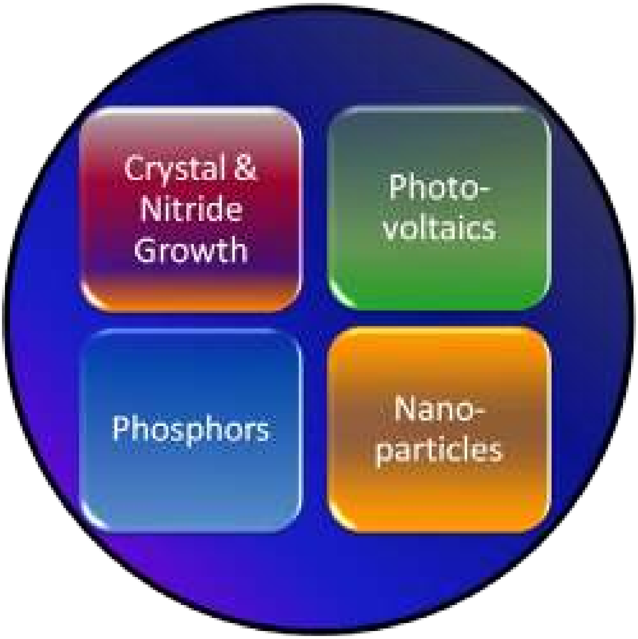
FRIEDRICH-ALEXANDER
UNIVERSITÄT
ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT

Department of Materials Science and Engineering

i-MEET

Materials for Electronics and Energy Technology



ANNUAL REPORT 2015

Prof. Dr. Christoph J. Brabec
Prof. Dr.-Ing. Peter Wellmann
Prof. Dr. Wolfgang Heiß
PD Dr. Miroslaw Batentschuk
Prof. Dr. rer. nat. Albrecht Winnacker

Lehrstuhl Materialien der Elektronik und der Energietechnologie
Universität Erlangen-Nürnberg
Martensstraße 7
91058 Erlangen

Telefon: +49 (0)9131 85-27633
Fax: +49 (0)9131 85-28495
E-Mail: i-MEET@ww.uni-erlangen.de

Homepage: www.i-meet.ww.fau.de

Table of Contents

1. Preface

Semiconductor research is currently rocked by the rapid advances in persovskite materials and perovskite devices. Also at i-MEET we started to in-depth explore the potential of pervoskite semiconductors and we were amazed by the potential of this novel class of electronic materials.

Some of our research highlights were published in prestigious journals. The work on perovskite X-Ray detectors from Wolfgang came out in Nature Photonics (DOI: 10.1038/nphoton.2015.82), Gebhard's cooperation on hybrid X-Ray detectors with Siemens was published in Nature Photonics (DOI: 10.1038/nphoton.2015.216).

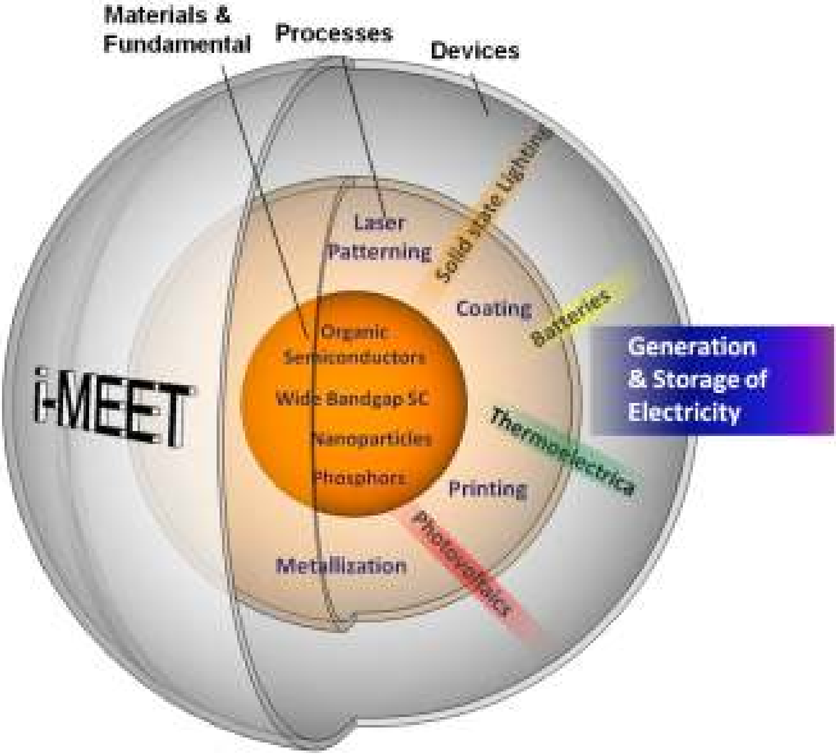
Fei's efforts to develop a novel tandem concept for organic/perovskite multilayer tandem cells found acknowledgement by publication in Nature Communications (DOI: 10.1038/ncomms8730). Personally I am very curious to learn about our further progress in perovskites in 2016.

I wish all the alumnis and friends of i-MEET further success. Please note that some of our highlights can be found on i-MEET's youtube channel (https://www.youtube.com/channel/UC6RHRl5xyzL1b-lcJ6FG3PA).

Please note also our alumni network at LinkedIn (Institute i-MEET).

With best regards

Christoph Brabec



(Christoph J. Brabec) (Peter Wellmann) (Wolfgang Heiß)

(Albrecht Winnacker) (Miroslaw Batentschuk)

Erlangen, June 2016

2. Members of the Chair

Professors

Prof. Dr.
Christoph J. Brabec
Head of the chair

Prof. Dr.-Ing.
Peter Wellmann

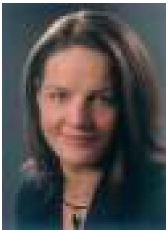
Prof. Dr.
Wolfgang Heiß

Secretaries

Manuela Baumer

Elisabeth Henneberger

Ulrike Knerr



Claudia Koch

Sandra Wehlmann

Academic administration

PD Dr. Miroslaw Batentschuk

Professors emeritus

Prof. Dr. rer. nat.
Georg Müller

Prof. Dr. rer. nat.
Albrecht Winnacker

Associate Professors

Prof. Dr. Dr.-Ing. habil.
Michael Thoms

Assistant lecturer

Dr.
Hans-Joachim Egelhaaf

Dr.-Ing.
Jochen Friedrich

Dr. rer. nat
Elke Meißner

Technical staff

Elena Epelbaum

Marwin Falter

Tina Foth

Winfried Habel

Silvan Heilscher

Leonid Kuper

Edeltraud Völkel

Corina Winkler

Ronald Wirth

Solar and Semiconductor Devices (SSD)

(Scientifical staff, doctoral candidates)

Prof. Dr.
Christoph J. Brabec
Group leader

Research of the device group is devoted to the design, simulation, processing and analysis of modern innovative semiconductors, electronic materials as well as advanced devices. Next generation concepts for electronic devices and future light harvesting techniques complete our research focus.

Development of low cost, long lived and highly efficient printed solar cells is one major vision of this research group. This includes the development of stable and efficient materials, the development of printed multilayer tandem technologies, ternary sensitization and controlling microstructure formation. Advanced organic semiconductors, p-type & n-type interface layers, printed transparent / opaque electrodes, flexible substrates and low cost barriers are further activities of this research group.
Organic semiconductors, perovskite hybrid composite semiconductors as well as colloidal quantum dots are the material fundament of our device engineering and process development activities. Further activities include low temperature processed chalcogenides and kesterites.

Dr. (Postdoc)
Hamed Azimi
Postdoc
i-MEET

Haiwei Chen
MSc
Doctoral candidate
i-MEET

Shi Chen
MEng
Doctoral candidate
i-MEET

Ening Gu
MEng
Doctoral candidate
i-MEET

Nusret Sena Güldal
MSc (Hons)
Doctoral candidate
i-MEET

Diana Galli
MSc
Doctoral candidate
i-MEET

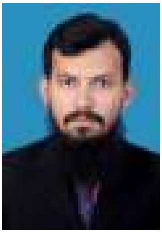
Thomas Heumüller
MSc
Doctoral candidate
i-MEET

Shuai Gao
MSc
Doctoral candidate
i-MEET

Yi Hou
MEng
Doctoral candidate
i-MEET

Simon Kahmann
MSc
Doctoral candidate
i-MEET

Lili Ke
MSc
Doctoral candidate
i-MEET



Laraib Khanzada
MEng
Doctoral candidate
i-MEET

Stefan Langner
MSc
Doctoral candidate
i-MEET

Dr.
Ning Li
Postdoc
i-MEET

Jie Min
MSc
Doctoral candidate
i-MEET

Dr.
Reza Mokhtari
Postdoc
i-MEET

J. D. Parea Ospina
MSc
Doctoral candidate
i-MEET

C.O. Ramirez Quiroz
MSc
Doctoral candidate
i-MEET

Dr.
Michael Salvador
Postdoc
i-MEET

George Spyropoulos
MSc
Doctoral candidate
i-MEET

Tobias Stubhan
Postdoc
Doctoral candidate
i-MEET

Chen Xie
MSc
Doctoral candidate
i-MEET

Chaohong Zhang
MSc
Doctoral candidate
ZAE

Dipl.-Ing.
Hong Zhang
Doctoral candidate
i-MEET

Transport in Solution-Processed Semiconductors (TSC)

(Scientifical staff, doctoral candidates)

Dr. Dipl.-Ing. Gebhard Matt
Group leader

Our research focus is in the electro-optical characterization of solution processed semiconductors.

We are specially interested in the nature of the charge transport in these exciting material systems. Our experimental methods cover a wide spectral range from the UV/VIS to the mid-infrared and a broad transient regime from the nanoseconds to the seconds.

We employed sensitive methods for the detection of photo-currents and the dynamic response is measured with time-resolved techniques (transient photo-current, photo-voltage, time-of-flight (TOF) and various charge-extraction methods (Charge extraction by linearly increasing voltage CELIV).

Thomas Heumüller
MSc
Doctoral candidate
i-MEET

Simon Kahmann
MSc
Doctoral candidate
i-MEET

Moses Richter
MSc (Hons)
Doctoral candidate
i-MEET

Shreetu Shrestha
MSc
Doctoral candidate
i-MEET

Xiaofeng Tang
MSc
Doctoral candidate
i-MEET

Phosphors & Light (P&L)

(Scientifical staff, doctoral candidates)

Dr. rer. nat. (Postdoc)
Karen Forberich
Group leader **Light management**

The main aim of the 'light management' group is to improve the optical properties of printed electronic devices, particularly the light harvesting in printed solar cells.

The experimental activities include light conversion, i.e. the transformation of UV and infrared light into visible light that can be converted by the solar cell, solution-processed electrodes, solution-processed dielectric mirrors, and the experimental investigation of light propagation in particle-matrix systems.

Optical simulations are another important part of the activities. We are using several different methods like FIT-THIIM, Ray-Tracing, RCWA and the transfer matrix formalism, and we combine different methods, but also different techniques for optical modelling. Optical models are verified by experimental measurements before they are used for numerical optimization.
For each problem, we will choose the most suitable method, i.e. the one that delivers the most accurate results at a reasonable computational effort.

Carina Bronnbauer
MSc
Doctoral candidate
i-MEET

Shuai Gao
MSc
Doctoral candidate
i-MEET

Dipl.-Ing.
Fei Guo
Doctoral candidate
i-MEET

Julian Hornich
MSc
Doctoral candidate
i-MEET

Dipl.-Ing.
Johannes Krantz
Doctoral candidate
i-MEET

Kerstin Krebs
MSc
Doctoral candidate
i-MEET

Yilei Shen
MSc
Doctoral candidate
i-MEET

Ternary Sensitization (TS)

(Scientifical staff, doctoral candidates)

Dr.
Tayebeh Ameri
Group leader

This research group aims to overcome the photocurrent and the performance limitation of polymer:fullerene solar cells in a simple single-junction structure by introducing a sensitizer with complimentary absorption profile into the host matrix. To boost near infrared light harvesting, we examine different semiconductor systems such as low bandgap polymers, small molecules, dye compounds as well as hybrid and inorganic nanoparticles / nanostructures. We carry out in-depth investigations on how the structural properties of the host system as well as the sensitizer will be influencing microstructure formation and the functionality of ternary systems. To illuminate on the modified recombination mechanisms in ternary systems, we also investigate the charge or energy transfer and charge transport between the constituent components. We employ various advanced microscopic, spectroscopic and optoelectronic techniques to study the morphology and transport of ternary hybrid and organic solar cells.

Dr.
Stefanie Fladischer
Postdoc
i-MEET

Nicola Gasparini
MSc
Doctoral candidate
i-MEET

Lili Ke
MSc
Doctoral candidate
i-MEET

Rezvan Soltani
MSc
Doctoral candidate
i-MEET

Imaging and Thermosensorics (IMT)

(Scientifical staff, doctoral candidates)

Dr. Andreas Vetter
Group leader

The group “Imaging & Thermosensorics” is dedicated to developing imaging methods and exploring accelerated life time testing of materials, in particular at high temperature. One important task of the group is to develop and apply innovative test and measurement methods. The group has a strong experience in precise infrared imaging methods. Also, different imaging methods have been extensively applied to characterize PV-cells and PV-modules.

Dipl.-Phys.
Klaus Burlafinger
Doctoral candidate
i-MEET

Johannes Hepp
MSc
Doctoral candidate
ZAE

Amir Hashemi
MSc
Doctoral candidate
ZAE

Dr.
Gordana Jovicic
Postdoc
i-MEET

Dr.-Ing.
Michael Woiton
Postdoc
i-MEET

B. Eng.
Sergej Lohvitki
Technician
i-MEET

Phosphors & Light (P&L)

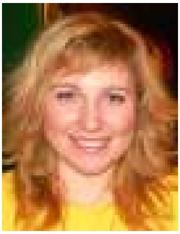
(Scientifical staff, doctoral candidates)

PD Dr.
Miroslaw Batentschuk
Group leader **Phosphors**

Dr. (Postdoc)
Andres Osvet
Group leader **Phosphors**

The research of the „Phosphors“ group is concentrated on the development of new phosphors, first of all for the light harvesting in solar cells, based on up and down conversion of the solar emission. In addition, new light-converting luminescent materials for white light emitting diodes, as well as storage phosphors for the application as markers in the medical and biological research are developed and studied. New phosphors for the high temperature thermometry are another part of activities, in co-operation with EnCN. Our expertize in optical spectroscopy is used in close cooperation with the Organic and Solution-based Photovaltaics Groups in the development and optical characterization of solar cell materials.

Amjad Ali
MSc
Doctoral candidate
i-MEET



Liudmyla Chepyga
MSc
Doctoral candidate
i-MEET

Dipl.-Chem.
Ievgen Levchuk
Doctoral candidate
i-MEET

Solution-Processed-Semiconductor-Materials (SOPSEM)

(Scientifical staff, doctoral candidates)

Prof. Dr.
Wolfgang Heiß
Group leader

Solution processed semiconductor materials are synthesized as a basis for the development of electronic devices. Topics cover solution processed perovskites to produce polycrystalline thin films and colloidal nanocrystals of perovskites, II-VI and VI-VI chalcogenides. These materials are applied in X-ray and infrared detectors, in solar cells, and in optically pumped lasers. Furthermore, organic pigments are synthesized as possible environmental friendly replacements for the toxic semiconductor nanocrystals.

Doctoral candidates i-MEET

Crystal Growth Lab (CGL)

(Scientifical staff, doctoral candidates)

Prof. Dr.-Ing. Peter Wellmann
Group leader

The research activities in the crystal growth lab of Prof. Dr.-Ing. Peter Wellmann at the electronic materials and energy technology (i-meet) division of the materials department (University of Erlangen-Nürnberg) are devoted to modern topics in semiconductor technology and include crystal growth, epitaxy and characterization of various electronic materials. In the current focus of research and development are materials for energy saving: (i) Silicon carbide for power electronic devices is a key player for energy saving. (ii) The CIGSSe thin film solar cell materials recently have reached a maturity that allows the realization of commercial solar panels. CZTSSe is believed to play the role of a succeeding thin film solar cell material. (iii) Printed electronic layers offer a great potential of a wide range of (opto-)electronic and photovoltaic device applications. (iv) In the field of characterization a large variety of electrical, spectroscopic and structural techniques are used which serve the better understanding of materials processing. Special emphasis is put on topographic methods. (v) In all fields service for industrial and institutional partners may be provided.

Soraya Abdelhaleem
MSc
Doctoral candidate
i-MEET

Dipl.-Ing.
Lars Fahlbusch
Doctoral candidate
i-MEET

Ayat Hassanien
MSc
Doctoral candidate
i-MEET

Hossein Khodamoradi
MSc
Doctoral candidate
i-MEET

Dr. Dipl.-Ing.
Ulrike Künecke
Scientifical staff
i-MEET

Dipl.-Ing.
Doctoral candidate
Stefan Möckel
i-MEET

Dipl.-Ing.
Georg Neubauer
Doctoral candidate
i-MEET

Saskia Schimmel
MSc
Doctoral candidate
i-MEET

Philipp Schuh
MSc
Doctoral candidate
i-MEET

Matthias Schuster
MSc
Doctoral candidate
i-MEET

Dipl.-Ing.
Martin Wilhelm
Doctoral candidate
i-MEET

Dipl.-Ing.
André Zweschke
Doctoral candidate
i-MEET

Bavarian Center for Applied Energy Research

(ZAE, doctoral candidates, postdocs)

The Bavarian Center for Applied Energy Research (ZAE Bayern) is a registered, non-profit association. The association was founded in December 1991 to promote energy research as well as education, further training, consultation, information and documentation in all fields significant to energy research. The association supports a scientific research institute with divisions in Würzburg, Garching, Erlangen, Nuremberg and Hof, employing more than 200 scientists, technicians, administrative personnel and students. Since the founding of ZAE Bayern in 1991, ZAE has become a both nationally and internationally recognized research institute.

ZAE Bayern works on the interface between evidence-based fundamental and applied industrial research. Every year the institute performs a great number of projects with the industry, from SME to large groups, as well as with university and non-university research partners. The core competences of the ZAE location in Erlangen with its subsidies in Nürnberg and Hof/Arzberg are renewable energies, with a strong focus on photovoltaics. Competences in materials science, theoretical understanding, and fundamental developments are linked in a knowledge- based chain of value with i-MEET. The close cooperation between i-MEET as well as further partners from FAU allows the ZAE Bayern in Erlangen to concentrate on finding effective solutions to remove the barriers on our way towards a green, sustainable and renewable future.

Dipl.-Phys.
Jens Adams

Iftikhar Channa
MEng

Dipl.-Phys.
Frank Fecher

Dr. Dipl.-Phys.
Maik Heßmann

Dipl.-Phys.
Ulrich Hoyer

Da Li
MSc

Luca Lucera
MSc

Philipp Maisch
MSc

Atif Makhdoom
MEng

Anastasiia Solodovnyk
MSc

G. Spyropoulos
MSc

Dipl.-Phys.
Arne Riecke

Dipl.-Ing.
Stephan Wittmann

External doctoral candidates

Dipl.-Phys.
Carina Ehrig
Siemens

Armin Heinrichsdobler
MSc
Osram

MEng
Tobias Kötter
Siemens

Dipl.-Pys.
Daniel Riedel
Osram

Dipl.-Ing.
Tobias Sauermann
Belectric

Dipl.-Ing
Philipp Schwamb
Osram

Visitors

04.05.2015-23.03.2016
Rezvan Soltani, MSc (Amirkabir University of Technology, Tehran, Iran)
Hybrid polymer solar cell based on PbS quantum dots/carbon nanotube nanoarchitectures

3. Bachelor Theses

Adler, Marius (Brabec)
Spray coating and characterization of homogeneous transparent electrodes of silver nanowires

Badschneider, Kevin (Brabec)
Einfluss von Beschichtungsmethoden und Tintenformulierung auf die optischen und elektrischen Eigenschaften von Silber Nanodraht Schichten

Barber, Alexander (Wellmann)
Bestimmung der Löslichkeit und der Lösungsgeschwindigkeit von Kohlenstoff in Siliziumschmelzen oberhalb von 2000 °C

Beickert, Leon (Batentschuk)
Synthesis and Characterization of Y-Ca-Al- and Ca-Al silicates with garnet and Anorthite structure for light conversion in solar cells

Bode, Alexander (Brabec)
Determination of Electric Parameters of Thin-Film Solar Cells with Imaging Measurements

Caliskan, Ayberg (Wellmann)
Untersuchung der Bandlücke von Siliziumgermaniumkarbid Epitaxieschichten

Dicke, Paul (Brabec)
Investigations of structural intermediate layers of multi-junction organics solar cells

Eichner, Stefan (Wellmann)
Einfluss von Verunreinigungen auf die Löslichkeit von GaN unter ammonosauren Bedingungen

Dörfler, Hannes (Wellmann)
Verbesserung der Keimstabilität bei der Siliziumkarbid Gasphasenzüchtung durch Rückseitenbeschichtung

Frank, Markus (Wellmann)
Untersuchung der Kohlenstoff-Rückseitenbeschichtung des Keims bei der SiC Einkristallzüchtung

Gall, Thomas (Brabec)
Herstellung organisch-anorganischer Hybridschichten aus Nanopartikel-Dispersionen

Henninger, Susanne (Wellmann)
Heteroepitaktische Abscheidung von 3C-SiC Halbleiterschichten auf Silizium

Herzog, Michael (Batentschuk)
Untersuchung des Driftverhaltens von gedruckten Widerständen auf einem HTCC-Schaltungsträger

Jordan, Dominik (Brabec)
Solution processed lead-free organic-inorganic halide perovskite solar cells

Kollwitz, Alexander (Wellmann)
Charakterisierung der Morphologie und chemischen Zusammensetzung von nanopartikulären $CuInSe_2$*-Schichten mittels Rasterelektronenmikroskopie*

Korn, Christian (Wellmann)
Strukturelle Charakterisierung von Siliziumkarbid-Einkristallscheiben mittels KOH_Defektätzen

Kornhas, Jakob (Batentschuk)
In search of effective flux materials for the optimisation of the synthesis and luminescent properties of $Sr_2Y_8(SiO_4)6O_2$*:Eu as a UV to VIS light converter*

Macher, Philipp (Wellmann)
Druckabhängigkeit der Löslichkeit von GaN unter ammonosaueren Bedingungen

Mattle, Patrick (Wellmann)
Anwendung eines induktiven Zweizonen-Beheizungssystem zur Einstellung des axialen Temperaturgradienten in einer Hochtemperatur-Kristallzüchtungsanlage

Meisel, Magnus (Wellmann)
Untersuchung der Korrosionsbeständigkeit von Siliziumkarbid, Diamant, Borkarbid und glasartigem Kohlenstoff unter ammonothermalen Bedingungen

Müller, Daniel (Wellmann)
Quantitative Untersuchung des Einflusses der Keim der Keimrückseitenbeschichtung auf die Defektdichte von SiC Einkristallen

Müller, Jonas (Brabec)
Ortsaufgelöste Messungen von Photostrom, Photo- und Elektrolumineszenz an karbazolbasierten und Perowskit-Solarzellen

Nguyen, Tien Linh (Wellmann)
Untersuchung der Schichtbildung eines dichten $Culn(S_xSe_{1-x})_2$ *Solarzellenabsorbers über eine Austauschreaktion von* $CulnS_2$ *Nanopartikeln mit Se*

Rössler, Anna (Brabec)
Realisierung eines Aufbaus zur Messung der Reflexions- und Emissionsspektren von Oberflächen bei hohen Temperaturen

Schnitzer Sarah (Wellmann)
Lösungszüchtung von SiC Einkristallen bei unterschiedlichen axialen Temperaturgradienten

Schöberl, Andrea (Batentschuk)
Synthese und Charakterisierung von Mikroskristallen mit der Granatstruktur für die Lichtkonversion in Leuchtdioden

Schuck, Kevin (Wellmann)
Transfer und Stabilisierung von kubischenSiC-Schichten für die Anwendung als Keim in der Sublimationsepitaxie

Sisterhenn, Philipp (Wellmann)
Herstellung und Charakterisierung eines dichten $CuInSe_2$- Solarzellenabsorbers aus Cu-In und Se Nanopartikel-Schichtstapeln

Sommerer, Lisa (Brabec)
Strukturelle Untersuchung an flüßigprozessierten Siliziumnanopartikelschichten auf Hochtemperatursubstraten

Steiner, Johannes (Batentschuk)
*Leuchtstoffe mit Granat – und Merwinit Struktur als Lichtkonverter für die Beschichtung von Solarzelle*n

Voll, Johannes C. (Brabec)
A detailed study of UV-soaking conditions and the effect on organic solar cell performance

Weghorn, Stefan (Brabec)
Prozessentwicklung zur Herstellung organischer Solarzellen für das EAM-Lab

4. Master Theses

Bergmann, Thore (Brabec)
Squaraine-sensitized Ternary Solar Cells based on Poly(3-hexylthiophene-2,5-diyl) (P3HT) and Phenyl-C61-butyric acid methyl ester (PCBM)

Besold, Sebastian (Brabec)
Organic solar cells - Investigation of charge transport dynamics

Doll, Bernd (Brabec)
Investigation of the film formation of doctor bladed perovskite layers for solar cell application as a function of humidity

Eisenhofer, Lena (Brabec)
Process development for inkjet printing of PEDOT:PSS hole injection layers

Fehn, Carsten (Brabec)
Fabrication and characterization of solvent processed and scaled-up OLECs

Göbel, Michaela (Batentschuk)
Homogenisierung des Gefüges der UFC-Keramik

Heinlein, Carina (Brabec)
Konzeptstudie zur thermochemischen Energiespeicherung

Högl, Florian (Brabec)
Generalized full solution-process fabrication of organic-inorganic metal halide perovskites for photovoltaic, X-ray and optoelectronic applications

Kazerouni, Negar (Brabec)
High efficient organic ternary solar cells

Kim, Damhee (Brabec)
Evaluation of solution-processed transparent electrodes for full-printed flexible Semitransparent polymer solar cells Non-halogenated and non-toxic fabrication of OPV Non-halogenated and non-toxic fabrication of OPV

Koch, Martina (Wellmann)
Löslichkeit von GaN unter ammonobasischen Bedingungen

Kogler, Willi (Brabec)
Growth and characterization of micron-sized inorganic semiconductors for solar cell applications

Schaumberger, Kerstin (Brabec)
Hybrid ternary solar cells based on CdSeTe nanoparticles

Udaya Shankar, Ashray (Brabec)
Investigation Of Ternary Organic Solar Cells Using Steady State Pump Probe Spectroscopy

Schwanke, Stanislaus (Wellmann)
Entwicklung einer Diffusionsbarriere für Metalle bei der gerichteten Erstarrung von Siliziumkristallen für die Photovoltaik

5. Doctoral Theses

Doctoral Theses in Preparation

Abdelhaleem, Soraya (Wellmann, i-MEET)
Determination of Homogeneity of CZTS Absorber Layers Prepared Entirely by Non-vacuum Process for Low cost and Radiation Hardness Solar Cell

Ali, Amjad (Batentschuk, i-MEET)
Developement of phosphors for light conversion in solar panels

Amin, Abbas Yousefi Amir (Heiss, i-MEET)
Inkjet printed nanocrystal devices

Bronnbauer, Carina (Brabec, i-MEET)
Printed dielectric mirrors for organic solar cells

Burlafinger, Klaus (Brabec, i-MEET)
Development of a high power illumination setup for accelerated photo-degradation

Channa, Iftikhar (Brabec, ZAE)
Development of solution processed thin film barriers for packaging thin film electronics

Chen Haiwei (Brabec, i-MEET)
Hihgh-Performance and stable perovskite solar cells

Chen, Shi (Brabec, i-MEET)
Designing and synthesizing novel pervoskite type semiconductors

Chepyga, Liudmyla (Batentschuk, i-MEET)
Developement of new phosphors for high-temperature thermometry

Fahlbusch, Lars (Wellmann, i-MEET)
Neue Ansätze beim PVT Wachstum von SiC Einkristallen

Fecher, Frank (Brabec, ZAE)
Electrical simulations of thin film photovoltaic modules

Galli, Diana (Brabec, i-MEET)
Near IR sensitization of polymer / fullerene solar cells

Gao, Shuai (Heiß, i-MEET)
Core-shell nanoparticles with enhanced properties for smart light management applications: engineering highly efficient upconversion composites

Gasparini, Nicola (Brabec, i-MEET)
Processing and characterization of small molecule type NIR sensitized BHJ solar cells / modules

Gu, Ening (Brabec, i-MEET)
Technological aspects of solution processed chalcopyrite solar cells

Güldal, Nusret Sena (Brabec, i-MEET)
Investigation of drying kinetics of hybrid/organic solar cells

Guo, Fei (Heiss, i-MEET)
Material and Process Engineering of Printed Semitransparent Organic Solar Cells and Advanced Multi-junction Architectures

Hassanien, Ayat (Wellmann, i-MEET)
Study of absorbing layer for thin film solar cells based on non-toxic, earth-abundant and low-cost elements

Heinrichsdobler Armin (Brabec extern, OSRAM OLED GmbH.)
Druckprozesse für OLED-Substrate

Hepp, Johannes (Brabec, ZAE)
Improving of Imaging Techniques for Quality Control of Thin Film Solar Cells

Heumüller, Thomas (Brabec, i-MEET)
Structure property correlation of microstructure modifications in semiconducting heterojunction composites

Hornich, Julian (Barbec, i-MEET)
Simulations of solar cells with FDTD methods

Hou, Yi (Brabec, i-MEET)
Multicomponet chalcopyrite and kesterite inorganic nanocrystals for solar cell applications

Hoyer, Ulrich (Brabec, ZAE)
Analyse von organischen Photovoltaik-Zellen mittels bildgebender Elektrolumineszenzmessung

Kahmann, Simon (Brabec, i-MEET)
Hybrid photovoltaics based on organic polymers / semiconductor nanoparticle composites

Ke, Lili (Brabec, i-MEET)
Synthesis & characterization of novel Phthalocyanine based small molecules

Killilea, Niall (Heiss, i-MEET)
Inkjet printed phototransistors

Kötter, Tobias (Brabec, external)
Hochleistungsdichte Phasenwechsel-Komposit-Materialien für das Thermomanagement von elektrotechnischen Systemen

Khodamoradi, Hossein (Wellmann, i-MEET)
Modeling of Crystal Growth from the Melt

Krantz, Johannes (Brabec, i-MEET)
Solution processed metallic nanorod electrodes as ITO replacement for thin film solar cells

Krebs, Kerstin (Brabec, i-MEET)
Transparent, leitfähige Beschichtungen als Elektroden für Touch Panel Displays

Langner, Stefan (Brabec, i-MEET)
Solubility investigation and green formulation based on HSPs

Levchuk, Ievgen (Batentschuk, i-MEET)
Synthesis and optimization of semiconductor colloidal nanocrystals for solar cell application

Lucera, Luca (Brabec, ZAE)
Coating and printing technologies for thin film solar cells

Makhdoom, Atif (Brabec, ZAE)
Low temperature route for the Development of Photovoltaic and optoelectronic devices using Silicon nanoparticles

Mashkov, Oleksandr (Heiss, i-MEET)
Organic pigment nanocrystals

Min, Jie (Brabec, i-MEET)
Design & fabrication of OPVs based on solution-processed small molecules

Neubauer, Georg (Wellmann, i-MEET)
Computertomographie bei der Kristallzüchtung

Perea Ospina, Jose Dario (Brabec, i-MEET)
Solubility investigation based on COSMO-RS approach

Ramirez Quiroz, César Omar (Brabec, i-MEET)
Hybrid tandem solar cells based on PbI perovskite

Richter, Moses (Brabec, i-MEET)
Transport properties of organic / inorganic hybrid composites

Riedel, Daniel (Brabec, external)
Internal light extraction in organic light emitting devices

Riecke, Arne (Brabec, ZAE)
Rekristallisation dünner Siliziumschichten auf Fremdsubstraten für photovoltaische Anwendungen und Anpassung der Zonenschmelzanlage (ZMR)

Sauermann, Tobias (Brabec, external)
Degradation Mechanisms in Organic Solar Cells

Schimmel, Saskia (Wellmann, i-MEET)
In situ Visualisierung des ammonothermalen Kristallisationsprozesses mittels Röntgenmesstechnik

Schuster, Matthias (Wellmann, i-MEET)
Solar Cells with Novel Materials

Schwamb, Philipp (Brabec, external)
Flexible white OLEDs

Shen, Yilei (Brabec, i-MEET)
Lösungsprozessierung für die semitransparenten Elektroden der organischen Leuchtdioden

Shrestha, Shreetu (Brabec, i-MEET)
Direct X-ray detectors based on PbI perovskite

Solodovnyk, Anastasiia (Brabec, ZAE)
Films with Particle Filled Systems for Solar Cell Applications

Spyropoulos, George (Brabec, ZAE)
Design and fabrication of novel and printable multi-junction organic solar cells

Wilhelm, Martin (Wellmann, i-MEET)
SiGeC Hetero-Epitaxie

Wittmann, Stephan (Brabec, ZAE)
Entwicklung und Optimierung von Zell- und Modulkonzepten für Dünnschicht-Silizium-Solarzellen auf Fremdsubstraten

Xie, Chen (Brabec, i-MEET)
Green formulation based on polymeric nanoparticles

Zhang, Chaohong (Brabec, i-MEET)
Synthesis & characterization of novel Fullerene-grafted compounds

Zhang, Hong (Brabec, i-MEET)
Design of Interfacial Layers for Organic Solar Cells

Zweschke, André (Wellmann, i-MEET)
Numerische Modellierung der Phasenbildung von CIS Solarzellenasorberschichten

Doctoral Theses Completed

12.03.2015
Möckel, Stefan (Wellmann, i-MEET)
Bildungsmechanismen bei der Herstellung von CIGSe Solarzellenabsorbern aus nanopartikulären Präkursorschichten

23.03.2015
Meier, Sebastian (Winnacker, i-MEET)
Organic Light-Emitting Electrochemical Cells for Lighting Applications / Organische licht-emittierende elektrochemische Zellen für Beleuchtungsanwendungen

16.09.2015
Guo, Fei (Brabec, i-MEET)
Material and Process Engineering of Printed Semitransparent Organic Solar Cells and Advanced Multi-junction Architectures / Material- und Prozessentwicklung von gedruckten semitransparenten organischen Solartzellen und innovativen Stapelarchitekturen

20.10.2015
Min, Jie (Brabec, i-MEET)
Solution-Processed Small Molecule Bulk Heterojunction Organic Solar Cells: Molecular, Morphological, Interfacial and Device Engineering / Lösungsprozessierte Bulk Heterojunction Solarzellen basierend auf kleinen Molekülen und Oligomeren: Charakterisierung und gezielte Entwicklung von Material-, Morphologie-, Interface- und Bauelement-Eigenschaften

21.10.2015
Adams, Jens (Brabec, ZAE)
Failure Analysis and Long Term Stability of Thin Film Solar Cells and Modules / Fehleranalyse und Langzeitstabiltitätsmessungen von Dünnschichtsolarzellen und Modulen

26.11.2015
Ehrig, Carina Miriam (Brabec, external)
Characterization of Inorganic Semiconductors for Solar Energy Conversion and their Stability in Aqueous Media / Charakterisierung von anorganischen Halbleitern für die Solarenergieumwandlung und ihre Stabilität in wässrigen Medien

30.11.2015
Li, Da (Brabec, ZAE)
Hydrogen and Surface Passivation of Thin-film Crystalline Silicon Solar Cells on Graphite Substrates / Wasserstoff- und Oberflächenpassivierung von kristallinen Silicium-Dünnschichtsolarzellen auf Graphitsubtraten

6. Awards

Derya Baran
Frauenpreis der Technischen Fakultät Universität Erlangen-Nürnberg

Simon Kahmann
won the poster prize of the international Next-Generation Organic Photovoltaics II Conference, Groningen, The Netherlands
"Lead sulphide quantum dot solar cells by blade coating from hybrid organic-inorganic solutions"

Ning Li
Excellent Doctoral Thesis Award 2015 of the "Freundeskreis der Technischen Fakultät", Friedrich-Alexander-Universität Erlangen-Nürnberg

Anastasiia Solodovnyk
Award of 2015 Optics and Photonics Education Scholarship by SPIE, the international society for optics and photonics for her potential contributions to the field of optics, photonics or related field

Hong Zhang
Student Award 2015 in Advanced Optical Technologies
Erlangen Graduate School in Advanced Optical Technologies, Friedrich-Alexander-Universität Erlangen-Nürnberg

7. Publications (Full Papers and Conference Proceedings)

Full Papers

Jens Adams, George D. Spyropoulos, Michael Salvador, Ning Li, Sebastian Strohm, Luca Lucera,Stefan Langner, Florian Machui, Hong Zhang, Tayebeh Ameri, Monika M. Voigt, Frederik C. Krebs and Christoph J. Brabec
Air-processed organic tandem solar cells on glass: toward competitive operating lifetimes
Energy & Environmental Science ***8****, pp.169-176, 2015*

Jens Adams, Michael Salvador, Luca Lucera, Stefan Langner, George D. Spyropoulos, Frank W. Fecher, Monika M. Voigt, Simon A. Dowland, Andres Osvet, Hans-Joachim Egelhaaf, and Christoph J. Brabec
Water Ingress in Encapsulated Inverted Organic Solar Cells: Correlating Infrared Imaging and Photovoltaic Performance
Advanced Energy Materials ***5 (20)****, art. no. 1501065, pages 11, 2015*

Hamed Azimi, Tayebeh Ameri, Hong Zhan , Yi Hou, Cesar Omar Ramirez Quiro, Jie Min, Mengyao H , Zhi-Guo Zhang, Thomas Przybilla, Gebhard J. Matt, Erdmann Spiecker, Yongfang Li, and Christoph J. Brabec
A Universal Interface Layer Based on an Amine-Functionalized Fullerene Derivative with Dual Functionality for Efficient Solution Processed Organic and Perovskite Solar Cells
Advanced Energy Materials ***5 (8)****,art. no. 1401692, pages 6, 2015*

Hamed Azimi, Susanne Kuhri, Melissa S. Stahl, Yi Hou, Dirk M. Guldi and Christoph J. Brabec
Elucidating the Excited-State Properties of $CuInS_2$ Nanocrystals upon Phase Transformation: Quasi-Quantum Dots Versus Bulk Behavior
Advanced Energy Materials ***1 (3)****,pages 7, 2015*

Baran, D., Erten-Ela, S., Kratzer, A., Ameri, T., Brabec, C.J., Hirsch, A.
Facile synthesis and photovoltaic applications of a new alkylated bismethano fullerene as electron acceptor for high open circuit voltage solar cells
RSC Advances ***5 (79)****,pp. 64724-64730, 2015*

Derya Baran, Michelle S Vezie, Nicola Gasparini, Florent Deledalle, Jizhong Yao, Bob C. Schroeder, Hugo Bronstein, Tayebeh Ameri, Thomas Kirchartz, Iain McCulloch, Jenny Nelson, and Christoph J Brabec
Role of Polymer Fractionation in Energetic Losses and Charge Carrier Lifetimes of Polymer: Fullerene Solar Cells
The Journal of Physical Chemistry C ***119 (34)****, pp. 19668-19673, 2015*

Brabec, C.J, Ameri, T.
Special section guest editorial: Solution-processable organic solar cells
Journal of Photonics for Energy ***5 (1)****, art. no. 057201, 2015*

Marco Brandl, Rameez Ahmad, Monica Distaso, Hamed Azimi , Yi Hoc, Wolfgang Peukert, Christoph J. Brabec, Rainer Hock
In-situ X-ray diffraction analysis of the recrystallization process in Cu_2ZnSnS_4 nanoparticles synthesised by hot-injection
Thin Solid Films ***582****,pp. 269-271, 2015*

Carina Bronnbauer, Julian Hornich, Nicola Gasparini, Fei Guo, Benjamin Hartmeier, Norman A. Luechinger, Christoph Pflaum, Christoph J. Brabec, and Karen Forberich
Printable Dielectric Mirrors with Easily Adjustable and Well-Defined Reflection Maxima for Semitransparent Organic Solar Cells
Advanced Optical Materials ***3****, pp. 1424-1430, 2015*

Patric Büchele, Moses Richter, Sandro F. Tedde, Gebhard J. Matt, Genesis N. Ankah, Rene Fischer, Markus Biele, Wilhelm Metzger, Samuele Lilliu, Oier Bikondoa, J. Emyr Macdonald, Christoph J. Brabec, Tobias Kraus, Uli Lemmer and Oliver Schmidt
X-ray imaging with scintillator-sensitized hybrid organic photodetectors
Nature Photonics, online 2015, pages 7, Article in press

Klaus Burlafinger, Andreas Vetter, Christoph J. Brabec
Maximizing concentrated solar power (CSP) plant overall efficiencies by using spectral selective absorbers at optimal operation temperatures
Solar Energy ***120****,pp. 428-438, 2015*

Wei Chen, Yi Hou, Andres Osvet, Fei Guo, Peter Kubis, Miroslaw Batentschuk, Benjamin Winter, Erdmann Spiecker, Karen Forberich, Christoph J. Brabec
Sub-bandgap photon harvesting for organic solar cells via integrating up-conversion nanophosphors
Organic Electronics ***19****, pp. 113-119, 2015*

Chaohua Cui, Xia Guo, Jie Min, Bing Guo, Xiao Cheng, Maojie Zhang, Christoph J. Brabec, and Yongfang Li
High-Performance Organic Solar Cells Based on a Small Molecule with Alkylthio-Thienyl-Conjugated Side Chains without Extra Treatments
Advanced Materials ***27 (45)****, pp. 7469-7475, 2015*

Vedran Derek, Eric Daniel Głowacki, Mykhailo Sytnyk, Wolfgang Heiss, Marijan Marcius, Mira Ristic, Mile Ivanda, and Niyazi Serdar Sariciftci
Enhanced near-infrared response of nano- and microstructured silicon/organic hybrid photodetectors
Applied Physics Letters ***107*** *(083302), pp. 1-5, 2015*

Ulf Dettinger, Hans-Joachim Egelhaaf, Christoph J. Brabec, Florian Latteyer, Heiko Peisert and Thomas Chassé
FTIR Study of the Impact of PC[60]BM on the Photodegradation of the Low Band Gap Polymer PCPDTBT under O_2 Environment
Chemistry of Materials ***27****, pp. 2299-2308, 2015*

Karen Forberich, Fei Guo, Carina Bronnbauer, and Christoph J. Brabec
Efficiency Limits and Color of Semitransparent Organic Solar Cells for Application in Building-Integrated Photovoltaics
Energy Technology ***3****, pp. 1-9, 2015*

Nicola Gasparini, Michael Salvador, Stefanie Fladischer, Athanasios Katsouras, Apostolos Avgeropoulos, Erdmann Spiecker, Christos L. Chochos, Christoph J. Brabec, and Tayebeh Ameri
An Alternative Strategy to Adjust the Recombination Mechanism of Organic Photovoltaics by Implementing Ternary Compounds
Advanced Energy Materials, art. no. 1501527, pages 7, 2015

Nicola Gasparini, Athanasios Katsouras, Mamantos I. Prodromidis, Apostolos Avgeropoulos, Derya Baran, Michael Salvador, Stefanie Fladischer, Erdmann Spiecker, Christos L. Chochos, Tayebeh Ameri, and Christoph J. Brabec
Photophysics of Molecular-Weight-Induced Losses in Indacenodithienothiophene-Based Solar Cells
Advanced Functional Materials ***25****, pp. 4898–4907, 2015*

Claudia Gollner, Johannes Ziegler, Loredana Protesescu, Dmitry N. Dirin, Rainer T. Lechner, Gerhard Fritz-Popovski, Mykhailo Sytnyk, Sergii Yakunin, Stefan Rotter, Amir Abbas Yousefi Amin, Cynthia Vidal, Calin Hrelescu, Thomas A. Klar, Maksym Kovalenko, and Wolfgang Heiss
Random Lasing with Systematic Threshold Behavior in Films of CdSe/CdS Core/Thick-Shell Colloidal Quantum Dots
ACS Nano ***9 (10)****, pp. 9792-9801, 2015*

J. Andres Guerra, Liz Montañez, Albrecht Winnacker, Francisco De Zela, and Roland Weingärtner
Thermal activation and temperature dependent PL and CL of Tb doped amorphous AlN and SiN thin films
Physica Status Solidi C ***12 (8)****, pp. 1183-1186, 2015*

Fei Guo, Peter Kubis, Thomas Przybilla, Erdmann Spiecker, Andre Hollmann, Stefan Langner, Karen Forberich, and Christoph J. Brabec
Nanowire Interconnects for Printed Large-Area Semitransparent Organic Photovoltaic Modules
Advanced Energy Materials, art. no. 1401779, pages 9, 2015

Fei Guo, Shi Chen, Zhang Chen, Hongjie Luo, Yanfeng Gao, Thomas Przybilla, Erdmann Spiecker, Andres Osvet, Karen Forberich, and Christoph J. Brabec
Printed Smart Photovoltaic Window Integrated with an Energy-Saving Thermochromic Layer
Advanced Optical Materials ***3****, pp. 1524-1529, 2015*

Fei Guo, Ning Li, Vuk V. Radmilovic, Velimir R. Radmilovic, Mathieu Turbiez, Erdmann Spiecker, Karen Forberich and Christoph J. Brabec
Fully printed organic tandem solar cells using solution-processed silver nanowires and opaque silver as charge collecting electrodes
Energy & Environmental Science ***8 (6)****, pp. 1690-1697, 2015*

Fei Guo, Hamed Azimi, Yi Hou, Thomas Przybilla, Mengyao Hu, Carina Bronnbauer, Stefan Langner, Erdmann Spiecker, Karen Forberich and Christoph J. Brabec
High-performance semitransparent perovskite solar cells with solution-processed silver nanowires as top electrodes
Nanoscale ***7****, pp. 1642-1649, 2015*

Fei Guo, Ning Li, Frank W. Fecher, Nicola Gasparini, Cesar Omar Ramirez Quiroz, Carina Bronnbauer, Yi Hou, Vuk V. Radmilovic, Velimir R. Radmilovic, Erdmann Spiecker, Karen Forberich & Christoph J. Brabec
A generic concept to overcome bandgap limitations for designing highly efficient multi-junction photovoltaic cells
Nature Commonications ***6:7730****,pages 9, 2015*

A Hashemi, A Vetter, G Jovicic, M Batentschuk and C J Brabec
Temperature measurements using YAG:Dy and YAG:Sm under diode laser excitation (405 nm)
Measurement Science and Technology ***26****, 075202, pages 7, 2015*

Felix Hermerschmidt, Andreas S. Kalogirou, Jie Min, Georgia A. Zissimou, Sachetan M. Tuladhar, Tayebeh Ameri, Hendrik Faber, Grigorios Itskos, Stelios A. Choulis, Thomas D. Anthopoulos, Donal D. C. Bradley, Jenny Nelson, Christoph J. Brabec and Panayiotis A. Koutentis
4H-1,2,6-Thiadiazin-4-one-containing small molecule donors and additive effects on their performance in solution-processed organic solar cells
Journal of Materials Chemistry C ***3****, pp. 2358-2365, 2015*

Benjamin Hertweck, Saskia Schimmel, Thomas G. Steigerwald, Nicolas S.A. Alt, Peter J. Wellmann, Eberhard Schluecker
Ceramic liner technology for ammonoacidic synthesis
Journal of Supercritical Fluids ***99****,pp. 76-87, 2015*

Thomas Heumueller, Timothy M. Burke, William R. Mateker, Isaac T. Sachs-Quintana, Koen Vandewal1, Christoph J. Brabec andMichael D. McGehee
Disorder-Induced Open-Circuit Voltage Losses in Organic Solar Cells During Photoinduced Burn-In
Advanced Energy Materials ***5 (14)****, art. no. 1500111, 2015*

Yi Hou, Hamed Azimi, Nicola Gasparini, Michael Salvador, Wei Chen, Laraib S. Khanzada, Marco Brandl, Rainer Hock, and Christoph J. Brabec
Low-temperature Solution-Processed Kesterite Solar Cell Based on in Situ Deposition of Ultrathin Absorber Layer
ACS Applied Materials and Interfaces ***7 (38)****, pp. 21100-21106, 2015*

Yi Hou, Hong Zhang, Wei Chen, Shi Chen, Cesar Omar Ramirez Quiroz, Hamed Azimi, Andres Osvet , Gebhard J. Matt, Eitan Zeira, Jan Seuring, Nina Kausch-Busies, Wilfried Lövenich, and Christoph J. Brabec
Inverted, Environmentally Stable Perovskite Solar Cell with a Novel Low-Cost and Water-Free PEDOT Hole-Extraction Layer
Advanced Energy Materials ***5 (15)****, art. no. 1500543, pages 7, 2015*

Yi Hou, Cesar Omar Ramirez Quiroz, Simon Scheiner, Wei Chen, Tobias Stubhan, Andreas Hirsch, MarcusHalik,Christoph J. Brabec
Low-Temperature and Hysteresis Free Electron Transporting Layers for Efficient, Inverted and Planar Structure Perovskite Solar Cells
Advanced Energy Materials ***5****, art. no. 1501056, pages 7, 2105*

Valdas Jokubavicius, Gholam R. Yazdi, Rickard Liljedahl, Ivan G. Ivanov, Jianwu Sun, Xinyu Liu,Philipp Schuh, Martin Wilhelm, Peter Wellmann, Rositsa Yakimova, and Mikael Syväjärvi
Single Domain 3C-SiC Growth on Off-Oriented 4H-SiC Substrates
Crystal Growth & Design ***15****, pp. 2940-2947, 2015*

Kahmann, S., Mura, A., Protesescu, L., Kovalenko, M.V., Brabec, C.J., Loi, M.A.
Opto-electronics of PbS quantum dot and narrow bandgap polymer blends
Journal of Materials Chemistry C ***3 (21)****, pp. 5499-5505, 2105*

Safakath Karuthedath, Tobias Sauermann, Hans-Joachim Egelhaaf, Reinhold Wannemacher, Christoph J. Brabec and Larry Lüer
The effect of oxygen induced degradation on charge carrier dynamics in P3HT:PCBM and Si-PCPDTBT:PCBM thin films and solar cells
Journal of Materials Chemistry A ***3****, pp.3399-3408, 2015*

Kassar, T., Güldal, N.S., Berlinghof, M., Ameri, T., Kratzer, A., Schroeder, B.C., Destri, G.L., Hirsch, A., Heeney, M., Mcculloch, I., Brabec, C.J., Unruh, T.
Real-Time Investigation of Intercalation and Structure Evolution in Printed Polymer:Fullerene Bulk Heterojunction Thin Films
Advanced Energy Materials, online 2105, art. no. 150205, Article in press

Athanasios Katsouras, Nicola Gasparini, Chrysanthos Koulogiannis, Michael Spanos, Tayebeh Ameri, Christoph J. Brabec, Christos L. Chochos, Apostolos Avgeropoulos
Systematic Analysis of Polymer Molecular Weight Influence on the Organic Photovoltaic Performance
Macromolecular Rapid Communications ***36 (20)****, pp. 1778-1797, 2015*

Renate Kellermann, Dan Taroata, Anna Maltenberger, David Hartmann, Christoph J. Brabec, and Guenter Schmid
Low-cost copper complexes as p-dopants in solution processable hole transport layers
Applied Physics Letters ***107****, pp. 103305-1 - 103305-4, 2015*

Maksym V. Kovalenko, Liberato Manna, Andreu Cabot, Zeger Hens, Dmitri V. Talapin, Cherie R. Kagan, Victor I. Klimov, Andrey L. Rogach, Peter Reiss, Delia J. Milliron, Philippe Guyot-Sionnnest, Gerasimos Konstantatos, Wolfgang J. Parak, Taeghwan Hyeon, Brian A. Korgel, Christopher B. Murray, and Wolfgang Heiss
Prospects of Nanoscience with Nanocrystals
ACS Nano ***9 (2)****, pp. 1012-1057, 2015*

Johannes Krantz, Karen Forberich, Peter Kubis, Florian Machui, Jie Min, Tobias Stubhan, Christoph J. Brabec
Printing high performance reflective electrodes for organic solar cells
Organic Electronics ***17****, pp. 334-339, 2015*

Peter Kubis, Ning Li, Tobias Stubhan, Florian Machui, Gebhard J. Matt, Monika M. Voigt and Christoph J. Brabec
Patterning of organic photovoltaic modules by ultrafast laser
Progress in Photovoltaics: Research and Applications ***23****, pp. 238-246, 2015*

Thomas Lenz, Moses Richter, Gebhard J. Matt, Norman A. Luechinger, Samuel C. Halim, Wolfgang Heiss and Christoph J. Brabec
Charge transport in nanoparticular thin films of zinc oxide and aluminum-doped zinc oxide
Journal of Materials Chemistry C ***3****, pp. 1468-1472, 2015*

Da Li, Stephan Wittmann, Thomas Kunz, Taimoor Ahmad, Nidia Gawehns, Maik T. Hessmann, Jan Ebser, Barbara Terheiden, Richard Auer, and Christoph J. Brabec
Recrystallized thin-film silicon solar cell on graphite substrate with laser single side contact and hydrogen passivation
EPJ Photovoltaics ***6****, 60301, pages 7, 2015*

Da Li, Thomas Kunz, NadineWolf, Jan Philipp Liebig, Stephan Wittmann, Taimoor Ahmad, Maik T. Hessmann, Richard Auer, Mathias Göken, Christoph J. Brabec
Silicon nitride and intrinsic amorphous silicon double antireflection coatings for thin-film solar cells on foreign substrates
Thin Solid Films ***583****, pp. 25-33, 2015*

Ning Li and Christoph J. Brabec
Air-processed polymer tandem solar cells with power conversion efficiency exceeding 10%
Energy & Environmental Science ***8 (10)****, pp. 2902-2909, 2015*

Benjamin Lipovšek,1 Anastasiia Solodovnyk, Karen Forberich, Edda Stern, Janez Krč, Christoph J. Brabec, and Marko Topič
Optical model for simulation and optimization of luminescent down-shifting layers filled with phosphor particles for photovoltaics
Optics Express ***23 (15)****, pp. A882-A895, 2015*

Ning Liu, Volker Häublein, Xuemei Zhou, Umamaheswari Venkatesan, Martin Hartmann, Mirza Mačković, Tomohiko Nakajima, Erdmann Spiecker, Andres Osvet, Lothar Frey, and Patrik Schmuki
“Black” TiO_2 Nanotubes Formed by High-Energy Proton Implantation
Show Noble-Metal-co-Catalyst Free Photocatalytic H_2-Evolution
Nano Letters ***15 (10)****, pp. 6815-6820, 2015*

Francesco Livi, Roar R. Søndergaard, Thomas R. Andersen, B¦renger Roth, Suren Gevorgyan, Henrik F. Dam, Jon E. Carl,Martin Helgesen, George D. Spyropoulos, Jens Adams, Tayebeh Ameri, Christoph J. Brabec, Mathilde Legros, NoÜlla Lemaitre, Stephane Berny, Owen R. Lozman, Stefan Schumann,Arnulf Scheel, P•lvi Apilo, Marja Vilkman, Eva Bundgaard, and Frederik C. Krebs
Round-Robin Studies on Roll-Processed ITO-free Organic Tandem Solar Cells Combined with Inter-Laboratory Stability Studies
Energy Technology 3, pp. 423-427, 2015

L. Lucera, F. Machui, P. Kubis, H. D. Schmidt, J. Adams, S. Strohm, T. Ahmad, K. Forberich, H.-J. Egelhaaf and C. J. Brabec
Highly efficient, large area, roll coated flexible and rigid OPV modules with geometric fill factors up to 98.5% processed with commercially available materials
Energy & Environmental Science, online 2015, pages 6, Article in press

Luca Lucera, Peter Kubis, Frank W. Fecher, Carina Bronnbauer, Mathieu Turbiez, Karen Forberich, Tayebeh Ameri, Hans-Joachim Egelhaaf, and Christoph J. Brabec
Guidelines for Closing the Efficiency Gap between Hero Solar Cells and Roll-To-Roll Printed Modules
Energy Technology 3, pp. 373-384, 2015

Luponosov, Y.N., Min, J., Khanin, D.A, Baran, D., Pisarev, S.A., Peregudova, S.M., Dmitryakov, P.V., Chvalun, S.N., Cherkaev, G.V., Svidchenko, E.A., Ameri, T., Brabec, C.J., Ponomarenko, S.A.
Synthesis and photovoltaic effect in red/near-infrared absorbing A-D-A-D-A-type oligothiophenes containing benzothiadiazole and thienothiadiazole central units
Journal of Photonics for Energy ***5 (1)****, pp. 057213-1 - 057213-17, 2015*

Yuriy N. Luponosov, Jie Min, Artem V. Bakirov, Petr V. Dmitryakov, Sergei N. Chvalun, Svetlana M. Peregudova, Tayebeh Ameri, Christoph J. Brabec, Sergei A. Ponomarenko
Effects of bridging atom and p-bridge length on physical and photovoltaic properties of Aep-Dep-A oligomers for solution processed organic solar cells
Dyes and Pigments ***122****,pp. 213-223, 2015*

Florian Machui, Philipp Maisch, Ignasi Burgues-Ceballos, Stefan Langner, Johannes Krantz, Tayebeh Ameri, and Christoph J. Brabec
Classification of Additives for Organic Photovoltaic Devices
Chem. Phys. Chem. ***16****, pp. 1275-1280, 2105*

Jie Min, Zhi-Guo Zhang, Yi Hou, Cesar Omar Ramirez Quiroz, Thomas Przybilla, Carina Bronnbauer, Fei Guo, Karen Forberich, Hamed Azimi, Tayebeh Ameri, Erdmann Spiecker, Yongfang Li and Christoph J. Brabec
Interface Engineering of Perovskite Hybrid Solar Cells with Solution-Processed Perylene−Diimide Heterojunctions toward High Performance
Chemistry of Materials ***27****, pp. 227-234, 2015*

Jie Min, Yuriy N. Luponosov, Nicola Gasparini, Moses Richter, Artem V. Bakirov, Maxim A. Shcherbina, Sergei N. Chvalun, Linda Grodd, Souren Grigorian, Tayebeh Ameri, Sergei A. Ponomarenko, and Christoph J. Brabec
Effects of Alkyl Terminal Chains on Morphology, Charge Generation, Transport, and Recombination Mechanisms in Solution-Processed Small Molecule Bulk Heterojunction Solar Cells
Advanced Electronic Materials ***5****, art. no. 1500386, pages 13, 2015*

Jie Min, Yuriy N. Luponosov, Nicola Gasparini,a Lingwei Xue, Fedor V. Drozdov, Svetlana M. Peregudova, Petr V. Dmitryakov, Kirill L. Gerasimov, Denis V. Anokhin, Zhi-Guo Zhang, Tayebeh Ameri, Sergei N. Chvalun, Dimitri A. Ivanov, Yongfang Li, Sergei A. Ponomarenko and Christoph J. Brabec
Integrated molecular, morphological and interfacial engineering towards highly efficient and stable solution-processed small molecule solar cells interfacial engineering towards highly efficient and stable solution-processed small molecule solar cells
Journal of Materials Chemistry A ***3****, pp. 22695–22707, 2015*

Mohamad Insan Nugraha, Roger Häusermann, Satria Zulkarnaen Bisri, Hiroyuki Matsui, Mykhailo Sytnyk, Wolfgang Heiss, Jun Takeya, and Maria Antonietta Loi
High Mobility and Low Density of Trap States in Dual-Solid-Gated PbS Nanocrystal Field-Effect Transistors
Advanced Materials ***27****, pp. 2107-2112, 2015*

César Omar Ramírez Quiroz, Ievgen Levchuk, Carina Bronnbauer, Michael Salvador, Karen Forberich, Thomas Heumüller, Yi Hou, Peter Schweizer, Erdmann Spiecker, Christoph J. Brabec
Pushing Efficiency Limits for Semitransparent Perovskite Solar Cells
Journal of Materials Chemistry A ***3****, pp. 24071-24081, 2015*

Saskia Schimmel, Michael Lindner, Thomas G.Steigerwald, Benjamin Hertweck, Theresia M.M.Richter, Ulrike Künecke, Nicolas S.A. Alt, Rainer Niewa, Eberhard Schlücker, Peter J. Wellmann
Determination of GaN solubility in supercritical ammonia with NH_4F and NH_4Cl mineralizerby in situ x-ray imaging of crystal dissolution
Journal of Crystal Growth ***418****, pp. 64-69, 2015*

R. Clayton Shallcross, Tobias Stubhan, Erin L. Ratcliff, Antoine Kahn, Christoph J. Brabec, and Neal R. Armstrong
Quantifying the Extent of Contact Doping at the Interface between High Work Function Electrical Contacts and Poly(3 hexylthiophene) (P3HT)
The Journal of Physical Chemistry Letters ***6 (8)****, pp. 1303-1309, 2015*

Anastasiia Solodovnyk, Karen Forberich, Edda Stern, Janez Krc, Marko Topic, Miroslaw Batentschuk, Benjamin Lipovšek and Christoph J. Brabec
Highly transmissive luminescent down-shifting layers filled with phosphor particles for photovoltaics
Optical Materials Express ***5 (6)****, pp. 1296-1305, 2015*

Benedetta M. Squeo, Nicola Gasparini, Tayebeh Ameri, Alex Palma-Cando, Sybille Allard, Vasilis G. Gregoriou, Christoph J. Brabec, Ullrich Scherf and Christos L. Chochos
Ultra low band gap a,b-unsubstituted BODIPY-based copolymer synthesized by palladium catalyzed cross-coupling polymerization for near infrared organic photovoltaics
Journal of Materials Chemistry A ***3****, pp. 16279–16286, 2015*

Melissa S. Stahl, Hamed Azimi and Christoph J. Brabec
A facile one-step method to reduce surface impurities in solution-processed CuInS2 nanocrystal solar cells
Journal of Materials Chemistry A ***3****, pp. 14116-14120, 2015*

Mikael Syväjärvi, Quanbao Ma, Valdas Jokubavicius, Augustinas Galeckas, Jianwu Sun, Xinyu Liu, Mattias Jansson, Peter Wellmann, Margareta Linnarsson, Paal Runde, Berti Andre Johansen, Annett Thøgersen, Spyros Diplas, Patrici Almeid Carvalho, Ole Martin Løvvik, Daniel Nilsen Wright, Alexander Yu Azarov, Bengt G. Svensson
Cubic silicon carbide as a potential photovoltaic material
Solar Energy Materials & Solar Cells, online 2015, pages 5, Article in press

Harald Unterweger, Daniel Subatzus, Rainer Tietz, Christina Janko, Marina Poettler, Alfons Stiegelschmitt, Matthias Schuster, Caroline Maake, Aldo R Boccaccini, Christoph Alexiou
Hypericin-bearing magnetic iron oxide nanoparticles for selective drug delivery in photodynamic therapy
International Journal of Nanomedicine ***10****, pp. 6985-6996, 2015*

Virginia Voland, Ulrich Hoyer, Richard Auer, Michael Salamon, Norman Uhlmann and Christoph J. Brabec
Defect recognition in crystalline silicon solar cells by X-ray tomosynthesis with layer resolution
Progress in Photovoltaics: Research and Applications 23, pp. 124-130, 2015

Hai-Qiao Wang , Mirza Mackovic, Andres Osvet, Ivan Litzov, Elena Epelbaum, Alfons Stiegelschmitt, Miroslaw Batentschuk, Erdmann Spiecker, and Christoph J. Brabec
A New Crystal Phase Molybdate $Yb_2Mo_4O_{15}$: The Synthesisand Upconversion Properties
Particle & Particle Systems Characterization ***32****, pp. 340-346, 2015*

Peter Wellmann, Georg Neubauer, Lars Fahlbusch, Michael Salamon, and Norman Uhlmann
Growth of SiC bulk crystals for application in power electronic devices – process design, 2D and 3D X-ray in situ visualization and advanced doping
Crystal Research and Technology ***50 (1)****, pp. 2-9, 2015*

Martin Wilhelm, Marcel Rieth, Marco Brandl, Rachmat Adhi Wibowo, Rainer Hock, Peter Wellmann
Optimization of growth parameters for growth of high quality heteroepitaxial 3C–SiC films at 1200 °C
Thin Solid Films ***577****, pp.88-93, 2015*

Sergii Yakunin, Mykhailo Sytnyk, Dominik Kriegner, Shreetu Shrestha, Moses Richter, Gebhard Matt, Hamed Azimi, Christoph Brabec, Julian Stangl, Maksym Kovalenko, and Wolfgang Heiss
Detection of X-ray photons by solution-processed lead halide perovskites
*Nature Photonics **9 (7)**, pp. 444-449, 2015*

Sergii Yakunin, Loredana Protesescu, Franziska Krieg, Maryna I. Bodnarchuk, Georgian Nedelcu, Markus Humer, Gabriele De Luca, Manfred Fiebig, Wolfgang Heiss & Maksym V. Kovalenko
Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites
*Nature Commonications **6:8056**, pp. 1-8, 2015*

Kai Zheng, Anastasiia Solodovnyk, Wei Li, Ourania-Menti Goudouri, Christoph Stähli, Showan N. Nazhat, and Aldo R. Boccaccini
Aging Time and Temperature Effects on the Structure and Bioactivity of Gel-Derived 45S5 Glass-Ceramics
*Journal of the American Ceramic Society **98 (1)**, pp. 30-38, 2015*

Yu.Zorenko, V.Gorbenko, T.Zorenko, K.Paprocki, A.Osvet, M.Batentschuk, C. Brabec, A.Fedorov
Enhancement of up-conversion luminescence in Er,Ce doped $Y_{3-x}Yb_x$ AG single crystalline films
Journal of Luminescence, online 2015, Article in press

Zorenko, Y., Zorenko, T., Gorbenko, V., Voznyak, T., Popielarski, P., Batentschuk, M., Osvet, A., Brabec, C., Kolobanov, V., Spasky, D., Fedorov, A.
Luminescent properties of LuAG: Yb and YAG: Yb single crystalline films grown by Liquid Phase Epitaxy method
Radiation Measurements, online 2015, Article in press

Energy &
Environmental
Science

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: Energy Environ. Sci., 2015, 8, 169

Received 14th August 2014
Accepted 12th September 2014

DOI: 10.1039/c4ee02582b

www.rsc.org/ees

Air-processed organic tandem solar cells on glass: toward competitive operating lifetimes†

Jens Adams,‡[a] George D. Spyropoulos,‡*[ab] Michael Salvador,*[ab] Ning Li,[b] Sebastian Strohm,[a] Luca Lucera,[a] Stefan Langner,[b] Florian Machui,[b] Hong Zhang,[b] Tayebeh Ameri,[b] Monika M. Voigt,[ab] Frederik C. Krebs[c] and Christoph J. Brabec[ab]

Photovoltaic devices based on organic semiconductors (OPVs) hold great promise as a cost-effective renewable energy platform because they can be processed from solution and deposited on flexible plastics using roll-to-roll processing. Despite important progress and reported power conversion efficiencies of more than 10% the rather limited stability of this type of devices raises concerns towards future commercialization. The tandem concept allows for both absorbing a broader range of the solar spectrum and reducing thermalization losses. We designed an organic tandem solar cell with an inverted device geometry comprising environmentally stable active and charge-selecting layers. Under continuous white light irradiation, we demonstrate an extrapolated operating lifetime in excess of one decade. We elucidate that for the current generation of organic tandem cells one critical requirement for long operating lifetimes consists of periodic UV light treatment. These results suggest that new material approaches towards UV-resilient active and interfacial layers may enable efficient organic tandem solar cells with lifetimes competitive with traditional inorganic photovoltaics.

Broader context

Low-cost, thin-film solar cells represent a potentially sustainable pathway towards replacing fossil fuel-based technologies. In this context, organic semiconductor based solar cells (OPVs) are particularly attractive because they can be deposited from solution on plastic substrates, making them compatible with large-scale industry standards. One possible setback when evaluating the commercial potential of organic photovoltaics is related to the limited lifetime that is typically observed for this type of devices. Most device performance reported in the literature is based on photovoltaic devices that have remained in an inert environment from the initial fabrication steps up to the final characterization process. However, it is clear that commercialization will only be possible under the premise of long-term air and UV stable materials. We adopted an innovative combination of device geometry and choice of active as well as charge selecting materials that allowed us to fabricate efficient organic tandem solar cells in air. The tandem OPVs feature stable performance over 1000 h of operation and an extrapolated lifetime in excess of one decade. Furthermore, we show that periodic UV light treatment during operation is an essential requirement for attaining long operating lifetimes. This progress suggests that operating lifetimes closer to what is known from traditional inorganic thin-film photovoltaics are within reach.

Introduction

Organic photovoltaics (OPVs) bears the potential for highly efficient, low-cost solar energy conversion. The emergence of new device architectures and material concepts led to a fast development in the recent past with reported efficiencies >10%.[1,2] Yet, all the advantages of organic materials, which provide OPVs with the well-known versatility of flexible, light weight and transparent devices, are accompanied with challenges when considering the next level of device efficiency towards commercialization. For instance, the photon harvesting efficiency and open circuit voltage (V_{oc}) are affected by the relatively narrow absorption spectrum of the vast majority of organic donor materials and by thermalization losses due to electronic mismatching, respectively.[3-5] The tandem solar cell design is one of the most promising concepts to mitigate these limitations.[6-9] Theoretical predictions based on already proven device parameters of short-circuit current density (J_{sc}), fill factor (FF) and V_{oc} point to possible power conversion efficiencies (PCEs) of >20% using multi-layer tandem stacks.[9] Recently, triple-junction devices with 11.5% and 12% conversion efficiency have been announced by Yang Yang's group[10] and by Heliatek,[11] respectively, which clearly states the potential of this technology.

---

[a] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a, 91058 Erlangen, Germany

[b] Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstraße 7, 91058 Erlangen, Germany. E-mail: michael.salvador@fau.de; George.Spyropoulos@zae-bayern.de

[c] Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ee02582b

‡ These authors contributed equally to this work.

Water Ingress in Encapsulated Inverted Organic Solar Cells: Correlating Infrared Imaging and Photovoltaic Performance

Jens Adams, Michael Salvador, Luca Lucera, Stefan Langner, George D. Spyropoulos, Frank W. Fecher, Monika M. Voigt, Simon A. Dowland, Andres Osvet, Hans-Joachim Egelhaaf, and Christoph J. Brabec*

Understanding the degradation and failure mechanisms of organic photovoltaic devices is a key requirement for this technology to mature toward a reliable product. Here, a report on accelerated temperature and moisture long-term stability testing (>20 000 h) of inverted and glass-encapsulated poly(3-hexylthiophene)/phenyl-C_{61}-butyric acid methyl ester solar cells is presented. The degradation kinetics using the Arrhenius model is analyzed and the activation energy for the diffusion of water is measured to be ≈43 kJ mol^{-1}. Through comparison of electroluminescence imaging, lock-in thermography, and photoluminescence mapping, the device performance is correlated with the loss of effective cell area and it is shown that the reaction of water at the hole extraction/active layer interface is likely to be the dominant cause for long-term device failure. The diffusion of water through the packaged solar cell using classical diffusion theory is described here. Based on an analytical solution of a simple diffusion model, the diffusion coefficient is estimated to be 4×10^{-13} m^2 s^{-1} and a shelf life of 100 000 h is anticipated at 65 °C/85% RH using a 9.3 cm wide protective adhesive rim. The findings of this study may inform strategies for predicting lifetimes of organic solar cells and modules based on local in situ tracking of moisture-induced device performance loss using IR imaging.

1. Introduction

Due to intense efforts over the last 10 years, solar cells and modules based on organic absorber materials have experienced a steady increase in power conversion efficiency (PCE).[1] Record PCEs for single cell organic photovoltaics (OPVs) above 10% and of about 12% for tandem OPVs are reported and 21% are predicted.[2–4]

The prospect of implementing fully solution based device fabrication makes this solar technology uniquely suited for roll-to-roll printing applications with potentially very low costs.[5,6] In addition to the need for higher efficiencies, the long-term stability of OPVs is essential for practical and economically viable outdoor applications.[7] Investigating the underlying degradation mechanisms and macroscopic defects in organic solar cells is thus an indispensable condition for achieving competitive lifetimes.[8]

Several research groups have provided fundamental insight into different aspects affecting the aging process of organic solar cells and modules. In this context, the blend poly(3-hexylthiophene)/phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM) has been an important model system.[9–14] It is still one of the most widely employed high band gap polymer blends, e.g., for tandem OPVs, because of its reliable photovoltaic performance and processability in air. Multiple degradation routes have been identified in operating devices featuring P3HT:PCBM, which are related to the influence of ambient conditions (temperature, moisture, oxygen) in combination with light but also to material diffusion, and physical stress.[9,10,15,17–24] More recently, the focus has been shifted toward correlating photochemical degradation reactions, such as photobleaching of the polymer,[9,25,26] fullerene dimerization,[27] cross-linking of photoactive components,[28] and interfacial reactions, with the observation of trap states[18,29,30] and charge carrier accumulation in the bulk and at the electrode interfaces of photovoltaic devices.[31,32]

While elucidating the relationship between observed performance loss and cause is often difficult, the underlying

---

J. Adams, L. Lucera, G. Spyropoulos, F. W. Fecher, Dr. M. M. Voigt, Dr. H.-J. Egelhaaf, Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Solar Factory of the Future
Fürther Str. 250, 90429 Nürnberg, Germany
E-mail: jens.adams@zae-bayern.de

Dr. M. Salvador, S. Langner, Dr. M. M. Voigt, Dr. A. Osvet, Prof. C. J. Brabec
Institute of Materials for Electronics and Energy Technology (i-MEET)
Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)
Martensstraße 7, 91058 Erlangen, Germany

Dr. M. Salvador
Instituto de Telecomunicações
Instituto Superior Técnico
Av. Rovisco Pais, P-1049-001 Lisboa, Portugal

Dr. S. A. Dowland
Belectric OPV GmbH
Landgrabenstr. 94, 90443 Nürnberg, Germany

DOI: 10.1002/aenm.201501065

A Universal Interface Layer Based on an Amine-Functionalized Fullerene Derivative with Dual Functionality for Efficient Solution Processed Organic and Perovskite Solar Cells

Hamed Azimi, Tayebeh Ameri, Hong Zhang, Yi Hou, Cesar Omar Ramirez Quiroz, Jie Min, Mengyao Hu, Zhi-Guo Zhang,* Thomas Przybilla, Gebhard J. Matt, Erdmann Spiecker, Yongfang Li, and Christoph J. Brabec*

The emergence of novel and efficient solution processed organic and organic–inorganic hybrid absorber semiconducting materials exhibits the promising path to ubiquitous and low-cost solar cells.[1–5] An interesting class of solution-processable materials suitable for solar energy conversion is the inorganic–organic perovskites that displayed a remarkable boost in device efficiency within the last two years.[5–7] With regard to the performance optimization of solar cells, one of the grand challenges is to control the interfacial losses at the interface of the photoactive layer with the hole or electron extracting electrode. In this context, the establishment of stable and universal interface layers that provide full functionality and junction selectivity for different solution processed semiconductors is of paramount importance. The opportune selection of interface materials provides a platform to systematically control the work function (WF), surface energy, and recombination induced by surface states and/or imperfections.[8–10] For instance, it is shown that the direction of the vertical segregation in organic bulk-heterojunction (oBHJ) can be effectively controlled by modifying the surface energy.[11] Another popular approach is the employment of surface modifiers that create interface dipoles and shift the WF of the conductor.[8] Here, we report the use of a chemisorbed dipolar interface layer, based on an amine functionalized fullerene derivative, (DMAPA-C_{60}, chemical structure is shown in **Figure 1a**, synthetic route is previously described by Zhang et al.[12], which effectively reduces surface recombination at the electron selective interface of various semiconductor types. Although our focus is mainly dedicated to the organometallic halide perovskite devices, we also demonstrate the functionality of this surface modifier in oBHJ solar cells. We show that, depending on the device architecture and the photoactive material systems, DMAPA-C_{60} enhances the performance of organic as well as perovskite solar cells. DMAPA-C_{60} is processed under ambient conditions from environmentally friendly solvents, such as alcohols, guaranteeing compatibility with the large-scale printing techniques. Previous work demonstrated that surface modifiers based on various aliphatic amine functionalized polymers markedly reduce the WF of various metals, transparent conductive metal oxides as well as conducting polymers.[13] It is also shown that the surface modifiers based on fullerene C_{60} can modulate the electronic and orbital interactions with subsequently deposited interfaces.[14–16] Figure 1a depicts the schematics of the $CH_3NH_3PbI_{3-x}Cl_x$ perovskite solar cell architecture. The device structure is based on a planar heterojunction that employs phenyl-C61-butyric acid methyl ester ($PC_{60}BM$) and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) (PEDOT:PSS) as electron and hole transporting interface layers, respectively. The possibility of implementing mixed halide $CH_3NH_3PbI_{3-x}Cl_x$ in planar p–i–n heterojunction configurations is directly related to high charge carrier diffusion lengths (larger than 1 μm) in this material system.[17,18] Such remarkably high diffusion lengths arise from small effective masses for electrons and holes, caused by a strong s–p antibonding coupling in halide perovskites.[19,20] Figure 1c shows a cross-sectional scanning electron microscopy (SEM) image of the complete device comprising a 350-nm-thick mixed halide

---

Dr. H. Azimi, Dr. T. Ameri, H. Zhang, Y. Hou,
C. O. R. Quiroz, J. Min, M. Hu, Dr. G. J. Matt,
Prof. C. J. Brabec
Institute of Materials for Electronics
and Energy Technology (i-MEET)
Department of Materials Science and Engineering
Friedrich-Alexander University Erlangen-Nuremberg
Martensstrasse 7, 91058 Erlangen, Germany
E-mail: hamed.azimi@fau.de

H. Zhang, Y. Hou
Erlangen Graduate School in Advanced Optical Technologies (SAOT)
Paul-Gordan-Straße 6
91052 Erlangen, Germany

Dr. Z.-G. Zhang, Prof. Y. Li
CAS Key Laboratory of Organic Solids
Institute of Chemistry
Chinese Academy of Sciences
Beijing 100190 China
E-mail: zgzhangwhu@iccas.ac.cn

T. Przybilla, Prof. E. Spiecker
Center for Nanoanalysis and Electron Microscopy
Friedrich-Alexander-Universität Erlangen-Nürnberg
Cauerstraße 6, 91058 Erlangen, Germany

Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Haberstr. 2a, 91058 Erlangen, Germany

DOI: 10.1002/aenm.201401692

AELM201500040(201500040)

ADVANCED ELECTRONIC MATERIALS

Elucidating the Excited-State Properties of $CuInS_2$ Nanocrystals upon Phase Transformation: *Quasi*-Quantum Dots Versus Bulk Behavior

By Hamed Azimi, Susanne Kuhri, Melissa S. Stahl, Yi Hou, Dirk M. Guldi, and Christoph J. Brabec*

Keywords: chalcopyrite, $CuInS_2$ nanocrystals, exciton generation, localized surface plasmon resonance, transient absorption spectroscopy

New insights into the complex relation between the thermal phase transformation and the excited state properties of chalcopyrite $CuInS_2$ nanocrystals (CIS NCs) are presented. An in situ solution processing method via depositing molecular precursors is applied, offering advantages in terms of simplicity, low-temperature processability, and control over crystallite size, and optical properties. At low annealing temperatures, strong carrier quantum confinement and small crystallite sizes are realized for CIS NC films. CIS crystal growth is found to set in at higher annealing temperatures inducing a complete transformation from quasi-quantum-dot (QD) via bulk-like to bulk behavior. The transition of a near-infrared localized surface plasmon resonance (LSPR) towards a bulk-like plasmon resonance documents the crystal growth and further acts as a valuable probe to relate crystallite size with copper-deficient stoichiometries. In addition, time-resolved photophysical investigations help to shed light on the dynamics and mechanisms of exciton and charge carrier generation of CIS NC films as a function of annealing temperature. The in situ-prepared CIS NC films are further passivated by a thin CdS layer, leading to the formation of long-lived excitons and an effective CIS ground-state depletion.

1. Introduction

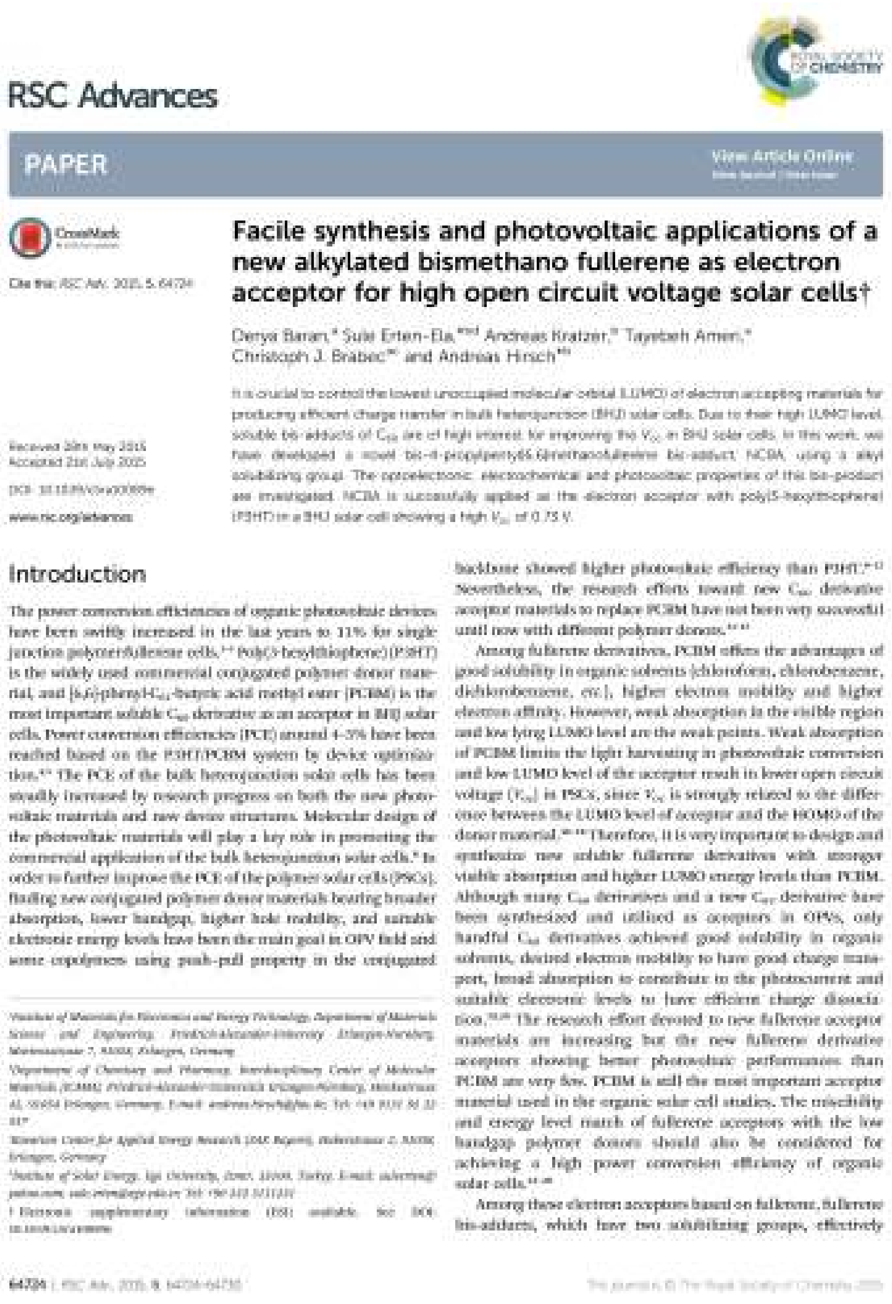
The chalcopyrite nanocrystals (NCs) of $CuInS_2$ (CIS), $CuInSe_2$ (CISe), and $\mathrm{CuIn1-xGa_xS_{2-y}Se_y}$ (CIGSSe) ($0 \le x \le 1$, $0 \le y \le 2$) have recently drawn a great deal of attention as potential absorber materials for low-cost solar cells.[1–5] The current fabrication methods of high-efficient solution processed chalcopyrite solar cells involve; however, the use of toxic solvents and/or complex post-crystallization processes in the presence of toxic gases.[6–7] Among various solution processing methods, the in situ synthesis via deposition of molecular precursor solution is regarded as the most promising technique to produce low-cost absorber layers.[8–10] It offers advantages in terms of processing simplicity, low-temperature processability, and easier control over stoichiometry.[11–12]

In chalcopyrites solar cells, a sound understanding of the relation between defects and secondary phases, on one hand, and mechanistic insights into charge generation and charge recombination, on the other hand, is of key importance to improve device performances. Previous work demonstrated that indium-on-copper-antisites ($\mathrm{In_{Cu}}$) and copper vacancies ($\mathrm{V_{Cu}}$) are the dominant donors and acceptor defects, respectively, in ternary chalcopyrite CIS and CISe.[13,14] Owing to the energetically favorable compensations between $\mathrm{V_{Cu}}$ and $\mathrm{In_{Cu}}$, the formation of defect clusters like $[2\mathrm{V_{Cu}}+\mathrm{In_{Cu}}]$ is likely to

---

H. Azimi, M. S. Stahl, Y. Hou, C. J. Brabec, Institute of Materials for Electronics and Energy Technology (i-MEET), Department of Materials Science and Engineering, Friedrich-Alexander University Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany
(E-mail: hamed.azimi@fau.de)
S. Kuhri, D. M. Guldi, Department of Chemistry and Pharmacy and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-University Erlangen-Nuremberg, Egerlandstr. 3 91058 Erlangen, Germany
Y. Hou, Erlangen Graduate School in Advanced Optical Technologies (SAOT), Paul-Gordan-Straße 6 91052 Erlangen, Germany
C. J. Brabec, Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstr. 2a 91058 Erlangen, Germany
Correspondence to: H. Azimi (E-mail: hamed.azimi@fau.de)

10.1002/aelm.201500040



RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: RSC Adv., 2015, 5, 64724

Facile synthesis and photovoltaic applications of a new alkylated bismethano fullerene as electron acceptor for high open circuit voltage solar cells†

Derya Baran,[a] Sule Erten-Ela,*[acd] Andreas Kratzer,[b] Tayebeh Ameri,[a] Christoph J. Brabec[ac] and Andreas Hirsch*[b]

Received 28th May 2015
Accepted 21st July 2015

DOI: 10.1039/c5ra09869e

www.rsc.org/advances

It is crucial to control the lowest unoccupied molecular orbital (LUMO) of electron accepting materials for producing efficient charge transfer in bulk heterojunction (BHJ) solar cells. Due to their high LUMO level, soluble bis-adducts of C_{60} are of high interest for improving the V_{OC} in BHJ solar cells. In this work, we have developed a novel 'bis-(1-propylpentyl)6,6-dimethanofullerene' bis-adduct, NCBA, using a alkyl solubilizing group. The optoelectronic, electrochemical and photovoltaic properties of this bis-product are investigated. NCBA is successfully applied as the electron acceptor with poly(3-hexylthiophene) (P3HT) in a BHJ solar cell showing a high V_{OC} of 0.75 V.

Introduction

The power conversion efficiencies of organic photovoltaic devices have been swiftly increased in the last years to 11% for single junction polymer/fullerene cells.[1–4] Poly(3-hexylthiophene) (P3HT) is the widely used commercial conjugated polymer donor material, and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) is the most important soluble C_{60} derivative as an acceptor in BHJ solar cells. Power conversion efficiencies (PCE) around 4–5% have been reached based on the P3HT/PCBM system by device optimization.[5,6] The PCE of the bulk heterojunction solar cells has been steadily increased by research progress on both the new photovoltaic materials and new device structures. Molecular design of the photovoltaic materials will play a key role in promoting the commercial application of the bulk heterojunction solar cells.[7] In order to further improve the PCE of the polymer solar cells (PSCs), finding new conjugated polymer donor materials bearing broader absorption, lower bandgap, higher hole mobility, and suitable electronic energy levels have been the main goal in OPV field and some copolymers using push–pull property in the conjugated backbone showed higher photovoltaic efficiency than P3HT.[8–12] Nevertheless, the research efforts toward new C_{60} derivative acceptor materials to replace PCBM have not been very successful until now with different polymer donors.[13–15]

Among fullerene derivatives, PCBM offers the advantages of good solubility in organic solvents (chloroform, chlorobenzene, dichlorobenzene, etc.), higher electron mobility and higher electron affinity. However, weak absorption in the visible region and low lying LUMO level are the weak points. Weak absorption of PCBM limits the light harvesting in photovoltaic conversion and low LUMO level of the acceptor result in lower open circuit voltage (V_{oc}) in PSCs, since V_{oc} is strongly related to the difference between the LUMO level of acceptor and the HOMO of the donor material.[16–18] Therefore, it is very important to design and synthesize new soluble fullerene derivatives with stronger visible absorption and higher LUMO energy levels than PCBM. Although many C_{60} derivatives and a new C_{70} derivative have been synthesized and utilized as acceptors in OPVs, only handful C_{60} derivatives achieved good solubility in organic solvents, desired electron mobility to have good charge transport, broad absorption to contribute to the photocurrent and suitable electronic levels to have efficient charge dissociation.[19–21] The research effort devoted to new fullerene acceptor materials are increasing but the new fullerene derivative acceptors showing better photovoltaic performances than PCBM are very few. PCBM is still the most important acceptor material used in the organic solar cell studies. The miscibility and energy level match of fullerene acceptors with the low bandgap polymer donors should also be considered for achieving a high power conversion efficiency of organic solar cells.[22–26]

Among these electron acceptors based on fullerene, fullerene bis-adducts, which have two solubilizing groups, effectively

---

[a] Institute of Materials for Electronics and Energy Technology, Department of Materials Science and Engineering, Friedrich-Alexander-University Erlangen-Nürnberg, Martensstrasse 7, 91058, Erlangen, Germany

[b] Department of Chemistry and Pharmacy, Interdisciplinary Center of Molecular Materials (ICMM), Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, 91054 Erlangen, Germany. E-mail: andreas.hirsch@fau.de; Tel: +49 9131 85 22 [illegible]

[c] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstrasse 2, 91058 Erlangen, Germany

[d] Institute of Solar Energy, Ege University, Bornova, 35100, Izmir, Turkey. E-mail: [illegible]; Tel: +90 232 3111231

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra09869e

THE JOURNAL OF
PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Role of Polymer Fractionation in Energetic Losses and Charge Carrier Lifetimes of Polymer: Fullerene Solar Cells

Derya Baran,*,† Michelle S. Vezie,‡ Nicola Gasparini,† Florent Deledalle,‡ Jizhong Yao,‡
Bob C. Schroeder,§ Hugo Bronstein,§ Tayebeh Ameri,† Thomas Kirchartz,∥,⊥ Iain McCulloch,§
Jenny Nelson,‡ and Christoph J. Brabec†,¶

†Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander University of Erlangen-Nuremberg, Martensstraße 7, 91058 Erlangen, Germany

‡Center for Plastic Electronics, Department of Physics and §Center for Plastic Electronics, Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom

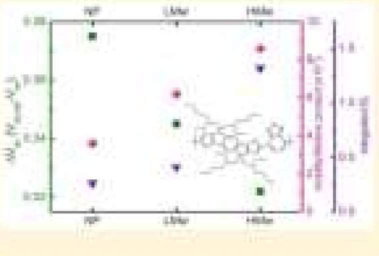
∥IEK5-Photovoltaics, Forschungszentrum Jülich, 52425 Jülich, Germany

⊥Faculty of Engineering and CENIDE, University of Duisburg-Essen, Carl-Benz-Straße 199, 47057 Duisburg, Germany

¶Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstrasse 2a, 91058 Erlangen, Germany

Supporting Information

ABSTRACT: Nonradiative recombination reduces the open-circuit voltage relative to its theoretical limit and leads to reduced luminescence emission at a given excitation. Therefore, it is possible to correlate changes in luminescence emission with changes in open-circuit voltage and in the charge carrier lifetime. Here we use luminescence studies combined with transient photovoltage and differential charging analyses to study the effect of polymer fractionation in indacenodithiophene-co-benzothiadiazole (IDTBT):fullerene solar cells. In this system, polymer fractionation increases electroluminescence emission at the same injection current and reduces nonradiative recombination. High-molecular-weight and fractionated IDTBT polymers exhibit higher carrier lifetime−mobility product compared to that of their nonfractionated analogues, resulting in improved solar cell performance.



INTRODUCTION

In polymer:fullerene solar cells, the open-circuit voltage (V_{oc}) is usually limited by recombination at the interface between donor and acceptor. Thus, it varies with the energy difference between the highest occupied molecular orbital of the donor ($HOMO_D$) and the lowest unoccupied molecular orbital of the acceptor ($LUMO_A$).[1−3] In practice, the $HOMO_D - LUMO_A$ difference is insufficient to predict V_{oc} because of differences in nonradiative recombination.[4] The highest possible V_{oc} denoted $V_{oc,rad}$ can be achieved only when (a) radiative recombination occurs and (b) the absorbed photon flux is balanced exactly by the emitted flux under open-circuit conditions; this is called the radiative limit.[5−10] In a practical solar cell, both V_{oc} and the LED quantum efficiency, Q_{LED}, are reduced relative to their thermodynamic limits by nonradiative recombination pathways, the degree of which can be quantified via a reciprocity theorem.[11−17] Therefore, it is of high interest in the field of organic photovoltaics to reduce these nonradiative recombination losses, thereby bringing V_{oc} closer to the radiative limit. Recently, indacenodithiophene (IDT) copolymers have shown promising field-effect transistor mobilities and solar cell performance.[18−22] Enhanced coplanarity of the polymer backbone has been hypothesized to lead to reduced energetic disorder.[23,24] IDT-co-benzothiadiazole polymers have achieved up to 6.5% PCE with device optimization and material purification.[25] The role of polymer molecular weight on solar cell performance has been well studied;[26−29] however, the detailed analysis of the recombination processes in fractionated polymer devices remains comparatively unexplored.[28,30]

In this work, we describe how fractionation has an impact on energetic losses and charge transport in IDTBT:$PC_{70}BM$ bulk-heterojunction (BHJ) solar cells. In particular, we use the reciprocity relation between nonradiative recombination and electroluminescence to explain the reduced energetic losses in IDTBT-HMW:$PC_{70}BM$ solar cells induced by fractionation and higher molecular weight by combining electroluminescence spectroscopy (EL) and Fourier-transform photocurrent spectroscopy (FTPS). The degree of nonradiative recombination, defined as the difference between $V_{oc,rad}$ and V_{oc} and denoted $\Delta V_{oc,nr}$, is found to decrease upon fractionation and with

Received: June 15, 2015
Revised: August 7, 2015
Published: August 18, 2015

DOI: 10.1021/acs.jpcc.5b05709
J. Phys. Chem. C 2015, 119, 19668−19673

Solution-Processable Organic Solar Cells

Christoph J. Brabec[a,b] **and Tayebeh Ameri**[a]
[a]Friedrich-Alexander University Erlangen-Nürnberg, Materials for Electronics and Energy
Technology, Department of Materials Science and Engineering, Martensstrasse 7,
91058 Erlangen, Germany
[b]Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstr. 2a,
91058 Erlangen, Germany

This special section of JPE focuses on the science and technology of organic solar cells. Tremendous progress has been made in the synthesis and production of organic solar cells. Companies like Merck, BASF, Polyera, etc. have started to commercialize organic semiconducting materials, while companies like BELECTRIC OPV, Heliatek, and others have begun commercialization of organic solar modules.

Compared to inorganic solar cells, organic photovoltaics (OPVs) offer many advantages, such as low cost, high throughput production, flexible devices, and lightweight products, as well as custom-designed colors. On the down side, OPVs still have significantly lower efficiency values and lifetime expectations as compared to their inorganic counterparts. Nevertheless, the most recent NREL-certified power conversion of 10.5% reported by UCLA, and the record conversion efficiency of 11.8% reported by Kyung Hee University position OPVs as the next generation of solar cells and a follow-up technology for thin film inorganic PVs.

Several things need to take place in order to achieve higher efficiency and longer lifetime. For example, stable and low bandgap semiconductors are required, and they must have excellent charge carrier transport properties, as well as implementation of more advanced approaches such as tandem and ternary solar cells. It is also necessary to find ways to control the microstructure in bulk heterojunction composites. In addition, efficient and environmentally stable interface materials must be developed. Finally, a cost-efficient and long-time stable packaging process needs to be established. For the final product release, light propagation and light management needs to become integrated into organic solar modules.

The papers presented in this special section are a small snapshot of the evolving and ongoing progress in this field, addressing aforementioned issues and challenges.

Christoph J. Brabec holds the chair of Materials for Electronics and Energy Technology (i-MEET) at the Materials Science Department of the Friedrich Alexander University Erlangen-Nürnberg. He is the scientific director of the Erlangen division of the Bavarian Research Institute for Renewable Energy (ZAE Bayern, Erlangen), a board member of the ZAE Bavaria, and a board member of the Energy Campus Nürnberg. He received his PhD in 1995 in physical chemistry from Linz University. His research interests are organic photovoltaics, all aspects of solution-processed semiconductors, and technologies for renewable energy scenarios.

Tayebeh Ameri is a postdoctoral research fellow in the group of Prof. Brabec in the chair of Materials for Electronics and Energy Technology (i-MEET) at the Friedrich-Alexander University Erlangen-Nürnberg, where she leads the organic photovoltaics team. She studied physics and solid state physics at Isfahan University of Technology and Ferdowsi University of Mashhad, Iran. In early 2007, she joined Konarka Austria to study for a PhD and received her PhD in engineering sciences from Johannes Kepler University of Linz in 2010. Her main research interests include investigation and development of organic and hybrid solar cells.

Thin Solid Films 582 (2015) [illegible]

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

In-situ X-ray diffraction analysis of the recrystallization process in Cu_2ZnSnS_4 nanoparticles synthesised by hot-injection

Marco Brandl [a,*], Rameez Ahmad [b], Monica Distaso [b], Hamed Azimi [c], Yi Hou [c], Wolfgang Peukert [b], Christoph J. Brabec [c], Rainer Hock [a]

[a] Chair for Crystallography and Structural Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg, [illegible], Germany
[b] Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, [illegible], Germany
[c] Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-Universität Erlangen-Nürnberg, [illegible], Germany

ARTICLE INFO

Available online 30 October 2014

Keywords:
Thin film solar
Copper zinc tin sulphide
Hot-injection synthesis
In-situ X-ray diffraction
Cubic phase
Tetragonal phase

ABSTRACT

Kesterite Cu_2ZnSnS_4 (CZTS) is a promising material for thin film solar cell applications. The biggest advantages of this compound lie in the abundance and non-toxicity of the contained elements. Low temperature hot-injection synthesis can provide an economic way to produce CZTS nanoparticles for application in solution processed solar cells. Powder X-ray diffraction (PXRD) measurements on the as-synthesised particles suggest that the crystal structure for this material can be best described as sphalerite-like. This means that the cations in the [illegible] structure. An in-situ PXRD [illegible] annealing of the particles up to 550 °C. The [illegible] recrystallization process [illegible] transforms the structure from cubic to tetragonal including an ordering of the cations.

1. Introduction

In recent research for thin film photovoltaics, the chalcogenide material Cu_2ZnSnS_4 (CZTS) has attracted interest as a potential future absorber material in photovoltaics. The interest in CZTS is driven by its high absorption coefficient of visible light, earth abundant and mostly non-toxic constituting elements and the possibility to tune the band gap by substitution of chemically similar elements like tin by germanium or sulphur by selenium or tellurium [1]. Many techniques to prepare CZTS absorber layers have been established, including vacuum deposition like sputtering, evaporation or solution based methods using for example molecular precursors or nanoparticles [2,3]. Nanoparticle approaches hold the potential to reduce the required synthesis temperatures and in consequence the costs for the production of solar cells. Using CZTSSe as the absorber material, cells with efficiency of 12.6% have been achieved [4]. Concerning CZTS, there is a major issue connected with the synthesis of absorber layers free of unwanted secondary phases such as zinc sulphide, copper sulphides and ternary phases like copper tin sulphide forming during the reaction. Second, there is a stability problem of CZTS at elevated temperatures arising during the post-processing of CZTS thin films: synthesis temperatures often are close to the decomposition temperature of CZTS. If the sulphur pressure is too low, it was shown that CZTS decomposes via the reaction [5]:

$$Cu_2ZnSnS_4 \rightarrow Cu_2S + ZnS + SnS + S. \quad (1)$$

Furthermore, CZTS can crystallise in two tetragonal structures, the kesterite structure with space group $I\bar{4}$ and the stannite structure with the space group $I\bar{4}2m$ [2,7]. The main difference between these structures is the arrangement of Cu and Zn in the unit cell [7]. CZTS can also crystallise in a hexagonal wurtzite type structure in the space group $P6_3mc$ [8]. Via an order–disorder phase transition kesterite adopts the cubic sphalerite structure (space group $F\bar{4}3m$) at temperatures above 877 °C [9]. This means that the three metal cations Cu, Zn and Sn randomly occupying a single crystallographic site in space group $F\bar{4}3m$.

In this experiment, we have used X-ray powder diffraction (PXRD) to investigate the crystal structure of CZTS nanoparticles after synthesis by hot-injection, and during annealing in inert gas atmosphere at temperatures up to 550 °C.

2. Experimental details

The CZTS nanoparticles were synthesised by a hot-injection method similar to the one described in [10] and [11]. A solution of elemental sulphur is injected into a solution of $Zn(Ac)_2$, [illegible], $CuCl_2$ and $SnCl_2$ [illegible] at a temperature of 225 °C. Details of the synthesis protocol can be found in [12]. After synthesis the particles were isolated by centrifugation at 4000 rpm for 10 min, washed twice through centrifugation and redispersion cycles with methanol/chloroform and finally air dried to get powder. The dried powder was used in the diffraction experiments.

PXRD measurements were carried out on nanoparticulate CZTS in powder form on the as-synthesised particles, as well as during and after annealing up to 550 °C. The measurements done before and after

---

[*] Corresponding author.

http://dx.doi.org/10.1016/j.tsf.2014.10.[illegible]
0040-6090/© 2014 Elsevier B.V. All rights reserved.

Printable Dielectric Mirrors with Easily Adjustable and Well-Defined Reflection Maxima for Semitransparent Organic Solar Cells

Carina Bronnbauer, Julian Hornich, Nicola Gasparini, Fei Guo, Benjamin Hartmeier, Norman A. Luechinger, Christoph Pflaum, Christoph J. Brabec, and Karen Forberich*

Building integrated semitransparent thin-film solar cells is a strategy for future eco-friendly power generation. Organic photovoltaics in combination with dielectric mirrors (DMs) are a potential candidate as they promise high efficiencies in parallel to the possibility to adjust the color and thus the transparency of the whole device. A fully solution processed and printable DM with an easily adjustable reflection maximum is presented that can be facilely attached to solar cells. The DM is optimized via optical simulations to the particular needs of the device with regard to photocurrent enhancement. The excellent agreement between experimental and theoretical results confirms the high optical quality of the printed layers with respect to homogeneity and surface roughness. The used inks are organic–inorganic nanocomposites with a large refractive index contrast of ~0.7. The short-circuit current is enhanced by up to ~24% for a semitransparent polymer solar cell.

1. Introduction

Semitransparent thin-film photovoltaics are a competitive photovoltaic technology to supply our global energy demand.[1] Besides the development towards high power conversion efficiencies (PCE) and printability, such devices supply high transparencies and even offer the possibility to adapt the absorption spectrum to a desired color by the use of different photoactive materials.[illegible] These characteristics enable the production of power generating smart windows, awnings, building facades etc.[illegible] Still, semitransparent solar cells show lower efficiencies than their opaque counterparts due to the inherent tradeoff between transmission and absorption. To overcome this problem different light trapping approaches such as microcavities, dielectric scatters, microlenses, and wavelength selective mirrors have been investigated.[illegible] Particularly the last approach allows to precisely adjust the transparency as well as the color of a device. Wavelength selective filters are also known as 1D photonic crystals, Bragg mirrors or dielectric mirrors (DMs). The working principle of DMs relies on constructive or destructive interference of thin layers. For this purpose, a high refractive index (HRI) and a low refractive index (LRI) material have to be arranged alternatingly and fulfill the equation $n_{\mathrm{HRI}}d_{\mathrm{HRI}} = n_{\mathrm{LRI}}d_{\mathrm{LRI}} = \frac{\lambda_0}{4}$, with n being the refractive index (RI), d being the layer thickness, and λ_0 being the wavelength with maximum reflection at perpendicular incidence. An high RI contrast is desirable as this leads to a broad stopband with a large reflection at λ_0.[illegible] The production of a DM, however, is challenging as only slight variations in layer thicknesses cause a shift in λ_0 (see Figure S1, Supporting Information). Conventional techniques for DM fabrication are evaporation of inorganic materials under high vacuum conditions, electron beam evaporation, and magnetron sputtering.[illegible] However, polymers or organic–inorganic nanocomposites are much more promising because they allow a controlled variation of n, better processability, and highly flexible films.[illegible] Methods such as spin coating or dip coating can be carried out with these ink-based materials.[illegible] However, while these techniques allow precise settings in layer thickness, they only offer limited potential with respect to commercial and large-area processing as they are cost-intensive and difficult in terms of upscaling. In addition, DMs directly processed on the top of solar cells further complicate the whole device structure. For example, up to 16 additional layers are necessary to increase the short-circuit current (J_{sc}) by ~20% compared to a device without DM.[illegible]

C. Bronnbauer, J. Hornich, N. Gasparini, F. Guo, Prof. C. J. Brabec, Dr. K. Forberich
Institute of Materials for Electronics and Energy Technology (i-MEET)
Friedrich-Alexander-Universität Erlangen-Nürnberg
Martensstrasse 7, 91058 Erlangen, Germany
E-mail: Carina.Bronnbauer@fau.de

C. Bronnbauer, J. Hornich
Erlangen Graduate School in Advanced Optical Technologies (SAOT)
Friedrich-Alexander-Universität Erlangen-Nürnberg
Paul-Gordan-Strasse 6, 91052 Erlangen, Germany

J. Hornich, Prof. C. Pflaum
Department of Computer Science 10 (LSS)
Friedrich-Alexander-Universität Erlangen-Nürnberg
Cauerstr. 11, 91058 Erlangen, Germany

B. Hartmeier, Dr. N. A. Luechinger
Nanograde Ltd
Laubisrütistrasse 50, 8712 Stäfa, Switzerland

Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Haberstrasse 2a, 91058 Erlangen, Germany

DOI: 10.1002/adom.201500216

Volume 9, Issue 12, 27 November 2015, Pages 843-848

nature photonics

ARTICLES

| DOI: 10.1038/NPHOTON.2015.216

X-ray imaging with scintillator-sensitized hybrid organic photodetectors

Patric Büchele[1,2]*, Moses Richter[3], Sandro F. Tedde[1], Gebhard J. Matt[3], Genesis N. Ankah[4], Rene Fischer[1,3], Markus Biele[1,3], Wilhelm Metzger[1], Samuele Lilliu[5], Oier Bikondoa[6], J. Emyr Macdonald[7], Christoph J. Brabec[3], Tobias Kraus[4], Uli Lemmer[2] and Oliver Schmidt[1]*

Medical X-ray imaging requires cost-effective and high-resolution flat-panel detectors for the energy range between 20 and 120 keV. Solution-processed photodetectors provide the opportunity to fabricate detectors with a large active area at low cost. Here, we present a disruptive approach that improves the resolution of such detectors by incorporating terbium-doped gadolinium oxysulfide scintillator particles into an organic photodetector matrix. The X-ray induced light emission from the scintillators is absorbed within hundreds of nanometres, which is negligible compared with the pixel size. Hence, optical crosstalk, a limiting factor in the resolution of scintillator-based X-ray detectors, is minimized. The concept is validated with a 256 × 256 pixel detector with a resolution of 4.75 lp mm^{-1} at a MTF = 0.2, significantly better than previous stacked scintillator-based flat-panel detectors. We achieved a resolution that proves the feasibility of solution-based detectors in medical applications. Time-resolved electrical characterization showed enhanced charge carrier mobility with increased scintillator filling, which is explained by morphological changes.

Today's most common flat-panel X-ray detectors for medical imaging consist of a scintillator that converts X-ray photons into light and a photodetector array made out of amorphous silicon[1,2]. The light emitted from the scintillator then propagates isotropically from the point of generation. This causes optical crosstalk between pixels, resulting in a low resolution. In addition to optical crosstalk, the detectors resolution is also limited by pixel size and electrical crosstalk due to trapped charges[3], for example. The resolution can be determined with the modulation transfer function (MTF), which describes the detectors' ability to transfer the input signal modulation of a given spatial frequency in relation to its output. An MTF value of 1 indicates the perfect detection of a given spatial frequency. To compare different detectors, it is practicable to determine the value of the spatial frequency *f* (measured in linepairs (lp) per mm) at which the MTF drops to 0.2. Advanced scintillators, such as thallium-doped cesium iodide (CsI:Tl), have a needle-type structure that behaves like a waveguide and decreases the optical crosstalk[4], resulting in f = 2–3 lp mm^{-1} at MTF = 0.2, depending on the thickness of the CsI:Tl[5]. However, CsI:Tl deposition is an expensive process and the material loses its crystal structure when exposed to humidity[5].

Direct-conversion detectors consist of a semiconductor material such as amorphous selenium (a-Se) that provides a high intrinsic X-ray absorption coefficient[6]. Because X-rays generate charges directly inside the semiconductor, these detectors have almost no optical crosstalk. While their resolution can be very high, it is limited by pixel size, electrical crosstalk and the operating electrical field. Current a-Se detectors have achieved f = 4.75 lp mm^{-1} at MTF = 0.2 (ref. 7). The field dependence of the ionization energy and the weak X-ray absorption necessitate thick layers, which result in very high operating voltages to achieve the electrical field required for an efficient charge extraction (~30 V μm^{-1}) (ref. 8).

Recently, several concepts have been proposed to leverage the advantages of organic semiconductors in medical flat-panel X-ray detectors requiring a size of up to 43 × 43 cm^2 (ref. 9). Organic photodiodes (OPDs) are attractive and cost-effective for this application as they can be processed from the solution phase over large, and even flexible, substrates[10,11]. OPD technology is based on an interpenetrating donor–acceptor network of an electron conductor, such as phenyl-C61-butyric acid methyl ester (PCBM), and a hole conductor, such as poly(3-hexylthiophene-2,5-diyl) (P3HT), which is known as a bulk heterojunction (BHJ)[12]. When a photon is absorbed by the BHJ, a Frenkel exciton is generated and can travel to the donor–acceptor interface, where it splits into an electron and a hole. The free charges can diffuse through the donor and acceptor percolation paths and reach their respective electrodes, thus enabling photodetection[13–15].

Appropriate nanoparticles can sensitize the absorption spectrum of pure P3HT:PCBM blends from the near-infrared to the X-ray region. Recently, OPDs have been enhanced with lead sulfide quantum dots for near-infrared detection[16]. Likewise, X-ray detection was demonstrated by adding small amounts of metal nanoparticles into a hole-conducting polymer[17].

Results and discussion

In this Article, we demonstrate that scintillating terbium-doped gadolinium oxysulfide (GOS:Tb) X-ray absorbers in the BHJ create a quasi-direct X-ray detector. The re-emitted photons from the scintillator particles are absorbed by the BHJ very close to the scintillator, minimizing optical crosstalk and enabling a high MTF. Low-cost micrometre-sized scintillator particles are used to achieve an optimum balance between high X-ray absorption and efficient charge extraction. The attenuation of GOS:Tb is above

---

[1]Siemens Healthcare GmbH, Technology Center, 91058 Erlangen, Germany. [2]Light Technology Institute and Institute of Microstructure Technology, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany. [3]Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany. [4]INM – Leibniz Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany. [5]Masdar Institute of Science and Technology, Abu Dhabi 54224, UAE. [6]XMaS, The UK-CRG Beamline, ESRF-The European Synchrotron, CS40220, Grenoble Cedex 9, 38043, France. [7]School of Physics and Astronomy, Cardiff University, Queens Buildings, The Parade, Cardiff CF24 3AA, UK. *e-mail: patric.buechele@gmx.de; schmidt.oliver@siemens.com

Available online at www.sciencedirect.com

ScienceDirect

Solar Energy 120 (2015) 428–439

SOLAR ENERGY

www.elsevier.com/locate/solener

Maximizing concentrated solar power (CSP) plant overall efficiencies by using spectral selective absorbers at optimal operation temperatures

Klaus Burlafinger [a,b], Andreas Vetter [a,b,*], Christoph J. Brabec [a,b,c]

[a] Institute of Materials for Electronics and Energy Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Martensstraße 7, 91058 Erlangen, Germany
[b] Energie Campus Nürnberg (EnCN), Fürther Straße 250, 90429 Nürnberg, Germany
[c] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a, 91058 Erlangen, Germany

Received 17 February 2015; received in revised form 7 July 2015; accepted 8 July 2015

Communicated by: Associate Editor Antoine Bittar

Abstract

Selective absorbers for CSP plants to suppress thermal losses and to increase the efficiency is a promising topic and strong scientific efforts have been spent on how to design and realize such materials. However, there has been no comprehensive optimization analysis of the overall efficiency of CSP plants with selective absorbers.

We performed a comprehensive computational parameter study of operation temperature and optical properties of the absorber and investigated their effect on the overall plant efficiency in dependance of sun light concentration up to $C = 2000$ suns. Optimal operation temperatures were shown not to exceed 1383 K. By using selective absorbers instead of a black body or currently used materials, our assessment yields a potential electrical power output gain of up to around 35%. Our investigations also provide the optical parameters of an ideal (perfect selective) absorber. Its optimal cut off wavelength λ_{cut} lies around 2.4 μm for concentration factors below 120 and above 600 suns. For C in the range of 120–600 suns the value of the cut off wavelength is 1.79 μm. Simulating non-ideal (realistic) absorption properties, it was found that the strongest influence is caused by high absorption at low wavelengths. Low emittance at longer wavelengths plays a less important role. Also the sharpness of the transition from high absorption to low emittance plays a minor role regarding overall plant efficiency. As a rule of thumb, the cut-off wavelength should be at around 2.4 μm when assuming realistic (non-ideal) spectral selectivity. Finally, the theoretical maximum overall efficiency of a CSP plant achievable by an ideal selective absorber was calculated to up to 73% at 2000 suns and even up to 65% for a selective absorber with realistic optical properties.

Keywords: Absorber; Selective; Spectral; CSP; Overall efficiency; Optimal operation temperature

1. Introduction

Because of environmental pollution and the finite nature of resources one of the most urgent challenges of today and tomorrow will be the power supply by renewable energy sources. Therefore, to keep power supply affordable and reliably available, a mix of sun, water and wind exploitation is inevitable. One part of future power generation can be provided by concentrating solar power (CSP)

---

* Corresponding author at: Institute of Materials for Electronics and Energy Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Martensstraße 7, 91058 Erlangen, Germany. Tel.: +49 911 568 54 9204.

E-mail addresses: klaus.burlafinger@fau.de (K. Burlafinger), andreas.vetter@fau.de (A. Vetter), christoph.brabec@ww.uni-erlangen.de (C.J. Brabec).

http://dx.doi.org/10.1016/j.solener.2015.07.023
0038-092X/© 2015 Elsevier Ltd. All rights reserved.

Organic Electronics 19 (2015) 113–118

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Letter

Sub-bandgap photon harvesting for organic solar cells via integrating up-conversion nanophosphors

Wei Chen[a,c,*], Yi Hou[a,c], Andres Osvet[a], Fei Guo[a], Peter Kubis[a,c], Miroslaw Batentschuk[a], Benjamin Winter[d], Erdmann Spiecker[d], Karen Forberich[a], Christoph J. Brabec[a,b,c]

[a] Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander Universität Erlangen-Nürnberg, Martensstrasse 7, 91058 Erlangen, Germany
[b] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a, 91058 Erlangen, Germany
[c] Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich-Alexander Universität Erlangen-Nürnberg, Germany
[d] Center of Nanoanalysis and Electron Microscopy (CENEM), Friedrich-Alexander Universität Erlangen-Nürnberg, Cauerstraße 6, 91058 Erlangen, Germany

ARTICLE INFO

Article history:
Received 17 December 2014
Received in revised form 27 January 2015
Accepted 27 January 2015
Available online 7 February 2015

Keywords:
Organic photovoltaics
Up-conversion
Nanophosphors
IR light harvesting

ABSTRACT

Lanthanide-doped up-conversion nanophosphors were employed as up-conversion converters (UC-converters) combined with organic solar cells (OSCs). The optical properties of the external up-conversion layers were investigated, and the optimized layers were laminated with OSCs. Strong photocurrents were observed when OSCs with an UC converter were illuminated by a NIR laser. An improvement of photocurrent and efficiency were also observed under AM 1.5 G sun irradiation. Our investigations show a proof-of-concept that organic solar cells could utilize sub-bandgap photons via integrating up-conversion nanophosphors, which provide us a promising approach to exceed the efficiency limit of single junction organic solar cells.

Organic solar cells (OSCs) have been extensively investigated due to their promising properties such as solution processability, low cost and light weight over the past decade [1–3]. The photoelectric conversion efficiency of single junction OSCs has recently achieved over 9% [4]. The key part of OSCs is the active layers which are composed of conjugated polymers or small molecules as donors and fullerene derivatives or metal oxide as acceptors [5–7]. The solar radiation is harvested and converted to photocurrent by the donor–acceptor blends. Nevertheless, there is a quest for donors that can effectively harvest the sub-bandgap photons, thus increasing the photocurrent density compared to the currently used donors and also surpass the Shockley-Queisser limit of single threshold organic solar cells. The optical bandgap (E_g) of the most commonly used donors is ~1.5–2.0 eV, allowing them to absorb sunlight only up to ca. 800 nm [8–11].

In order to achieve the harvesting of sub-bandgap photons (NIR and IR regions) of solar spectrum for organic solar cells, several approaches have been developed, such as designing new low band-gap donors [12], inorganic nanocrystals sensitizers [13] or so-called ternary system consisting of two different donors, in which one donor is sensitive to the NIR photons [14]. An alternative approach for improving light-harvesting in the NIR and IR regions is the utilization of up-conversion nanophosphors (UCNPs), which can convert NIR or IR photons into visible photons [15–17]. Recently, rare earth doped up-conversion systems have been integrated into photovoltaic devices to enhance NIR light absorption and performances [18–20]. Among those up-conversion nanophosphors, due to the low phonon energy of lattices, hexagonal $NaYF_4$ (β-$NaYF_4$) crystals have been reported as the most-efficient host material for

---

[*] Corresponding author at: Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander Universität Erlangen-Nürnberg, Martensstrasse 7, 91058 Erlangen, Germany.
E-mail address: wei.chen@fau.de (W. Chen).

http://dx.doi.org/10.1016/j.orgel.2015.01.036

MaterialsViews
www.MaterialsViews.com

ADVANCED MATERIALS
www.advmat.de

High-Performance Organic Solar Cells Based on a Small Molecule with Alkylthio-Thienyl-Conjugated Side Chains without Extra Treatments

Chaohua Cui, Xia Guo, Jie Min, Bing Guo, Xiao Cheng, Maojie Zhang,* Christoph J. Brabec, and Yongfang Li**

Due to their unique advantages of light weight, easy fabrication, and the capability to be fabricated into large area flexible devices, the bulk-heterojunction (BHJ) organic solar cells (OSCs) offer a very promising outlook for low-cost renewable energy technology.[1–3] Photovoltaic performance of OSCs has been significantly improved by a combination of materials innovation, morphology control, and interface engineering.[4–10] Photoactive materials innovation, especially the innovation of donor materials (including conjugated polymers and solution processable conjugated organic small molecules) is one of the key issues currently in the studies of BHJ OSCs. The molecular design of donor materials generally includes engineering their bandgap (reducing bandgap) and energy levels (downshifting HOMO (highest occupied molecular orbital) energy level) to achieve high short-circuit current density (J_{sc}) and higher open-circuit voltage (V_{oc}), improving molecular planarity to enhance interchain interaction for higher hole mobility, controlling well-defined molecular order and restricting crystal size of blend film for efficient charge generation. Remarkable power conversion efficiency (PCE) of over 10% has been achieved recently for polymer-based single-junction OSCs.[11–15]

Compared to their polymer counterpart, small-molecule donor materials possess unique features of easy purification, well-defined molecular structure and fixed molecular weight which can circumvent the batch-to-batch variations of their photovoltaic performance.[16] Benefitted from the research progress of planar A–D–A-type organic molecular donors, notable PCE of over 9% has been reported for the small molecule-based OSCs (SM-OSCs), which is comparable to polymer-based OSCs.[17–21] However, most of the high PCE of the SM-OSCs rely heavily on extra treatments of their active layer, such as thermal annealing (TA),[21,22–24] solvent additive processing (SAP),[25–27] and solvent vapor annealing (SVA)[21,28–30] to optimize the morphology and to form nanoscaled donor/acceptor (D/A) interpenetrating network of their active layer to reach the high PCE values. **Table 1** summarized the photovoltaic performance of the SM-OSCs with PCE over 9% reported in literatures. Without the extra treatments, only moderate PCEs from 3.46% to 6.7% were obtained. The PCEs were greatly improved to over 9% by SAP, TA, SVA, or dual treatments of TA and SVA to fine-tune the morphology of the active layer. However, the extra treatments will be a challenge in the fabrication of large area flexible SM-OSCs. Obviously, it is very important to develop highly efficient small-molecule donor materials without the need of extra treatments to optimize the morphology of the active layer for the high photovoltaic performance.

In our previous work, the engineering of alkylthio side chain in a 2D-conjugated polymer PBDTT-S-TT effectively downshifted the HOMO energy level, slightly redshifted the absorption, and enhanced hole mobility of the corresponding polymer, leading to an overall improvement of photovoltaic properties without extra treatments.[31] In addition, we ever reported the positive effect of the thienyl conjugated side chain on the photovoltaic performance of the linear A–D–A-type small molecules with benzo[1,2-b:4,5-b′] (BDT) as central unit.[32] Bearing in mind that the promising alkylthio side-chain effect in enhancing the photovoltaic properties of the polymer without the need of extra treatments and the positive effect of the thienyl conjugated side chains, herein we tried to investigate the synergistic effect of the alkylthio-thienyl-conjugated side chain in small molecule donor materials for SM-OSCs. From this consideration, we synthesized a new 2D-conjugated small-molecule donor material (designated as BDTT-S-TR, as shown in **Scheme 1**) with alkylthio-thienyl-substituted BDT (BDTT-S) as central unit, terthiophene end-capped with electron-withdrawing group rhodanine (TR) as two arms. The theoretical calculation and molecular simulation with density functional theory (Figure S1, Supporting Information) reveal that the strategically introducing alkylthio side chain in BDTT-S-TR effectively downshifts the molecular HOMO energy level (−5.09 eV) by 0.1 eV in comparison to the analogous molecule with alkyl side chain (−4.99 eV), while it has almost no influence on the

---

Dr. C. Cui, Dr. X. Guo, B. Guo, X. Cheng,
Prof. M. Zhang, Prof. Y. Li
Laboratory of Advanced Optoelectronic Materials
College of Chemistry
Chemical Engineering and Materials Science
Soochow University
Suzhou 215123, China
E-mail: mjzhang@suda.edu.cn; liyf@iccas.ac.cn

J. Min, Prof. C. J. Brabec
Institute of Materials for Electronics
and Energy Technology (i-MEET)
Friedrich-Alexander-University Erlangen-Nuremberg
Martensstraße 7, 91058 Erlangen, Germany
E-mail: Min.Jie@ww.uni-erlangen.de

Prof. Y. Li
Beijing National Laboratory of Molecular Sciences
CAS Key Laboratory of Organic
Solids, Institute of Chemistry
Chinese Academy of Sciences
Beijing 100190, P. R. China

DOI: 10.1002/adma.201503815

APPLIED PHYSICS LETTERS 107, 083302 (2015)

Enhanced near-infrared response of nano- and microstructured silicon/organic hybrid photodetectors

Vedran Đerek,[1] Eric Daniel Głowacki,[2,a)] Mykhailo Sytnyk,[3] Wolfgang Heiss,[3]
Marijan Marciuš,[1] Mira Ristić,[1] Mile Ivanda,[1,a)] and Niyazi Serdar Sariciftci[2]
[1]*Center of Excellence for Advanced Materials and Sensing Devices, Research Unit for New Functional Materials, Ruđer Bošković Institute, Bijenička c. 54, Zagreb 10000, Croatia*
[2]*Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University, Altenbergerstraße 69, Linz 4040, Austria*
[3]*Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander Universität Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany and Energie Campus Nürnberg (EnCN), Fürther Straße 250, Nürnberg 90429, Germany*

(Received 19 June 2015; accepted 19 August 2015; published online 28 August 2015)

Heterojunctions between an organic semiconductor and silicon are an attractive route to extending the response of silicon photodiodes into the near infrared (NIR) range, up to 2000 nm. Silicon-based alternatives are of interest to replace expensive low band-gap materials, like InGaAs, in telecommunications and imaging applications. Herein, we report on the significant enhancement in NIR photodetector performance afforded by nano- and microstructuring of p-doped silicon (p-Si) prior to deposition of a layer of the organic semiconductor Tyrian Purple (TyP). We show how different silicon structuring techniques, namely, electrochemically grown porous Si, metal-assisted chemical etching, and finally micropyramids produced by anisotropic chemical etching (Si μP), are effective in increasing the NIR responsivity of p-Si/TyP heterojunction diodes. In all cases, the structured interfaces were found to give photodiodes with superior characteristics as compared with planar interface devices, providing up to 100-fold improvement in short-circuit photocurrent, corresponding with responsivity values of 1–5 mA/W in the range of 1.3–1.6 μm. Our measurements show this increased performance is neither correlated to optical effects, i.e., light trapping, nor simply to geometric surface area increase by micro- and nanostructuring. We conclude that the performance enhancement afforded by the structured p-Si/organic diodes is caused by a yet unresolved mechanism, possibly related to electric field enhancement near the sharp tips of the structured substrate. The observed responsivity of these devices places them closer to parity with other, well-established, Si-based NIR detection technologies. [http://dx.doi.org/10.1063/1.4929841]

Infrared photodetectors are a major component of many optoelectronic devices used in telecommunications, sensing, and imaging technologies.[1,2] Long distance telecommunications are enabled by silica optical fibers, where near-infrared (NIR) wavelengths in the range of 1.3–1.6 μm are used due to the superior transparency of silica in this range. NIR photodetectors are typically fabricated using low-band gap semiconductors, where InGaAs is dominant in most applications.[1–3] Though currently the industry standard due to excellent performance in terms of responsivity and bandwidth, GaAs based technologies are expensive and problematic due to toxicity of precursor materials and difficulties in integration with silicon-based microelectronics. Silicon-based NIR detector solutions would be a highly attractive alternative to incumbent InGaAs technologies.[4] Various methods of sensitizing silicon to function in NIR optoelectronics have been explored in the past. Most early work had focused on doping Si in order to introduce states capable of mid-band gap absorption (MBA).[3] The trade-off between increased responsivity with doping and accompanying decline in electrical performance is a major obstacle for MBA devices. An alternative concept relies on internal photoemission of electrons from a metallic electrode over a Schottky barrier and into the conduction band of Si.[6,7] These devices are promising; however, their low quantum efficiency has precluded application in telecommunications.[7] "Black silicon" technologies which combine concepts of MBA with nanostructured surfaces to increase absorption have achieved responsivity close to competitive levels for telecom applications.[5,8,9] However, such approaches are still plagued by low charge carrier mobility and overall poor electrical characteristics. In principle, a sensitization approach that does not adversely affect the superior electrical properties of Si is favorable. Silicon/organic heterojunction photodiodes are both low-cost and ecological in comparison with the InGaAs technology, and compatible with silicon-based CMOS. Interest in organic/inorganic heterojunction devices began in the 1980s, and since then several models have been developed to understand the electrical characteristics of such junctions.[9–11] In 2010, it was reported that a heterojunction of a solution-processed fullerene (C_{60}) derivative and p-Si displayed a photovoltaic effect down to photon energies of around 0.55 eV (2.25 μm),[12] with mediocre NIR responsivity

---

a) Authors to whom correspondence should be addressed. Electronic addresses: eric_daniel.glowacki@jku.at and ivanda@irb.hr.

CHEMISTRY OF MATERIALS

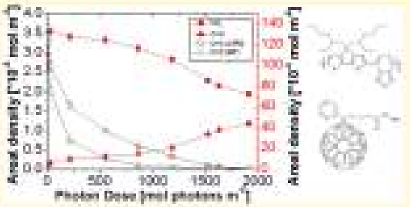
FTIR Study of the Impact of PC[60]BM on the Photodegradation of the Low Band Gap Polymer PCPDTBT under O_2 Environment

Ulf Dettinger,† Hans-Joachim Egelhaaf,‡ Christoph J. Brabec,‡,§ Florian Latteyer,† Heiko Peisert,*,† and Thomas Chassé†

†Institute for Physical and Theoretical Chemistry, Eberhard-Karls-University, Auf der Morgenstelle 18, 72076 Tübingen, Germany
‡ZAE Bayern, Haberstrasse 2a, 91058 Erlangen, Germany
§Institute of Materials for Electronics and Energy Technology (I-MEET), Department of Materials Science and Engineering, Friedrich-Alexander-University, Martensstrasse 7, 91058, Erlangen, Germany

Supporting Information

ABSTRACT: The photodegradation of the low band gap polymer poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT) during irradiation under white light (AM 1.5 conditions) has been studied in pristine polymer films as well as in blend films with [6,6]-phenyl C_{61} butyric acid methyl ester (PC[60]BM). In order to gain insight into the degradation process, FTIR spectroscopy has been used to follow the evolution of different subunits of the polymer and to probe the chemical product formation. In contrast to other polymers, not the alkyl side chains but the π-conjugated system is preferentially oxidized during the first stages of degradation. Furthermore, it has been shown that the subunits of the polymer backbone are differently affected by the degradation. Blending the polymer with PC[60]BM leads to a significantly larger impact on the stability of the cyclopentadiene group compared to the benzene ring of the benzothiadiazole group.



1. INTRODUCTION

Organic photovoltaics (OPVs) offer a promising low-cost technology for the increasing energy demand of the future. While present device efficiencies of about 10%[1] are sufficient for market entry of this technology, device lifetime remains an important issue for the commercial success of organic photovoltaics.[2] Because module lifetimes of at least 20 years are required, which can only be realized by encapsulating them into expensive barrier materials, it is indispensable to gain a detailed insight into the polymer degradation itself to identify the weak points of the conjugated polymers to achieve intrinsically more stable polymers. The degradation of the active layer of an organic solar cell is mainly driven by the lack of the materials resistances against molecular oxygen, water, temperature, and light;[3] the detailed degradation mechanism is often discussed controversially and depends on the material under consideration.[4−12] Already the initial degradation can have dramatic consequences on the electrical transport and charge extraction in devices.[13,14] Moreover, it was shown that the electron acceptor (EA) in bulk-heterojunction solar cells can affect the stability of electron donor (ED) materials in different ways significantly.[15] The commonly used EA [6,6]-phenyl C_{61} butyric acid methyl ester (PC[60]BM, Figure 1) exhibits several stabilizing effects on conjugated polymers, namely, screening from UV light, radical scavenging, hydroperoxide cleavage, and excited state quenching[7,16−18] in which these stabilizing effects predominate for polymers such as poly(3-hexylthiophene-2,5-diyl) (P3HT),[15] poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV),[7,18] and Si-PCPDTBT (PCPDTBT = poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)]).[15] PC[60]BM has been shown to

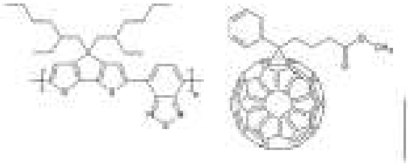


Figure 1. Left: π-conjugated polymer poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT). Right: [6,6]-Phenyl C_{61} butyric acid methyl ester (PC[60]BM).

Received: July 25, 2014
Revised: March 4, 2015
Published: March 13, 2015

ACS Publications

DOI: 10.1021/[illegible]
Chem. Mater. 2015, 27, 2299−2308

Energy Technology FULL PAPER

DOI: 10.1002/ente.201500131

Efficiency Limits and Color of Semitransparent Organic Solar Cells for Application in Building-Integrated Photovoltaics

Karen Forberich,*[a] Fei Guo,[a] Carina Bronnbauer,[a, b] and Christoph J. Brabec[a, b, c]

We have modified the well-known Scharber model for the efficiency limits of organic solar cells for the case of semitransparent devices, which are considered as one of the most promising applications for this photovoltaic (PV) technology. We introduce a modified external quantum efficiency (EQE) relation and derive the transparency from the convolution of the calculated transmittance spectrum with the human eye sensitivity. We find that the design guidelines for the optimum band gap of the absorber material have to be carefully adapted for the desired transparency, especially for transparency values exceeding 40%. In addition, we examine the relationship between efficiency, transmitted color, and band gap and conclude that high efficiencies can be achieved for a wide range of colors. Our model shows good agreement with experimental values from the literature and can be easily adapted to different applications (e.g., greenhouses) by using the appropriate spectrum.

Introduction

Over the last decade, bulk-heterojunction organic solar cells (OSCs) have emerged as a low-cost alternative to more-established technologies such as silicon solar cells. A seminal study based on a semi-empirical model on the efficiency limits of single-junction OSCs was published in 2006 by Scharber et al., which predicts a maximum efficiency value of slightly over 10%.[1]

At that time, the certified record efficiencies were only about 5%, but in thefollowing years this value was increased to 11%.[2] This remarkable progress was due to the emergence of many high-performance polymer donors with improved transport properties and with energy levels optimized according to the guidelines for the optimum band gap of approximately 1.4 eV given by Scharber. Consequently, the prediction was updated to account for the increased values of fill factor (FF) and external quantum efficiency (EQE), to yield a maximum efficiency of over 15%.[3] The model implicitly assumes opaque solar cells as the EQE value was derived from devices with an evaporated top metal electrode. However, one of the unique properties of organic solar cells is their inherent semitransparency, and the ability to adjust the color by engineering the band gap of the absorber polymer. These characteristics lead to many new opportunities for applications in building-integrated photovoltaics (BIPV) such as glass windows, greenhouses, architectural structures, etc.[4–6] Figure 1 shows a digital image of modules with the appearance of leaves which are already commercially available in different colors. In fact, it is widely believed that aesthetic semitransparent applications will be the main market in which OSCs will be able to compete against alternative solar cell technologies.

Figure 1. Digital image of functional aesthetic semitransparent OSC modules with the appearance of leaves, fabricated in three different colors. Source: Belectric OPV GmbH.

Many groups have published reports about semitransparent solar cells, including optical simulations correlating efficiency and transparency depending on the absorber polymer, the electrode material, and the specific device architecture and layer thicknesses.[7–17] However, a systematic study investigating the interdependency between the energy levels of the absorber polymer on the one hand and efficiency and color on the other hand is still missing. The polymers used

---

[a] Dr. K. Forberich, F. Guo, C. Bronnbauer, Prof. C. J. Brabec
Institute of Materials for Electronics and Energy Technology (i-MEET)
Friedrich-Alexander University Erlangen-Nürnberg
Martensstrasse 7, 91058 Erlangen (Germany)
E-mail: karen.forberich@fau.de

[b] C. Bronnbauer, Prof. C. J. Brabec
Erlangen Graduate School in Advanced Optical Technologies (SAOT)
Friedrich-Alexander University Erlangen-Nürnberg
Paul-Gordan-Str. 6, 91052 Erlangen (Germany)

[c] Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Haberstrasse 2a, 91058 Erlangen (Germany)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ente.201500131.

Materials Views
www.MaterialsViews.com

ADVANCED ENERGY MATERIALS
www.advenergymat.de

An Alternative Strategy to Adjust the Recombination Mechanism of Organic Photovoltaics by Implementing Ternary Compounds

Nicola Gasparini, Michael Salvador, Stefanie Fladischer, Athanasios Katsouras, Apostolos Avgeropoulos, Erdmann Spiecker, Christos L. Chochos, Christoph J. Brabec, and Tayebeh Ameri**

The concept of ternary blend bulk-heterojunction (BHJ) solar cells based on organic semiconductors constitutes an exciting opportunity to further extend the spectral absorption of current generation organic photovoltaics, thus achieving a better match to the solar irradiance spectrum.[1–3] Ternary blend organic solar cells, typically consisting of two donor materials and one acceptor (or one donor and two acceptors),[4–7] represent a real chance to considerably improving the light-to-current conversion efficiency while maintaining the simplicity of the processing conditions used for single active layer devices. However, the introduction of a third component with generally dissimilar optoelectronic and chemical characteristics compared to the binary matrix may introduce recombination centers or morphological traps for charge carriers, thereby affecting the fill factor (FF) and open-circuit voltage (V_{oc}). Particularly, the sensitive active layer morphology often makes it challenging to translate a potential sensitization effect into high power conversion efficiency (PCE).[8]

Significant research effort has been directed toward understanding the opportunities and limitations of ternary organic solar cells with respect to charge generation and charge transport as well as establishing morphology and performance relations.[7–9] Advanced material design has recently led to record efficiencies, exceeding the commercially important 10% threshold.[10,11] Despite these advances, the photophysics and device performance is still not fully understood, limiting the full potentiality of this technology. Importantly, the introduction of a third component (acceptor or donor) to the BHJ has been shown to induce different working mechanisms. Specifically, depending on the sensitizer content, the relative frontier orbital alignment of the constituting components, and the sensitizer location in the photoactive layer, i.e., the morphological composition, it is possible to discriminate between three main mechanisms reported so far: cascade charge transfer,[12] energy transfer,[13] and parallel-like charge transfer.[14]

Here, we demonstrate that the introduction of an additional donor polymer can be used to beneficially modify both the absorption properties and the recombination landscape in a binary blend system, particularly at very low light levels. We report a ternary organic solar cell system processed in air that features a pronounced sensitization effect, resulting in a PCE of more than 6% at 0.01 suns (1 mW cm^{-2}). As sensitizer, we incorporate the near infrared (NIR) active polymer poly[(4,4′-bis(2-ethylhexyl)dithieno[3,2-b:2′,3′-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5′-diyl] (Si-PCPDTBT) into a host system based on indacenodithieno[3,2-b]thiophene,2,3-bis(3-(octyloxy)phenyl)quinoxaline (PIDTTQ) and [6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$) (see Figure S1 in the Supporting Information for the absorption spectra of the aforementioned polymers). Importantly, the efficiency of the ternary system under low light levels surpasses the overall efficiency of the corresponding binary blend. We present photovoltaic device performance and charge transport measurements of the binary and ternary system and compare these with photoinduced absorption (PIA) spectra. We find that a strong sensitization effect combined with reduced charge carrier recombination at low light levels overcomes the morphological limitations of the ternary BHJ. These results may stimulate new material avenues toward high-efficiency photovoltaics at low light levels based on organic ternary blend semiconductors.

The performance of the binary and ternary blend was tested in BHJ solar cells using an inverted device configuration based on indium tin oxide (ITO)/ZnO[15]/active layer/MoO_x/Ag (see Experimental Section). The ZnO and active layers were doctor-bladed in air. The MoO_x interface layer and the silver top electrode were applied by vacuum deposition. The amount of Si-PCPDTBT in the active blend was varied while the overall

N. Gasparini, Dr. M. Salvador, Dr. S. Fladischer,
Prof. C. J. Brabec, Dr. T. Ameri
Institute of Materials for Electronics
and Energy Technology (i-MEET)
Friedrich-Alexander University Erlangen-Nuremberg
Martensstraße 7, 91058 Erlangen, Germany
E-mail: nicola.gasparini@fau.de; tayebeh.ameri@fau.de
Dr. M. Salvador
Instituto de Telecomunicações
Instituto Superior Técnico
Av. Rovisco Pais, P-1049-001 Lisboa, Portugal
Dr. S. Fladischer, Prof. E. Spiecker
Center for Nanoanalysis and Electron Microscopy (CENEM)
Friedrich-Alexander University Erlangen-Nuremberg
Cauerstraße 6, 91058 Erlangen, Germany
A. Katsouras, Prof. A. Avgeropoulos, Dr. C. L. Chochos
Department of Materials Science Engineering
University of Ioannina
Ioannina 45110, Greece
Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Haberstrasse 2a, 91058 Erlangen, Germany

DOI: 10.1002/aenm.201501527

ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

www.MaterialsViews.com

Photophysics of Molecular-Weight-Induced Losses in Indacenodithienothiophene-Based Solar Cells

Nicola Gasparini, Athanasios Katsouras, Mamantos I. Prodromidis, Apostolos Avgeropoulos, Derya Baran, Michael Salvador, Stefanie Fladischer, Erdmann Spiecker, Christos L. Chochos, Tayebeh Ameri,* and Christoph J. Brabec*

The photovoltaic performance and optoelectronic properties of a donor–acceptor copolymer are reported based on indacenodithienothiophene (IDTT) and 2,3-bis(3-(octyloxy)phenyl)quinoxaline moieties (PIDTTQ) as a function of the number-average molecular weight (M_n). Current–voltage measurements and photoinduced charge carrier extraction by linear increasing voltage (photo-CELIV) reveal improved charge generation and charge transport properties in these high band gap systems with increasing M_n, while polymers with low molecular weight suffer from diminished charge carrier extraction because of low mobility–lifetime ($\mu\tau$) product. By combining Fourier transform photocurrent spectroscopy (FTPS) with electroluminescence spectroscopy, it is demonstrate that increasing M_n reduces the nonradiative recombination losses. Solar cells based on PIDTTQ with M_n = 58 kD feature a power conversion efficiency of 6.0% and a charge carrier mobility of 2.1×10^{-4} cm^2 V^{-1} s^{-1} when doctor bladed in air, without the need for thermal treatment. This study exhibits the strong correlations between polymer fractionation and its optoelectronics characteristics, which informs the polymer design rules toward highly efficient organic solar cells.

1. Introduction

High band gap (HBG) conjugated polymers (E_g^{opt} ≥ 1.7 eV) with excellent photovoltaic properties, promising environmental stability, and up-scaling ability are highly desirable complementary absorbers for efficient organic tandem solar cells.[1] Contrary to the extensive efforts devoted to the development of low band gap (LBG) donor polymers, the investigation of HBG polymers with suitable photovoltaic properties in inverted architecture solar cells, particularly when processed in air using roll-to-roll compatible printing methods, is barely examined. Regioregular poly(3-hexyl thiophene) (rrP3HT) is the most widely employed high band gap polymer for tandem organic photovoltaics (OPVs) because of its reliable photovoltaic performance.[1] The rrP3HT-based solar cells with reasonable performances usually rely on time-consuming device fabrication processes such as thermal treatment and solvent vapor annealing, representing a limiting factor in high-throughput device manufacturing. Furthermore, the photovoltaic performance of most high efficiency HBG polymers is demonstrated in conventional device architectures, usually processed through spin coating in combination with solvent additives or with the help of thermal posttreatment.[2–9] OPVs based on regular device architecture typically suffer from oxidation of low work function metals and consequently low operating lifetimes.[10]

Donor–acceptor (D–A) conjugated polymers based on indacenodithiophene (IDT) or indacenodithieno[2,3] thiophene (IDTT) usually exhibit HBGs, depending on the choice of electron deficient unit. These polymers have demonstrated great promise as p-type polymers in OPVs.[7,11] IDT comprises two thiophene rings held in a rigid arrangement via a central phenyl ring (**Scheme 1**). It has emerged as a favorable electron rich building block because of its highly planar structure, which enables copolymers with improved charge carrier mobility. Additionally, good solubility is achieved because of the four alkyl side chains anchored on the periphery of the monomer.[11] Ting et al. synthesized random and alternating copolymers based on IDT and benzothiadiazole with an optical band gap E_g^{opt} = 1.75 eV. OPVs fabricated with this material resulted in

N. Gasparini, Dr. D. Baran, Dr. M. Salvador,
Dr. S. Fladischer, Dr. T. Ameri, Prof. C. J. Brabec
Institute of Materials for Electronics
and Energy Technology (I-MEET)
Friedrich-Alexander-University Erlangen-Nuremberg
Martensstraße 7, 91058 Erlangen, Germany
E-mail: nicola.gasparini@fau.de; tayebeh.ameri@fau.de
A. Katsouras, Dr. A. Avgeropoulos, Dr. C. L. Chochos
Department of Materials Science Engineering
University of Ioannina
Ioannina 45110, Greece
Dr. M. I. Prodromidis
Department of Chemistry
University of Ioannina
Ioannina 45110, Greece
Dr. M. Salvador
Instituto de Telecomunicações
Instituto Superior Técnico
Av. Rovisco Pais, P-1049-001 Lisboa, Portugal
Dr. S. Fladischer, Prof. E. Spiecker
Center for Nanoanalysis and Electron Microscopy (CENEM)
Friedrich-Alexander-University Erlangen-Nuremberg
Cauerstraße 6, 91058 Erlangen, Germany
Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Haberstrasse 2a, 91058 Erlangen, Germany

DOI: 10.1002/adfm.201501062

Random Lasing with Systematic Threshold Behavior in Films of CdSe/CdS Core/Thick-Shell Colloidal Quantum Dots

Claudia Gollner,[†] Johannes Ziegler,[#] Loredana Protesescu,[§,⊥] Dmitry N. Dirin,[§,⊥] Rainer T. Lechner,[∥] Gerhard Fritz-Popovski,[∥] Mykhailo Sytnyk,[†] Sergii Yakunin,[†,§,⊥] Stefan Rotter,[▽] Amir Abbas Yousefi Amin,[#,■] Cynthia Vidal,[‡] Calin Hrelescu,[‡] Thomas A. Klar,[‡] Maksym V. Kovalenko,[§,⊥] and Wolfgang Heiss[*,†,#,■]

[†]Institute of Semiconductor and Solid State Physics and [‡]Institute of Applied Physics, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria, [§]Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1, 8093 Zürich, Switzerland, [⊥]Empa – Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland, [∥]Institut für Physik, Montanuniversität Leoben, Franz-Josef-Strasse 18, A-8700 Leoben, Austria, [▽]Institute for Theoretical Physics, Vienna University of Technology, Wiedner Hauptstraße 8-10/136, 1040 Vienna, Austria, [#]Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany, and [■]Energie Campus Nürnberg (EnCN), Fürther Straße 250, 90429 Nürnberg, Germany

ABSTRACT While over the past years the synthesis of colloidal quantum dots (CQDs) with core/shell structures were continuously improved to obtain highly efficient emission, it has remained a challenge to use them as active materials in laser devices. Here, we report random lasing at room temperature in films of CdSe/CdS CQDs with different core/shell band alignments and extra thick shells. Even though the lasing process is based on random scattering, we find systematic dependencies of the laser thresholds on morphology and laser spot size. To minimize laser thresholds, optimizing the film-forming properties of the CQDs, proven by small-angle X-ray scattering, was found to be more important than the optical parameters of the CQDs, such as biexciton lifetime and binding energy or fluorescence decay time. Furthermore, the observed systematic behavior turned out to be highly reproducible after storing the samples in air for more than 1 year. These highly reproducible systematic dependencies suggest that random lasing experiments are a valuable tool for testing nanocrystal materials, providing a direct and simple feedback for further development of colloidal gain materials toward lasing in continuous wave operation.

KEYWORDS: giant shell quantum dots · successive ion layer adsorption and reaction · random lasing · exciton−exciton interactions · plasmonics

Colloidal quantum dots (CQDs) based on CdSe nanocrystals covered by protective inorganic shells are an attractive material system due to their simple fabrication in solution, their size-adjustable optical properties, and their high environmental stability.[1−11] They also exhibit a pre-eminent photoluminescence (PL) quantum yield,[12−14] which suggested their use as nanophotonic light sources, for example, as fluorescence markers for biolabeling[15−19] and as active material in quantum-dot-based light-emitting diodes,[20−25] or to study the emission of single photons[26−30] in quantum-optical systems. In contrast to these applications based on spontaneous emission, CQDs exhibit severe drawbacks with respect to bulk semiconductors or nanoparticles of higher dimensionality (rods[31] and platelets[32,33]) in laser devices. This is because in CQDs the desired population inversion effectively dissipates by nonradiative Auger recombination, whose efficiency increases rapidly with decreasing dot radius r by $1/r^3$, and competes with the stimulated emission.[34−39] Thus, stimulated emission from CQDs is observed solely under intense, pulsed laser excitation. Contradictory statements are

* Address correspondence to wolfgang.heiss@fau.de.

Received for review May 6, 2015 and accepted September 12, 2015.

10.1021/acsnano.5b02739

GOLLNER ET AL. VOL. 9 • NO. 10 • 9792–9801 • 2015 ACSNANO www.acsnano.org 9792

Phys. Status Solidi C 12, No. 8, 1183–1186 (2015) / DOI 10.1002/pssc.201400226

physica status solidi pss c
www.pss-c.com
current topics in solid state physics

Thermal activation and temperature dependent PL and CL of Tb doped amorphous AlN and SiN thin films

J. Andres Guerra[*,1,2], **Liz Montañez**[1], **Albrecht Winnacker**[2], **Francisco De Zela**[1], **and Roland Weingärtner**[**,1,2]

[1] Pontificia Universidad Católica del Perú, Departamento de Ciencias, Sección Física, Av. Universitaria 1801, Lima 32, Perú
[2] University of Erlangen-Nürnberg, Institute of Materials Science 6, Martensstr. 7, 91058 Erlangen, Germany

Received 10 September 2014, revised 1 June 2015, accepted 8 July 2015

Keywords terbium, thermal activation, temperature dependent, photoluminescence, cathodoluminescence

---

[*] Corresponding author: e-mail guerra.jorgea@pucp.edu.pe, Phone: +511 6262000 ext. 4146, Fax: +511 6262085
[**] e-mail rweingartner@pucp.edu.pe, Phone: +511 6262000 ext. 4146

The effect of terbium (Tb) doping on the photoluminescence (PL) and cathodoluminescence (CL) spectra of amorphous aluminum nitride (*a*-AlN) and amorphous silicon nitride (*a*-SiN) thin films has been investigated for different temperature conditions. The samples were prepared by RF dual magnetron reactive sputtering technique with a Tb concentration of about ~1 at%. An enhancement of the light emission is obtained after thermal annealing treatments following the activation of luminescent centers. Furthermore, the Tb related integrated light emission intensity is reported exhibiting a continuous increase with the samples temperature well below thermal quenching for both materials. This behavior suggests a phonon assisted energy migration mechanism which contributes to the effective energy transfer from the matrix to the Tb ions.

1 Introduction

Rare Earth (RE) ions are intensively investigated due to their unique optical and electronic properties. RE-doped amorphous wide-bandgap semiconductor systems have attracted special attention because they show sharp and temperature stable RE-related light emission spectra in the visible region, a feature that can be trace back to the effective excitation of the RE-ions through the host matrix [1-4]. It is well established that RE-related radiative electronic transitions are largely independent of the host material. Nonetheless, light emission intensity strongly depends on the host. Additionally, the interaction between RE-atoms allows energy down- and up-conversion paths and also produces the so called concentration quenching effect [5-7].

Different atomic environments give rise to slightly different RE-related emission spectra. Furthermore, thermal annealing treatments improve the quality of the electronic properties of the host material. They enhance the light emission intensity of the REs by reducing the non-radiative recombination paths. These facts reveal a close relationship between RE-related light emission intensity and host matrix.

The role played by amorphous matrices in excitation processes can be studied for instance by analysing how emission intensity depends on temperature. We performed temperature dependent PL and CL measurements in order to assess light emission features upon photon sub-bangap and electron band-to-band excitation under conditions for which Tb ions weakly interact with phonons. Typically, the decrease of lattice vibrations at low temperatures is expected to enhance the RE-related light emission intensity. This behaviour is attributed to the reduction of phonon-assisted processes and therefore the inhibition of the energy migration from the RE ion to the host matrix [8, 9]. However, a strong enhancement of the RE-related light emission with temperature has been reported previously for Sm^{3+}, Tb^{3+}, Tm^{3+} and Ce^{3+}, even after up to 200 degrees above room temperature in different amorphous and crystalline hosts [9-12].

In the present work, Tb^{3+} ions were incorporated into *a*-AlN and *a*-SiN thin films by reactive dual magnetron sputtering. These matrices exhibit a wide-bandgap about 5 eV and 4 eV for the *a*-AlN and *a*-SiN, respectively [13], thus overcoming thermal quenching at room temperature.

Materials Views
www.MaterialsViews.com

ADVANCED ENERGY MATERIALS
www.advenergymat.de

Nanowire Interconnects for Printed Large-Area Semitransparent Organic Photovoltaic Modules

Fei Guo, Peter Kubis,* Thomas Przybilla, Erdmann Spiecker, Andre Hollmann, Stefan Langner, Karen Forberich, and Christoph J. Brabec**

Semitransparent organic photovoltaic (OPV) cells promise applications in various transparent architectures where their opaque counterparts cannot contribute. Realizing practical applications of this technology requires the manufacturing of large-area modules without significant performance loss compared to the lab-scale devices. In this work, efficient semitransparent OPV modules based on ultrafast laser patterning on both glass and flexible substrates are reported. Solution-processed metallic silver nanowires (AgNWs) are used as transparent top electrodes. The efficient low-ohmic contact of the interconnects between the top AgNWs and the bottom electrode in combination with high-precision laser beam positioning system allow to fabricate semitransparent modules with high electrical fill factor of ≈63% and a remarkable geometric fill factor exceeding 95%, respectively. These results represent an important progress toward upscaling of high-performance OPV modules with reduced production costs.

1. Introduction

Semitransparent thin-film photovoltaic (PV) cells have recently drawn growing attention in both the scientific and industrial communities because of their attractive specific applications,[1-4] such as building integrated PV windows, translucent roof tops, curtain walls, and self-powered greenhouses. In addition, some modern fashion elements can also find their applications, such as shades, awnings, carports, car roofs, etc. Among several types of semitransparent photovoltaic technologies,[5-7] organic solar cells are one of the most promising technologies due to their low-cost processing potential. Moreover, the color tunability of conjugated organic semiconductors enabled by chemical and bandgap engineering allows for manufacturing of different color devices for a variety of specific applications.[8-12]

A key step toward commercial viability of the semitransparent organic photovoltaic (OPV) technology is to manufacture large-area modules with desired high operating voltage to power output loads.[13-15] When it comes to upscaling, inevitable decreases in the overall efficiency of large-area modules are observed due to the presence of dead area and resistance losses. Presently, record inorganic thin film solar modules show efficiencies routinely higher than 85% of their best small lab-scale devices.[11] In contrast, the retained efficiencies of the large-area organic solar modules are much lower than their inorganic counterparts, which can be mainly attributed to the low geometric fill factor (GFF) and the reduced electrical fill factor (FF).[16-19]

Creating an efficient series-interconnection between individual subcells is the most essential step in fabricating high-performance modules. Generally, there are two aspects which should be taken into account during module design and fabrication. First, the contact resistance of the interconnections should be sufficiently low to facilitate efficient charge recombination. Second, the dead area which does not contribute to the current generation should be minimized, thereby maximizing the utilization of the total active area. In terms of minimizing the dead area, choosing a suitable patterning technique to fabricate a narrow interconnection region is of great importance. Previously, organic solar cell modules were mostly fabricated in a "patterning-free" way where the series-interconnection is realized by overlapping the top and bottom contacts during the deposition of adjacent subcell stripes.[11-21] However, the inherent drawback of the inaccurate positioning characteristics of the involved coating techniques, such as gravure printing[9] and slot-die coating[20-22] requires a certain offset to achieve a sufficient overlap between the adjacent layers, which generally results in a width of the dead area as wide as several millimeters. Alternatively, ultrafast laser system can provide a high-precision, high-throughput, and mask-free patterning process. Laser patterning of inorganic thin-film solar modules such as amorphous silicon or copper indium gallium diselenide has

---

F. Guo, Dr. P. Kubis, A. Hollmann, S. Langner,
Dr. K. Forberich, Prof. C. J. Brabec
Institute of Materials for Electronics and Energy
Technology (I-MEET)
Friedrich-Alexander-University of Erlangen-Nuremberg
Martensstrasse 7, 91058 Erlangen, Germany
E-mail: fei.guo@ww.uni-erlangen.de;
peter.kubis@zae-bayern.de; christoph.brabec@ww.uni-erlangen.de
Dr. P. Kubis
Erlangen Graduate School in Advanced Optical Technologies (SAOT)
Paul-Gordan-Strasse 6, 91052 Erlangen, Germany
T. Przybilla, Prof. E. Spiecker
Center for Nanoanalysis and Electron Microscopy (CENEM)
WW7, Friedrich-Alexander-University of Erlangen-Nuremberg
Cauerstrasse 6, 91058 Erlangen, Germany
Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Am Weichselgarten 7, 91058 Erlangen, Germany

DOI: 10.1002/aenm.201401779

Printed Smart Photovoltaic Window Integrated with an Energy-Saving Thermochromic Layer

Fei Guo, Shi Chen, Zhang Chen, Hongjie Luo, Yanfeng Gao, Thomas Przybilla, Erdmann Spiecker, Andres Osvet, Karen Forberich, and Christoph J. Brabec**

The inherent semitransparency and color tunability of the organic semiconductors are the two biggest treasures for organic photovoltaic (OPV) technology, which allows to manufacture semitransparent devices.[1–4] These esthetical semitransparent organic solar cells (OSCs) offer fascinating applications in building-integrated transparent elements such as glass windows, shades, greenhouses, rooftops, etc. Employing high-performance photoactive materials and advanced light management, considerable effort is currently devoted to pursuing high-efficiency devices while maintaining acceptable visible transparency.[illegible] However, most of the high-performance organic semiconductors reported to date possess absorption onsets of below 800 nm, which is located at the border of the sensitivity of human eyes (Figure S1, Supporting Information).[8–12] It is therefore not surprising that most of these reported semitransparent OPV devices exclusively focused on the manipulation of visible light, leaving the large amount of NIR spectrum which accounts for ≈40% of the total solar energy wasted as thermal radiation (Figure S1, Supporting Information).

Vanadium dioxide (VO_2) known as a NIR-responsive thermochromic material exhibits a heat-driven reversible metal-insulator transformation (MIT) from an infrared-reflective metallic state at high temperatures to an infrared-transparent semiconducting state at low temperatures without obviously affecting the visible transmittance.[illegible] This phase transition property makes VO_2 an attractive material for the application to smart windows. Current studies are mainly focused on enhancing the optical properties of VO_2 films, for example, improving the solar modulation ability and visible transmittance by means of designing multilayered structures (TiO_2/VO_2 and SiO_2/VO_2)[illegible] or doping (Mg-doped VO_2 and Ti doped VO_2),[illegible] or forming nanoparticle composite foils (VO_2/SiO_2 core-shell and VO_2/ATO (antimony-doped tin oxide) composite).[illegible] There have been only a few attempts to integrate energy generation functions in these promising smart windows. Till recently, we demonstrated the first smart window with a mechanically bonded silicon solar cell surrounded on a VO_2-coated glass panel for electricity generation by using partially scattering of visible light.[illegible] Due to small cell areas comparing to glass and the very limited fraction of light scattered by VO_2 to the solar cells for power conversion, the devices achieved a fairly low efficiency of ≈0.5%.

In this work, we conceive and construct a smart photovoltaic window that combines a thin layer of thermochromic VO_2 nanoparticles and a semitransparent organic solar cell. Our smart window offers unprecedented advantages over conventional windows, fulfilling two essential functionalities, namely the generation of energy and the reduction of energy consumption. Specifically, the photovoltaic component of the smart window is capable of generating electricity by converting visible light and, simultaneously, the integrated VO_2 nanoparticle layer is able to intelligently regulate the fraction of NIR light passing through the device, depending on environmental temperature.

The crystalline structure of VO_2 (monoclinic/rutile) during phase transition is presented **Figure 1**a. The MIT temperature (T_c) of bulk VO_2 is appropriately 68 °C (heating cycle) and could be reduced to values approaching room temperature (25 °C) by elemental doping (i.e., W and Mo).[illegible] However, decreasing the T_c by introducing these dopants adversely reduces the solar modulation abilities as well as the visible transparency of the films. In order to exhibit the optimum optical property of VO_2, we shall incorporate the pristine VO_2 as the NIR switchable regulator for our smart window in this study. As schematically illustrated in Figure 1b, such a smart window can continuously generate electricity under solar illumination. And simultaneously, the smart window can block the incident NIR light when the ambient temperature is higher than T_c, whereas it allows the NIR light to pass through the window when the temperature drops below T_c. The automatic and reversible switching of the transmission of NIR solar energy in response to the environmental temperature enables the reduction of indoor power consumption, for example, from air conditioning in summer and from heating in winter. Significantly, it should be underlined that the NIR energy modulation process is completely reversible without consumption of any additional power.

VO_2 nanoparticles were synthesized via a hydrothermal approach as previously reported.[illegible] The X-ray diffraction (XRD) characteristic of the prepared VO_2 nanoparticles is

---

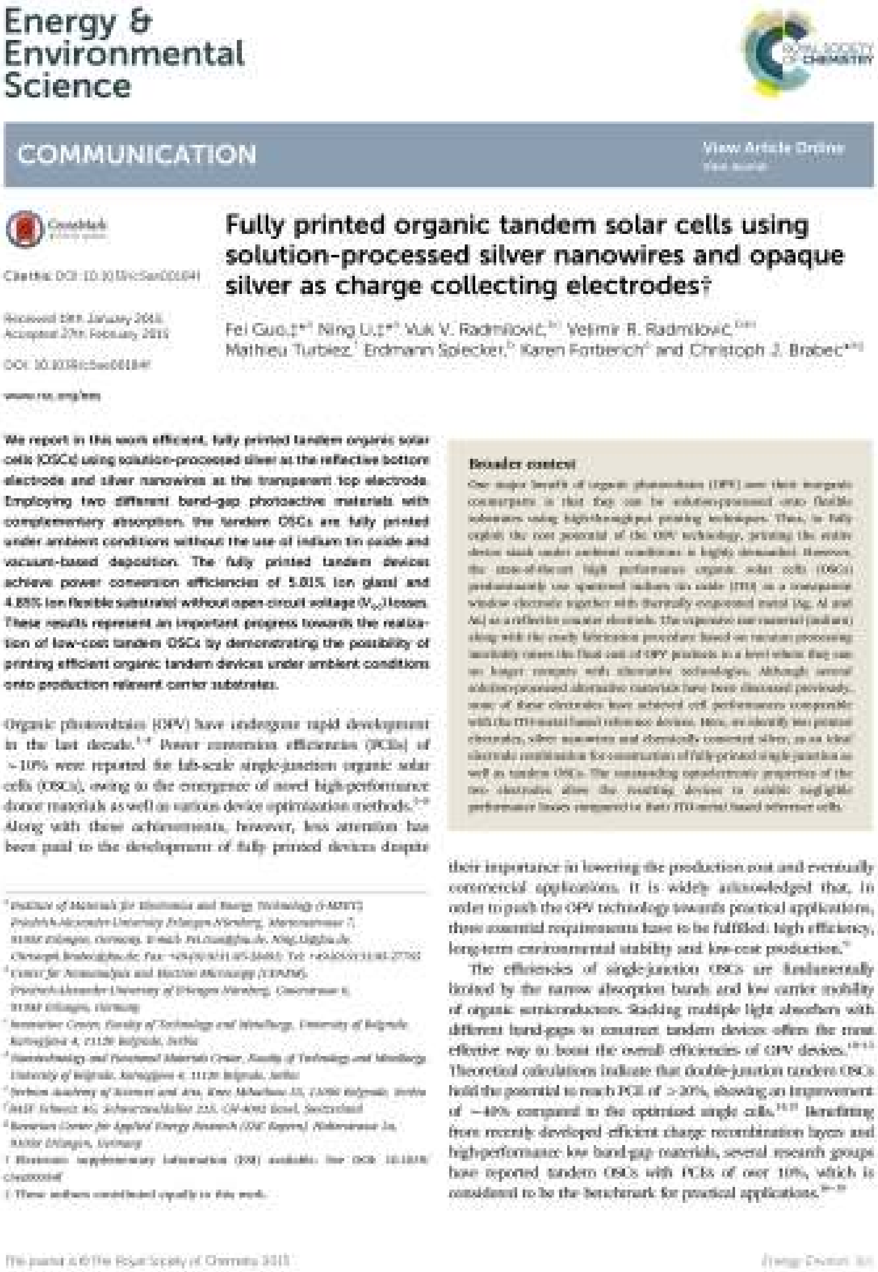
F. Guo, S. Chen, Dr. A. Osvet, Dr. K. Forberich,
Prof. C. J. Brabec
Institute of Materials for Electronics and Energy
Technology (i-MEET)
University Erlangen-Nuremberg
Martensstrasse 7, 91058 Erlangen, Germany
E-mail: christoph.brabec@fau.de

Dr. Z. Chen, Prof. H. Luo, Prof. Y. Gao
School of Materials Science and Engineering
Shanghai University
Shangda Road 99, 200444 Shanghai, China
E-mail: yfgao@shu.edu.cn

T. Przybilla, Prof. E. Spiecker
Center for Nanoanalysis and Electron Microscopy (CENEM)
University Erlangen-Nuremberg
Cauerstraße 6, 91058 Erlangen, Germany

Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Am Weichselgarten 7, 91058 Erlangen, Germany

DOI: 10.1002/adom.201500314



Energy & Environmental Science

COMMUNICATION

View Article Online

Cite this: DOI: 10.1039/c5ee00184f

Received 19th January 2015,
Accepted 27th February 2015

DOI: 10.1039/c5ee00184f

www.rsc.org/ees

Fully printed organic tandem solar cells using solution-processed silver nanowires and opaque silver as charge collecting electrodes†

Fei Guo,‡*[a] Ning Li,‡*[a] Vuk V. Radmilović,[b,c] Velimir R. Radmilović,[d,e] Mathieu Turbiez,[f] Erdmann Spiecker,[b] Karen Forberich[a] and Christoph J. Brabec*[a,g]

We report in this work efficient, fully printed tandem organic solar cells (OSCs) using solution-processed silver as the reflective bottom electrode and silver nanowires as the transparent top electrode. Employing two different band-gap photoactive materials with complementary absorption, the tandem OSCs are fully printed under ambient conditions without the use of indium tin oxide and vacuum-based deposition. The fully printed tandem devices achieve power conversion efficiencies of 5.81% (on glass) and 4.85% (on flexible substrates) without open-circuit voltage (V_{oc}) losses. These results represent an important progress towards the realization of low-cost tandem OSCs by demonstrating the possibility of printing efficient organic tandem devices under ambient conditions onto production relevant carrier substrates.

Broader context

Organic photovoltaics (OPV) have undergone rapid development in the last decade.[1-4] Power conversion efficiencies (PCEs) of ~10% were reported for lab-scale single-junction organic solar cells (OSCs), owing to the emergence of novel high-performance donor materials as well as various device optimization methods.[5-9] Along with these achievements, however, less attention has been paid to the development of fully printed devices despite their importance in lowering the production cost and eventually commercial applications. It is widely acknowledged that, in order to push the OPV technology towards practical applications, three essential requirements have to be fulfilled: high efficiency, long-term environmental stability and low-cost production.[9]

The efficiencies of single-junction OSCs are fundamentally limited by the narrow absorption bands and low carrier mobility of organic semiconductors. Stacking multiple light absorbers with different band-gaps to construct tandem devices offers the most effective way to boost the overall efficiencies of OPV devices.[10-13] Theoretical calculations indicate that double-junction tandem OSCs hold the potential to reach PCE of >20%, showing an improvement of ~40% compared to the optimized single cells.[14,15] Benefiting from recently developed efficient charge recombination layers and high-performance low band-gap materials, several research groups have reported tandem OSCs with PCEs of over 10%, which is considered to be the benchmark for practical applications.[16-18]

---

[a] Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-University Erlangen-Nürnberg, Martensstrasse 7, 91058 Erlangen, Germany. E-mail: Fei.Guo@fau.de, Ning.Li@fau.de, Christoph.Brabec@fau.de; Fax: [illegible]; Tel: [illegible]
[b] Center for Nanoanalysis and Electron Microscopy (CENEM), Friedrich-Alexander University of Erlangen-Nürnberg, Cauerstrasse 6, 91058 Erlangen, Germany
[c] Innovation Center, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia
[d] Nanotechnology and Functional Materials Center, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia
[e] Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia
[f] BASF Schweiz AG, Schwarzwaldallee 215, CH-4002 Basel, Switzerland
[g] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstrasse 2a, 91058 Erlangen, Germany

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ee00184f

‡ These authors contributed equally to this work.

Nanoscale

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: Nanoscale, 2015, 7, 1642

Received 13th October 2014,
Accepted 18th December 2014

DOI: 10.1039/c4nr06033d

www.rsc.org/nanoscale

High-performance semitransparent perovskite solar cells with solution-processed silver nanowires as top electrodes†

Fei Guo,*[a,d] Hamed Azimi,[a] Yi Hou,[a,c] Thomas Przybilla,[b] Mengyao Hu,[a] Carina Bronnbauer,[a,c] Stefan Langner,[a] Erdmann Spiecker,[b] Karen Forberich[a] and Christoph J. Brabec*[a,d]

In this work, we report efficient semitransparent perovskite solar cells using solution-processed silver nanowires (AgNWs) as top electrodes. A thin layer of zinc oxide nanoparticles is introduced beneath the AgNWs, which fulfills two essential functionalities: it ensures ohmic contact between the $PC_{60}BM$ and the AgNWs and it serves as a physical foundation that enables the solution-deposition of AgNWs without causing damage to the underlying perovskite. The as-fabricated semitransparent perovskite cells show a high fill factor of 66.8%, V_{oc} = 0.964 V, J_{sc} = 13.18 mA cm^{-2}, yielding an overall efficiency of 8.49% which corresponds to 80% of the reference devices with reflective opaque electrodes.

Inorganic–organic halide perovskite solar cells have recently emerged as a promising photovoltaic technology due to their high efficiencies and low-cost processing potential.[1–3] The exceptional optoelectronic properties of the perovskite crystals such as high carrier mobility and long charge diffusion length promise highly efficient charge separation.[4,5] These intriguing characteristics make perovskites ideal materials for photovoltaic applications. Since the first device demonstration in 2009, power conversion efficiency (PCE) of perovskite solar cells processed by both vacuum-deposition and solution-processing has surged to over 15%.[1,6,7–9] The continuous and fast progress in the research related to perovskite solar devices has established them as a serious contestant to the traditional silicon-based panels.

Together with the considerable efforts devoted to pursuing high efficiencies *via* improved crystallization of perovskite and searching for low-cost interface materials,[4,10–13] aesthetic semitransparent perovskite solar cells have been simultaneously receiving growing attention because of their specific application in transparent architectures,[14–17] such as windows, rooftops, greenhouses and other fashion elements. To achieve efficient semitransparent perovskite devices, both the anode and the cathode of the devices should be highly transparent and conductive in order to minimize the optical and resistance losses. To date, several studies have reported semitransparent perovskite solar cells, but most of these devices employed thin metal films (Al, Ag, Au) as top electrodes which were fabricated based on energy-intensive evaporation processes.[14–17] It is well known that, in addition to low-cost materials, the cost reduction of photovoltaic devices substantially depends on the ability to use high-throughput coating techniques in combination with roll-to-roll processing.[18] Despite its importance, however, less attention has been paid to the exploration of solution-processable transparent electrodes for perovskite solar cells.

Carbon based materials have received much attention for use as conducting electrodes for perovskite solar cells, due to their low-cost and high stability.[14,19,20] For example, Li *et al.* have recently reported semitransparent perovskite solar cells using carbon nanotubes as top electrodes. It was found that the high sheet resistance of the carbon nanotube films (2–25 kΩ $sq.^{-1}$) adversely limited the device's performance, resulting in low fill factors (FFs) due to the high series resistance of the device.[19] Moreover, the involved transfer and lamination procedures increased the complexity in device fabrication which is incompatible with large-scale, continuous roll-to-roll manufacturing. Simultaneously, Mei *et al.* reported the use of printed carbon black/graphite composite material as top electrodes for perovskite solar cells.[20,21] Although the devices with carbon electrodes exhibited high efficiency and long-term stability, to achieve the desired sheet resistance the carbon black/graphite layer had to be made rather thick (tens of micrometres) which makes the devices non-transparent.

---

[a] Institute of Materials for Electronics and Energy Technology (I-MEET), Friedrich-Alexander-University of Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany
[b] Center for Nanoanalysis and Electron Microscopy (CENEM), WW7, Friedrich-Alexander-University of Erlangen-Nuremberg, Cauerstrasse 6, 91058 Erlangen, Germany
[c] Erlangen Graduate School in Advanced Optical Technologies (SAOT), Paul-Gordan-Strasse 6, 91052 Erlangen, Germany
[d] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstrasse 2a, 91058 Erlangen, Germany. E-mail: fei.guo@ww.uni-erlangen.de, christoph.brabec@ww.uni-erlangen.de

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4nr06033d

nature
COMMUNICATIONS

ARTICLE

Received 2 Feb 2015 | Accepted 4 Jun 2015 | Published 16 Jul 2015 DOI: 10.1038/ncomms8730 OPEN

A generic concept to overcome bandgap limitations for designing highly efficient multi-junction photovoltaic cells

Fei Guo[1,*], Ning Li[1,*], Frank W. Fecher[2], Nicola Gasparini[1], Cesar Omar Ramirez Quiroz[1], Carina Bronnbauer[1,3], Yi Hou[1,3], Vuk V. Radmilović[4,5], Velimir R. Radmilović[4,6], Erdmann Spiecker[4], Karen Forberich[1] & Christoph J. Brabec[1,2,3]

The multi-junction concept is the most relevant approach to overcome the Shockley–Queisser limit for single-junction photovoltaic cells. The record efficiencies of several types of solar technologies are held by series-connected tandem configurations. However, the stringent current-matching criterion presents primarily a material challenge and permanently requires developing and processing novel semiconductors with desired bandgaps and thicknesses. Here we report a generic concept to alleviate this limitation. By integrating series- and parallel-interconnections into a triple-junction configuration, we find significantly relaxed material selection and current-matching constraints. To illustrate the versatile applicability of the proposed triple-junction concept, organic and organic-inorganic hybrid triple-junction solar cells are constructed by printing methods. High fill factors up to 68% without resistive losses are achieved for both organic and hybrid triple-junction devices. Series/parallel triple-junction cells with organic, as well as perovskite-based subcells may become a key technology to further advance the efficiency roadmap of the existing photovoltaic technologies.

---

[1] Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander University Erlangen-Nürnberg, Martensstrasse 7, 91058 Erlangen, Germany. [2] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstrasse 2a, 91058 Erlangen, Germany. [3] Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich-Alexander-University Erlangen-Nürnberg, Paul-Gordan-Str. 6, 91052 Erlangen, Germany. [4] Center for Nanoanalysis and Electron Microscopy (CENEM), Friedrich-Alexander University Erlangen-Nürnberg, Cauerstrasse 6, 91058 Erlangen, Germany. [5] Innovation Center, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia. [6] Nanotechnology and Functional Materials Center, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia. * These authors contributed equally to this work. Correspondence and requests for materials should be addressed to C.J.B. (email: christoph.brabec@fau.de).

IOP Publishing
Measurement Science and Technology
Meas. Sci. Technol. **26** (2015) 075202 (7pp)
doi:10.1088/0957-0233/26/7/075202

Temperature measurements using YAG : Dy and YAG : Sm under diode laser excitation (405 nm)

A Hashemi[1,2], **A Vetter**[1,2,3], **G Jovicic**[2,3,4], **M Batentschuk**[3] **and C J Brabec**[1,3]

[1] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a, 91058 Erlangen, Germany
[2] Energie Campus Nürnberg (EnCN), Fürther Straße 250, 90429 Nürnberg, Germany
[3] Institute of Materials for Electronics and Energy, Friedrich Alexander University Erlangen-Nuremberg, Martensstraße 7, 91058 Erlangen, Germany
[4] Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich Alexander University Erlangen-Nuremberg, Paul-Gordan-Str. 6, 91052 Erlangen, Germany

E-mail: andreas.vetter@fau.de

Received 29 December 2014, revised 23 March 2015
Accepted for publication 31 March 2015
Published 5 June 2015

Abstract

Temperature-sensitive phosphors offer an option of accurate contactless temperature measurement. The method can be applied to a wide temperature range and up to more than 1500 K. In the current paper, phosphor thermometry based on four rare earths doped in YAG was studied. The standard excitation of thermographic phosphors is carried out with a Nd : YAG laser often at 355 or 266 nm. We examined the temperature dependent luminescence at an excitation wavelength of 405 nm. The excitation with visible blue light offers two main advantages: the excitation sources are rather cheap and they involve less safety issues. Accordingly, a variety of new application of such remote-thermometry would be possible. The results show that YAG : Dy and YAG : Sm may be well utilized for phosphor thermometry excited by a 405 nm diode laser.

Keywords: phosphor thermometry, temperature, luminescence, phosphorescence, diode laser

(Some figures may appear in colour only in the online journal)

1. Introduction

Phosphor thermometry is a non-contact temperature measurement method, which can be used for temperature measurement up to 1500 K and more [1, 2]. It is one of the semi-noninvasive temperature measurement methods, which may be applied to cases in which no direct contact between a thermocouple and the test object is possible or would result in inaccurate measurements [3, 4]. In order to use this method for temperature measurements, a thin phosphor layer may be coated onto the sample surface and the sample is excited by a light source [5]. Another typical experiment aims to measure the temperature in the gas phase. In this case, the phosphor is introduced into the experimental setup as powder. In both cases, the luminescence signal of the phosphor is collected and analyzed, for example by using a spectrometer. In this introduction, we will give some examples of phosphor thermometry applications, we will briefly review the basics of the measurement technique and then outline the aim of this study. A comprehensive description of the photo-physics of phosphors can be found in the Phosphor Handbook [6].

Temperature measurement using thermographic phosphors is a very versatile tool due to its noninvasive way of measuring. The method has been intensively employed to study combustion processes [7, 8], for example with the aim to increase the efficiency of an engine. Many studies measured the local gas temperature inside the combustion chamber, often together with an analysis of the velocity of the gas flow [9] or the gas concentration [10] as well as surface temperature measurements of the walls of the combustion volume [11, 12] or measurements of the local surface temperature of porous burners [13] or a Swirl burner [14]. By choosing appropriate phosphors,

Journal of
Materials Chemistry C

PAPER

View Article Online
View Journal | View Issue

Cite this: J. Mater. Chem. C, 2015, 3, 2358

4H-1,2,6-Thiadiazin-4-one-containing small molecule donors and additive effects on their performance in solution-processed organic solar cells†

Felix Hermerschmidt,*[a] Andreas S. Kalogirou,[b] Jie Min,[c] Georgia A. Zissimou,[b] Sachetan M. Tuladhar,[d] Tayebeh Ameri,[c] Hendrik Faber,[d] Grigorios Itskos,[e] Stelios A. Choulis,[a] Thomas D. Anthopoulos,[d] Donal D. C. Bradley,[d] Jenny Nelson,*[d] Christoph J. Brabec*[c] and Panayiotis A. Koutentis*[b]

Received 22nd December 2014
Accepted 13th January 2015

DOI: 10.1039/c4tc02911c

www.rsc.org/MaterialsC

The optical, electrochemical, morphological and transport properties of a series of thiadiazinone (acceptor) and thienylcarbazoles (donor) containing π-extended donor–acceptor–donors (D–A–D) are presented. Systematic variations in the number of the thienyl units, the choice of branched or straight alkyl side chains and the use of a processing additive demonstrate their use as electron donors in bulk heterojunction solar cells blended with fullerene acceptors. The best power conversion efficiency (PCE) of 2.7% is achieved by adding to the D–A–D 5 : fullerene blend a polydimethylsiloxane (PDMS) additive that improves the morphology and doubles the hole mobility within the D–A–D : fullerene blend.

1. Introduction

Incident sunlight falling on Earth in 1 hour is sufficient to satisfy the average yearly human energy consumption;[1] not surprisingly, the interest in solar energy has grown rapidly. Organic photovoltaics (OPVs), which are free of expensive rare earth metals, can provide a low-cost, solution-processable and environmentally friendly alternative to generate electricity.

Bulk-heterojunction (BHJ) OPV devices, which use a bulk mixture of an electron donating and an electron accepting unit, to provide a flow of electrons and holes to the relevant electrodes, have reached certified power conversion efficiencies (PCEs) for single-junction devices >9%,[2,3] and >10% for tandem cells.[4,5] These devices typically contain an active layer comprising a conjugated polymer as the electron donating unit such as PTB7, PCDTBT, Si-PCPDTBT or P3HT and a soluble fullerene as electron acceptor such as PC60BM, PC70BM or ICBA.[6–9]

Small molecules have recently been used as donor and acceptor components in BHJ-OPVs[9] and device efficiencies of 7–9% have been achieved for single-junction solar cells,[10–12] while a 10.1% PCE has been achieved for a solution-based small molecule tandem cell.[13]

Advantages of small molecules include well-defined structures and characterisability, higher manufacturing yields, facile purification techniques,[14] and their reproducible, less complex syntheses.[15] Devices employing solution-processed small molecules as both donor and acceptor components gave device efficiencies of ~3%,[16] which is similar to the average device performance of the widely studied and extensively optimized polymer : fullerene P3HT : PC60BM system.[17] As a result of this progress, a wide variety of new small molecules for solution-processed organic photovoltaics are being prepared,[18–21] including efficient donor–acceptor–donor (D–A–D) systems.[22]

A recent electrochemical study of non-oxidised 4H-1,2,6-thiadiazines indicated electron affinities (LUMO energy values) of −3.25 to −3.66 eV with reversible oxidations and reductions.[23] As such, these heterocycles are promising as acceptor building blocks for D–A–D small molecule donors and for polymerization with various prominent comonomers to produce solar harvesting polymers. The presence of an appropriate electron-deficient 4H-1,2,6-thiadiazine in the donor molecule can be used to control the energy level of the LUMO while that of the HOMO can be regulated by the incorporation of electron-rich substituents such as thiophene and carbazole.

---

[a] Molecular Electronics and Photonics Research Unit, Department of Mechanical Engineering and Materials Science and Engineering, Cyprus University of Technology, 3041 Limassol, Cyprus

[b] Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus

[c] Institute of Materials for Electronics and Energy Technology, Friedrich-Alexander University Erlangen-Nürnberg, 91058 Erlangen, Germany

[d] Department of Physics, Imperial College London, London SW7 2AZ, UK

[e] Experimental Condensed Matter Physics Laboratory, Department of Physics, University of Cyprus, 1678 Nicosia, Cyprus

† Electronic supplementary information (ESI) available: Synthesis and structural characterisation of materials, ^{1}H and ^{13}C NMR spectra of D–A–D molecules, electrochemistry, cyclic voltammograms, fabrication and characterisation of organic solar cells. See DOI: 10.1039/c4tc02911c

J. of Supercritical Fluids 99 (2015) 76–87

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Reactions

Ceramic liner technology for ammonoacidic synthesis

Benjamin Hertweck[a,*], Saskia Schimmel[b], Thomas G. Steigerwald[a], Nicolas S.A. Alt[a], Peter J. Wellmann[b], Eberhard Schluecker[a]

[a] Institute of Process Machinery and Systems Engineering, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Cauerstr. 4, 91058 Erlangen, Germany
[b] Materials Department 6, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Martensstr. 7, 91058 Erlangen, Germany

ARTICLE INFO

Article history:
Received 21 November 2014
Received in revised form 13 January 2015
Accepted 14 January 2015
Available online 24 January 2015

Keywords:
Ammonothermal crystal growth
Liner technology
Ceramic materials
Corrosion
Supercritical ammonia
In situ X-ray imaging

ABSTRACT

The ammonoacidic crystal growth is a comprehensive method for the synthesis of novel compounds like nitrides or amides but also for the growth of bulk single crystals like gallium or aluminum nitride for power electronics and photonics. In this report we describe a novel liner technology for growth autoclaves, showing high potential for several research purposes. Thereby the applicability of several ceramic materials as liner materials was investigated for the first time. Moreover, the effectivity of the new apparatus was verified in experimental studies. The described concept based on a silicon nitride crucible is characterized by low costs and diverse possible applications. For example its use is of advantage in fundamental research to explore new nitride materials. Furthermore, it shows high potential for X-ray imaging to investigate basic principles in growth of gallium nitride.

1. Introduction

The ammonothermal synthesis as a technique of high industrial potential already allows the commercial growth of gallium and aluminum nitride [1–6] with high quality, inter alia low dislocation density and low strain level for the use in optoelectronics and high power electronics. Moreover, the ammonothermal route is of high scientific interest in fundamental chemical research, providing new synthesis routes which yield new compounds. Multinary nitrides like $Ca_2Si_5N_8$ or $Ba_2Si_5N_8$ are applicable in nonlinear optics [7]. Doped nitrides like $Ca_2Si_5N_8:Eu^{2+}$ or $Ca_2Si_5N_8:Ce^{3+}$ are of interest for the fabrication of LEDs due to their efficient luminescence [8,9]. The growth of ferromagnetic semiconductor materials, like metal nitrides of the form Me_xN_y (with Me = Mn, Fe, Ni and N = Nitrogen) are of interest for spintronics [10].

The ammonothermal growth takes place in high pressure/high temperature autoclaves made of a nickel base alloy. Depending on the alloy, pressure and temperature range is limited because the complete autoclave is placed in a heater to achieve high internal process temperatures. Although the maximum pressure is not only determined by the high-temperature strength, dimensioning is also an influencing factor. Common materials for ammonothermal autoclaves are alloys from the Inconel® group (composition Ni-Cr/Fe-Al/Ti) [11–13], alternative materials like alloy 41 allow the realization of higher process temperatures [14] (see Table 1).

In order to increase the growth rate of the nitride, so-called mineralizers are commonly used as additives to improve the solubility of the nitride in supercritical ammonia. Two different groups of mineralizers can be distinguished: ammonobasic and ammonoacidic mineralizers. Ammonobasic mineralizers (e.g. lithium amide $LiNH_2$, sodium amide $NaNH_2$ and potassium amide KNH_2) introduce amide ions NH_2^- causing an ammonobasic solution which contains the corresponding alkali metal ions Li^+, Na^+ or K^+. Ammonobasic solutions are connected to moderate corrosion but also to low growth rates with the use of a liner [5].

Ammonoacidic mineralizers (ammonium halides, e. g. ammonium chloride NH_4Cl, or ammonium fluoride NH_4F) introduce NH_4^+ ions causing an ammonoacidic solution that contains the corresponding halide ions Cl^- or F^-. Ammonoacidic environments are highly corrosive to the autoclave material, on the other hand, they enable higher growth rates than ammonobasic ones. As mineralizer also influences temperature dependence of solvent properties of the fluid, ammonoacidic conditions lead to a positive solubility coefficient and a forward solubility in the temperature range accessible in alloy 718 autoclaves [11]. The temperature profile of an ammonoacidic growth reactor is characterized by higher temperature in the dissolution region compared to the crystallization zone [3,12].

The corrosion of the autoclave material due to the supercritical ammonothermal fluid is a limiting factor for both growth routes,

---

[*] Corresponding author. Tel.: +49 9131 85 29457; fax: +49 9131 85 29449.
E-mail address: benjamin.hertweck@fau.de (B. Hertweck).

http://dx.doi.org/10.1016/j.supflu.2015.01.017

Materials Views
www.MaterialsViews.com

ADVANCED ENERGY MATERIALS
www.advenergymat.de

Disorder-Induced Open-Circuit Voltage Losses in Organic Solar Cells During Photoinduced Burn-In

*Thomas Heumueller, Timothy M. Burke, William R. Mateker, Isaac T. Sachs-Quintana, Koen Vandewal, Christoph J. Brabec, and Michael D. McGehee**

The photoinduced open-circuit voltage (V_{oc}) loss commonly observed in bulk heterojunction organic solar cells made from amorphous polymers is investigated. It is observed that the total charge carrier density and, importantly, the recombination dynamics are unchanged by photoinduced burn-in. Charge extraction is used to monitor changes in the density of states (DOS) during degradation of the solar cells, and a broadening over time is observed. It is proposed that the V_{oc} losses observed during burn-in are caused by a redistribution of charge carriers in a broader DOS. The temperature and light intensity dependence of the V_{oc} losses can be described with an analytical model that contains the amount of disorder broadening in a Gaussian DOS as the only fit parameter. Finally, the V_{oc} loss in solar cells made from amorphous and crystalline polymers is compared and an increased stability observed in crystalline polymer solar cells is investigated. It is found that solar cells made from crystalline materials have a considerably higher charge carrier density than those with amorphous materials. The effects of a DOS broadening upon aging are suppressed in solar cells with crystalline materials due to their higher carrier density, making crystalline materials more stable against V_{oc} losses during burn-in.

1. Introduction

With power conversion efficiencies over 10%, improving device stability has become a major challenge for organic solar cells. In a recent study,[1] we investigated the photoinduced burn-in of BHJ solar cells using several crystalline and amorphous materials under one sun light intensity and inert conditions. While an increased trap density upon degradation was found for all polymers, only the amorphous polymers showed a significant decrease in open-circuit voltage. Apparently, traps can have a different effect on device performance depending on the morphology of the active layer. We investigate this influence of morphology in the context of two fundamental mechanisms that are able to cause a V_{oc} loss. First, an increased trap-assisted recombination rate that lowers the charge carrier density[2,3] and second a broadening of the density of states that reduces V_{oc}[4,5] with the same charge carrier density and unchanged recombination dynamics. Answering this question is important not only for making more stable solar cells, but also for understanding in general how traps reduce the open-circuit voltage in organic solar cells. Aging is a convenient way to add traps into an organic solar cell and see their effect on recombination and V_{oc} without introducing additional materials into the active layer.

We illuminate BHJ solar cells of various materials in inert conditions for three days. Using transient photovoltage (TPV),[6] charge extraction (CE)[7] and temperature dependent measurements of the open-circuit voltage, we compare the recombination dynamics and charge carrier densities of fresh and aged solar cells and relate them to the observed V_{oc} losses. We find that in degraded solar cells of amorphous materials such as poly[9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), the recombination dynamics are basically unchanged. Instead, the observed open-circuit voltage losses appear to result from increased energetic disorder that causes a change in the relevant low-energy portion of the density of states such that for the same charge carrier density a lower quasi Fermi level splitting is obtained. We observe that solar cells made from crystalline materials do not show V_{oc} losses and have a higher charge carrier density than solar cells made from amorphous materials. Apparently crystalline materials are not affected by a moderate increase of energetic disorder, most likely due to a higher charge carrier density.

Besides reduced open-circuit voltages, also losses of fill factor[1,8] and short-circuit current[9,10] are observed upon burn-in. Often a convolution of degradation mechanisms at material interfaces and within the bulk of the absorbing layer is present. Recent work suggests that a decrease in fill factor during degradation is related to interface defects[10] which are most likely related to injection or extraction barriers at the electrodes.[11–13]

T. Heumueller, T. M. Burke, W. R. Mateker,
I. T. Sachs-Quintana, Dr. K. Vandewal,
Prof. M. D. McGehee
Department of Materials Science and Engineering
Stanford University
Stanford, CA 94305, USA
E-mail: mmcgehee@stanford.edu
T. Heumueller, Prof. C. J. Brabec
Institute of Materials for Electronics and Energy Technology (i-MEET)
Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)
91058 Erlangen, Germany
Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
91058 Erlangen, Germany

DOI: 10.1002/aenm.201500111

ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

Low-Temperature Solution-Processed Kesterite Solar Cell Based on in Situ Deposition of Ultrathin Absorber Layer

Yi Hou,*[†,§] Hamed Azimi,*[†] Nicola Gasparini,[†] Michael Salvador,[†,⊥] Wei Chen,[†,‡] Laraib S. Khanzada,[†,#] Marco Brandl,[∥] Rainer Hock,[∥] and Christoph J. Brabec[†,‡]

[†]Institute of Materials for Electronics and Energy Technology (I-MEET), Department of Materials Science and Engineering, Friedrich-Alexander University Erlangen-Nürnberg, Martensstrasse 7, 91058 Erlangen, Germany

[‡]Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstrasse 2a, 91058 Erlangen, Germany

[§]Erlangen Graduate School in Advanced Optical Technologies (SAOT), Paul-Gordan-Strasse 6, 91052 Erlangen, Germany

[∥]Chair for Crystallography and Structural Physics, Friedrich-Alexander-University Erlangen-Nürnberg, Staudtstrasse 3, 91058 Erlangen, Germany

[⊥]Instituto de Telecomunicações, Instituto Superior Técnico, Av. RovisscoPais, P-1049-001 Lisboa, Portugal

[#]Department of Metallurgical Engineering, NED University of Engineering and Technology, University Road, Karachi 75270, Pakistan

Supporting Information

ABSTRACT: The production of high-performance, solution-processed kesterite $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe) solar cells typically relies on high-temperature crystallization processes in chalcogen-containing atmosphere and often on the use of environmentally harmful solvents, which could hinder the widespread adoption of this technology. We report a method for processing selenium free Cu_2ZnSnS_4 (CZTS) solar cells based on a short annealing step at temperatures as low as 350 °C using a molecular based precursor, fully avoiding highly toxic solvents and high-temperature sulfurization. We show that a simple device structure consisting of ITO/CZTS/CdS/Al and comprising an extremely thin absorber layer (~110 nm) achieves a current density of 8.6 mA/cm². Over the course of 400 days under ambient conditions encapsulated devices retain close to 100% of their original efficiency. Using impedance spectroscopy and photoinduced charge carrier extraction by linearly increasing voltage (photo-CELIV), we demonstrate that reduced charge carrier mobility is one limiting parameter of low-temperature CZTS photovoltaics. These results may inform low energy demanding strategies for the production of CZTS optoelectronic layers compatible with large-scale processing techniques.

KEYWORDS: *CZTS, kesterite solar cells, molecular based precursor, low-temperature processing, device stability*

INTRODUCTION

Solution-processed inorganic semiconductors exhibit a broad range of attractive optoelectronic properties, and hold great promise for enabling inexpensive and large area roll-to-roll device fabrication.[1,2] Recently, low-temperature, solution-processed nanocrystalline inorganic and hybrid semiconductors, based on earth-abundant elements, have attracted broad attention.[3−6] Among these classes of materials, Pb based semiconductors such as PbS and inorganic−organic Pb based perovskites, demonstrated record high efficiencies of 8.6% and 20.1%, respectively.[7,8] However, multistep photovoltaic device fabrication, sometimes including complicated ligand exchange protocols, and concerns regarding the toxicity and the limited lifetime of these absorber materials may represent important hurdles when considering large-area deployment of these materials. Conversely, semiconductors based on environmentally benign, largely available materials like FeS_2, Cu_2O, and $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe) open up opportunities for large-scale photovoltaic implementation.[4,9−14] Particularly, the case of CZTSSe has regained significant interest through reports of high-efficiency solar cells based on molecular precursors and nanocrystal inks.[9−11] In theory, Cu_2ZnSnS_4 (CZTS) represents an optimum absorber material for solar cell mass production. It features p-type conductivity, an optimal direct band gap of ~1.5 eV, and a high absorption coefficient of ~10^4 cm^{-1}.[15] The latter suggests that devices with active layer thicknesses smaller than the typically employed 1−2 μm could function efficiently.

High-performance CZTSSe devices with power conversion efficiencies (PCEs) of up to 12.6% rely on high-temperature

Received: May 22, 2015
Accepted: September 10, 2015
Published: September 10, 2015

Materials Views
www.MaterialsViews.com

ADVANCED ENERGY MATERIALS
www.advenergymat.de

Inverted, Environmentally Stable Perovskite Solar Cell with a Novel Low-Cost and Water-Free PEDOT Hole-Extraction Layer

Yi Hou, Hong Zhang, Wei Chen, Shi Chen, Cesar Omar Ramirez Quiroz,*
Hamed Azimi, Andres Osvet, Gebhard J. Matt, Eitan Zeira, Jan Seuring,
*Nina Kausch-Busies, Wilfried Lövenich, and Christoph J. Brabec**

In the past few years, the performance of hybrid perovskite solar cell processed at low temperatures has rapidly surpassed that of dye-sensitized, organic, and quantum dot solar cells, now reaching a strikingly high certified efficiency of 20.1%.[1–4] Due to its desirable virtues of forming extended crystal structures under moderately low temperatures which possess long-range, balanced electron and hole diffusion lengths, perovskite solar cells provide advantages like high efficiency, low processing temperature, and low cost.[5–12] This positions perovskite-based solar cells as a promising third-generation solar cell technology, although the current usage of lead and iodine is certainly seen critical in terms of the restriction of hazardous substances (RoHS) of the European Commission as well as in terms of stability.[13]

Very recently, a fully printed planar-heterojunction perovskite solar cell fabricated by slot-die coating has been reported by Vak's group.[14,15] Importantly, this work underlines the feasibility of printing inorganic–organic lead halide perovskite materials on a large-scale roll-to-roll scheme. Low temperature "roll-to-roll" processing on an industrial scale was yet only demonstrated for the organic solar cell technology (oPV) by the pioneering work from Konarka. From an industrial point of view, the current hybrid lead halide perovskite solar cell technology is still limited in multiple aspects. The expensive HTM, the commonly used doped 2,2′,7,7′-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)-9,9′-spirobifluorene (spiro-MeOTAD), which greatly increase the materials and manufacturing cost of the device is one of the limitations. In addition, spiro-MeOTAD requires a relatively complex doping strategy by adding polar components into the solution for the benefit on an enhanced hole transport ability.[16] This not only increases the complexity of the fabrication steps, but also questions the reproducibility and standing time of this ink at industrial scales. The development of a low-cost HTM, which is stable in its solution form, is therefore among the most important issues to evolve this solar cell technology from lab to industry.

PEDOT is a well-known conductive polymer that is widely used in organic light emitting diodes and organic photovoltaics as a low-cost hole transporting layer.[17,18] Typically, PEDOT dispersions are water-based. It is well understood that the inorganic–organic lead halide perovskite material system is very sensitive to polar solvents,[9] and this made it impossible to deposit PEDOT:PSS on top of perovskite solar cell with routine processes. In this paper, we introduce a water-free dispersion of PEDOT to replace spiro-MeOTAD in perovskite solar cells. We present a device structure consisting of a low-temperature processed TiO_2 (LT-TiO_2) as electron transport layer, a perovskite layer fabricated by a mixed solvent precursor as absorber, and a water-free PEDOT as a hole transport layer. After the optimization of the water-free PEDOT (Clevios HTL Solar 3) layer thickness, the device shows a maximum PCE of 11.75% and more than 800 h stability under ambient environmental conditions without packaging. As the impact of the acid nature on the perovskite surface was a potential concern, we next investigated a pH neutralized PEDOT, formulated in Anisole (Clevios SEJ 372). Reducing the acidity of PEDOT allowed to further enhance the initial device performance to 14.2%, most likely by reducing the density of defect states at the surface of the perovskites. To the best of our knowledge, this is the first time that such a water-free PEDOT has been used in fabricating highly efficient perovskite-based solar cells, indicating its feasibility of being a scalable low-cost hole transport layer for perovskite solar cells in a industrial production.

The water-free PEDOT (Clevios HTL Solar 3) was prepared by polymerizing ethylenedioxythiophene (EDOT) in the presence of a partially sulfonated copolymer and *p*-toluenesulfonic acid in toluene. The work function of water-free PEDOT (Clevios HTL Solar 3) determined by Kelvin probe was found to be

---

Y. Hou, H. Zhang, W. Chen, S. Chen, C. O. R. Quiroz,
Dr. H. Azimi, Dr. A. Osvet, Dr. G. J. Matt,
Prof. C. J. Brabec
Department of Materials Science and Engineering
Institute of Materials for Electronics
and Energy Technology (i-MEET)
Friedrich-Alexander University Erlangen-Nuremberg
Martensstrasse 7, 91058 Erlangen, Germany
E-mail: yi.hou@fau.de; christoph.brabec@fau.de

Y. Hou, H. Zhang, W. Chen
Erlangen Graduate School in Advanced Optical Technologies (SAOT)
Paul-Gordan-Straße 6, 91052 Erlangen, Germany

Dr. E. Zeira
OneSun Inc., P.O. Box 1199
Sausalito, CA 94966, USA

J. Seuring, Dr. N. Kausch-Busies, Dr. W. Lövenich
Heraeus Deutschland GmbH and Co.KG
Chempark S138B, Leverkusen, Germany

Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Am Weichselgarten 7, 91058 Erlangen, Germany

DOI: 10.1002/aenm.201500543

Low-Temperature and Hysteresis-Free Electron-Transporting Layers for Efficient, Regular, and Planar Structure Perovskite Solar Cells

Yi Hou, Cesar Omar Ramirez Quiroz, Simon Scheiner, Wei Chen, Tobias Stubhan, Andreas Hirsch, Marcus Halik, and Christoph J. Brabec**

With the aim of fully utilizing the low processing temperatures of perovskite solar cells, significant progress in replacing high temperature processed TiO_2 by various low-temperature solution processed electron transporting layers (LT-ETLs) was recently reported. Here, recent progress in the development of LT-ETLs for regular planar structure perovskite solar cells, which is essential for achieving high efficiency in parallel to avoiding hysteresis, is reviewed. In addition, the application of a novel hysteresis-free LT-ETLs for regular planar perovskite solar cells in our laboratory is briefly discussed. By incorporating a low temperature processed WO_x nanoparticular layer in combination with a mixed fullerene functionalized self-assembled monolayers (SAMs), a regular, planar structure, and hysteresis-free perovskite solar cell with a maximum efficiency of almost 15% can be fabricated.

1. Introduction

Nowadays, silicon photovoltaics represent the majority of shares in the solar panel market. However, the required high purity and the necessary high-temperature processing conditions significantly increase the bill of modules (BOM). Hence, during the past two decades, numerous next-generation solar technologies were developed including organic photovoltaics (OPVs), dye-sensitized solar cells (DSCs), and quantum dot solar cells (QDSCs), which all share the goal of low-temperature solution processing by roll-to-roll printing and coating.[1–4] Although, Konarka already demonstrated the commercial feasibility of scaling up OPVs by roll-to-roll in 2009, no other printing technologies have proven a transition from the lab to the market due to their low efficiency and lifetime. Recently, perovskites have drawn tremendous research interest as they have demonstrated increased power conversion efficiency up to 20%, which is getting closer and closer to other thin-film technologies.[5,6] These results became even more impressive considering their short development period compared to other inorganic PV technologies.

By utilizing the concept of mesoscopic DSCs, the first perovskite solar cell was reported in 2009 from Miyasaka and co-workers.[7] At the beginning, perovskites have been employed as sensitizers in photoelectrochemical cells using iodine-based liquid electrolytes achieving a power conversion efficiency (PCE) of 3.8%. Subsequently, by using doped 2,2′,7,7′-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)9,9′-spirobifluorene (spiro-OMeTAD), as a solid state hole-transporting materials (HTMs), Snaith et al. dramatically increased the device performance to a PCE of 9.7%.[8] Furthermore, by using a double layer of mesoporous TiO_2 and ZrO_2 as a scaffold infiltrated with perovskite, Han et al. reported a PCE of 12.8% without a hole-conducting layer, which was stable for >1000 h in ambient air under full sunlight.[9] In all these devices, the perovskite was either deposited onto mesoporous TiO_2 (mp-TiO_2), Al_2O_3, or ZrO_2 scaffolds, which still is based on the typical device configuration of solid-state DSCs (**Figure 1**a).

Until now the reported highest efficiency devices still require a high temperature processed TiO_2 mesoporous layer. The perovskite roadmap forces the production of cheap materials by a simple solution process at low temperatures further reducing costs through production of large areas on plastic substrates. In 2013, Snaith group dramatically improved PCE to over 15.4% in a regular planar structure employing a high-temperature solution processed TiO_2 layer as a electron transporting

Y. Hou, C. O. R. Quiroz, W. Chen, Dr. T. Stubhan,
Prof. C. J. Brabec
Institute of Materials for Electronics and
Energy Technology (i-MEET)
Department of Materials Science and Engineering
Friedrich-Alexander University Erlangen-Nürnberg
Martensstrasse 7, 91058 Erlangen, Germany
E-mail: yi.hou@fau.de; christoph.brabec@ww.uni-erlangen.de
Y. Hou, W. Chen
Erlangen Graduate School in Advanced Optical Technologies (SAOT)
Paul-Gordan-Straße 6, 91052 Erlangen, Germany
S. Scheiner, Prof. M. Halik
Organic Materials & Devices (OMD)
Institute of Polymer Materials
Friedrich-Alexander University Erlangen-Nürnberg
Martensstraße 7, 91058 Erlangen, Germany
Prof. A. Hirsch
Department of Chemistry and Pharmacy
Friedrich-Alexander University Erlangen-Nürnberg
Henkestraße 42, 91054 Erlangen, Germany
Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Am Weichselgarten 7, 91058 Erlangen, Germany

DOI: 10.1002/aenm.201501056

CRYSTAL GROWTH & DESIGN

Article

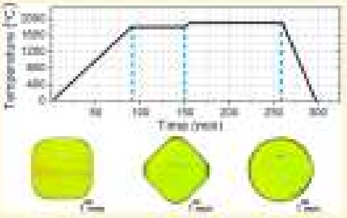
pubs.acs.org/crystal

Single Domain 3C-SiC Growth on Off-Oriented 4H-SiC Substrates

Valdas Jokubavicius,*,[†] Gholam R. Yazdi,[†] Rickard Liljedahl,[†] Ivan G. Ivanov,[†] Jianwu Sun,[†] Xinyu Liu,[†] Philipp Schuh,[‡] Martin Wilhelm,[‡] Peter Wellmann,[‡] Rositsa Yakimova,[†] and Mikael Syväjärvi[†]

[†]Department of Physics, Chemistry and Biology (IFM), Semiconductor Materials Division, Linköping University, SE 183 Linköping, Sweden
[‡]Materials Department 6 (i-meet), Crystal Growth Lab, University of Erlangen, Martensstr. 7, D-91058 Erlangen, Germany

ABSTRACT: We investigated the formation of structural defects in thick (~1 mm) cubic silicon carbide (3C-SiC) layers grown on off-oriented 4H-SiC substrates via a lateral enlargement mechanism using different growth conditions. A two-step growth process based on this technique was developed, which provides a trade-off between the growth rate and the number of defects in the 3C-SiC layers. Moreover, we demonstrated that the two-step growth process combined with a geometrically controlled lateral enlargement mechanism allows the formation of a single 3C-SiC domain which enlarges and completely covers the substrate surface. High crystalline quality of the grown 3C-SiC layers is confirmed using high resolution X-ray diffraction and low temperature photoluminescence measurements.



1. INTRODUCTION

The great challenge to obtain high crystalline quality cubic silicon carbide (3C-SiC) has hampered its use in semiconductor applications.[1−4] In order to accelerate the 3C-SiC application in electronics, high-quality thick 3C-SiC layers or substrates are needed. They could be used for homoepitaxial growth, e.g., by chemical vapor deposition (CVD), which allows reproducible growth of device quality 3C-SiC layers. In addition, thick layers could be explored as seeds in bulk growth techniques like seeded sublimation growth to obtain large 3C-SiC crystals/boules. However, thick layers of 3C-SiC with quality similar to that in commercially available hexagonal (4H and 6H) SiC substrates have not been demonstrated.

There are fundamental challenges in the growth of single crystal 3C-SiC. Heteroepitaxial layers of 3C-SiC grown on silicon substrates contain a high density of structural defects due to a large mismatch in the lattice parameter (~20%) and thermal expansion coefficient (~8%). In contrast, the mismatch problems are substantially smaller when using hexagonal SiC substrates (in-plane lattice mismatch ~0.08% for 3C/4H).[9] However, despite promising results,[5−8] the control of initial nucleation of 3C-SiC domains on hexagonal SiC, especially when growing on nominally on-axis substrates, and the reproducibility of high crystalline quality layers, in particular, thick ones, remain problematic.

Recently, a generic concept of producing 3C-SiC layers with substantially lower numbers of domains, compared to the 3C-SiC grown on nominally on-axis substrates, has been demonstrated using a lateral enlargement (LE) mechanism on off-oriented hexagonal SiC substrates.[10] The LE mechanism allows localization of the initial nucleation of 3C-SiC domains on an *in situ* formed large terrace with an on-axis area at the edge of the hexagonal substrate. These domains enlarge along the step-flow [11$\bar{2}$0] direction and completely cover the surface. It was shown that a reproducible growth of 3C-SiC layers without foreign polytype inclusions can be obtained using this approach. However, even though substantially reduced in number, the layers still contain incoherent twin boundaries, also called double positioning boundaries (DPBs), which have a pronounced influence on electrical characteristics[11,12] and thus have to be eliminated in order to unleash the full potential of 3C-SiC for various applications.

In this paper we present a two-step process combined with a geometrically controlled LE mechanism that leads to the growth of *single domain* 3C-SiC layers. Such a 3C-SiC growth approach has been developed on the grounds of detailed analysis of the formation of various structural defects in 3C-SiC layers grown under different growth conditions and different growth arrangements. In addition, we demonstrate that 3C-SiC layers with profound thickness (>1 mm) can be grown and used to obtain free-standing 3C-SiC substrates.

2. EXPERIMENTAL DETAILS

The 3C-SiC layers were grown via an LE mechanism using the sublimation epitaxial growth technique.[13] The schematic illustration of the growth setup is shown in Figure 1. The materials are placed inside an inductively heated graphite crucible on top of each other in a sandwich-like arrangement with a tantalum foil at the bottom, followed by a polycrystalline SiC plate (source material), a graphite spacer with an opening for vapor species transport, a substrate, and a graphite plate to prevent backside sublimation of the substrate. The tantalum foil acts as a carbon getter at elevated temperatures and leads to an increased concentration of silicon in the vapor phase inside the crucible. This is beneficial for the cubic polytype stabilization and expands the growth

Received: March 17, 2015
Revised: April 28, 2015
Published: April 30, 2015

DOI: 10.1021/acs.cgd.5b00368
Cryst. Growth Des. 2015, 15, 2940−2947

Journal of
Materials Chemistry C

PAPER

View Article Online
View Journal | View Issue

Opto-electronics of PbS quantum dot and narrow bandgap polymer blends†

Cite this: J. Mater. Chem. C, 2015, 3, 5499

Simon Kahmann,[ab] Andrea Mura,*[c] Loredana Protesescu,[de] Maksym V. Kovalenko,[de] Christoph J. Brabec[bf] and Maria A. Loi*[a]

Here we report on the interaction between the narrow bandgap polymer [2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta-[2,1-b;3,4-b′]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and lead sulphide (PbS) colloidal quantum dots (CQDs) upon photoexcitation. We show that the presence of both materials in a blend leads to a significant reduction of photoluminescence (PL) lifetime of the polymer. This observation is attributed, supported by transient absorption (TA) data, to an efficient electron transfer towards the QDs for excitons generated on the polymer. Furthermore, the ligand capping the QD surface exhibits a great impact on the dynamics of the PL, with the long-chain oleic acid (OA) largely suppressing any kind of interaction. By means of external quantum efficiency (EQE) measurements we find evidence that both components give rise to a contribution to the photocurrent, making this an interesting blend for future applications in hybrid organic–inorganic solar cells.

Received 17th March 2015,
Accepted 28th April 2015

DOI: 10.1039/c5tc00754a

www.rsc.org/MaterialsC

1 Introduction

The so-called third generation of photovoltaic technologies aims at a reduction of manufacturing costs and material consumption, while maintaining high efficiencies. A plethora of new materials and concepts is currently investigated in order to make future products more efficient and less expensive. Amongst them organic photovoltaics (OPV) especially have taken a leap from the proof of concept of a heterojunction by Tang in 1986[1] up to 10.6% power conversion efficiency (PCE) in 2012.[2] The relatively low permittivities of materials involved in organic solar cells demand an electron donor (D) and acceptor (A) couple to be applied in order to achieve an efficient photocurrent generation through separation of electrons and holes. The most widely spread D–A combination consists of a fullerene derivative as acceptor and a polymer as donor, forming a type-II heterojunction. Since most acceptors tend to exhibit low extinction coefficients, it is common that just the donor component gives rise to a significant solar light harvesting in these blends.

Colloidal quantum dot solar cells (QDSC) are a new class of devices that has been attracting interest for several years now. Here the active layer consists of a film of quantum dots – most commonly cadmium- or lead chalcogenides.[3–8] The absorption profile of these QDs can be tuned due to the quantum size effect.[9] Lead sulphide is of particular interest in QDSCs since its rather narrow bulk bandgap (0.41 eV) allows for harvesting photons in the near infrared region (IR) of the solar spectrum – a spectral region that is beyond reach for many other materials.

In order to fabricate working QDSCs the long insulating ligands (commonly oleic acid (OA)) that stabilise the QDs in solution, need to be exchanged for shorter entities, which establish a more efficient interconnection between the particles (without losing their confined nature). The exchange is often carried out as a solid state treatment involving thiol-containing short molecules such as 1,6-hexanedithiol (HDT), 1,2-ethanedithiol (EDT), or 3-mercaptopropionic acid (MPA) acting as bidentate linkers.

By intermixing both a narrow bandgap polymer with good performance in OPVs and QDs, one might overcome drawbacks of the two respective concepts.[10–13] Namely, the rather poor absorption of the acceptor species in OPV may be improved by using lead chalcogenides. From the QDSC point of view, the addition of the polymer into the inorganic matrix might be able to suppress the formation of cracks upon exchanging the ligand, hence offering the possibility for large-scale compatible

---

[a] Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, Groningen, NL-9747 AG, The Netherlands. E-mail: s.kahmann@rug.nl, m.a.loi@rug.nl

[b] Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander University Erlangen-Nürnberg, Martensstraße 7, D-91058 Erlangen, Germany. E-mail: christoph.brabec@fau.de

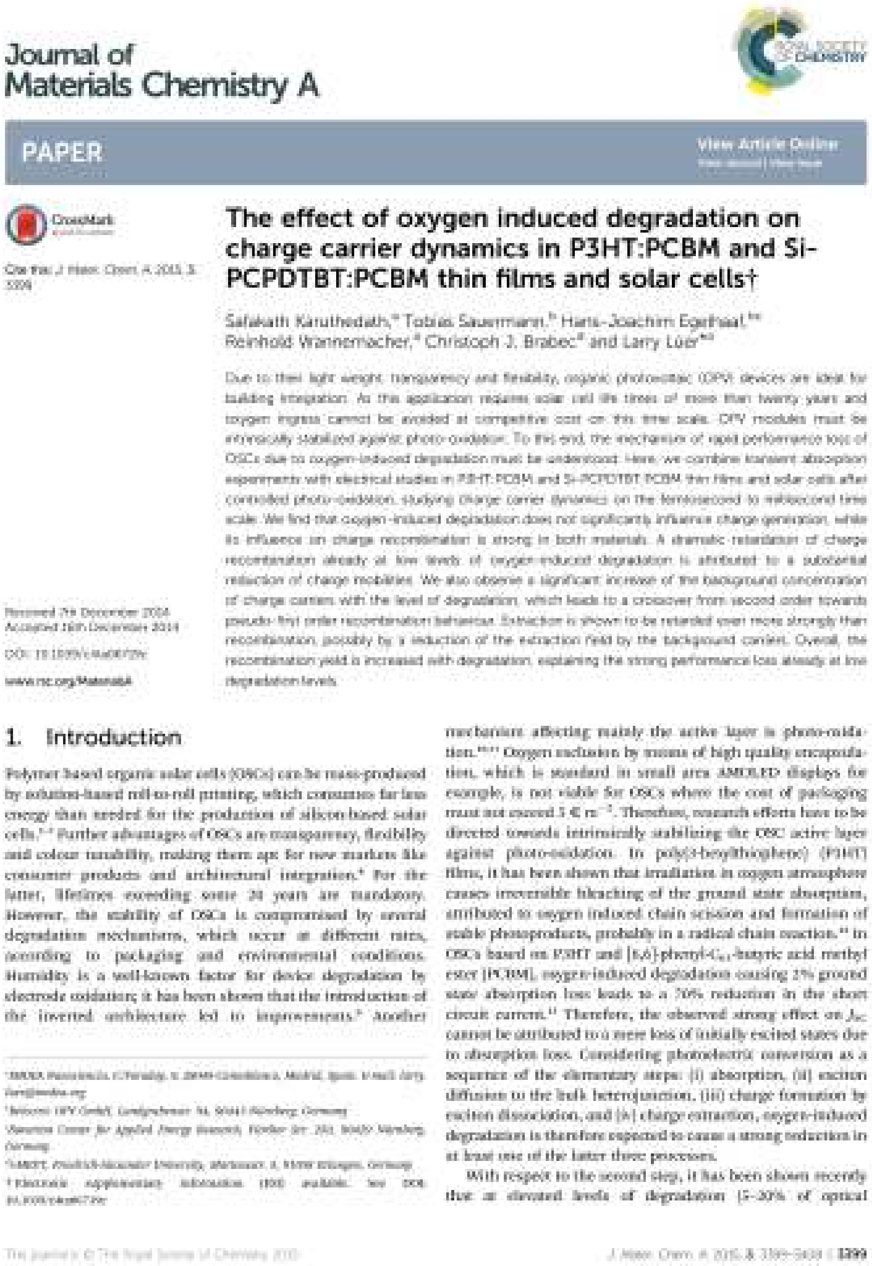
[c] Dipartimento di Fisica, Università di Cagliari, I-09042 Monserrato (CA), Italy. E-mail: andrea.mura@dsf.unica.it

[d] Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir Prelog Weg 1, Zürich, CH-8093, Switzerland. E-mail: mvkovalenko@ethz.ch

[e] EMPA-Swiss Federal Laboratories for Materials Science and Technology, Überlandstraße 129, Dübendorf, CH-8600, Switzerland

[f] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a, D-91058 Erlangen, Germany

† Electronic supplementary information (ESI) available: Fig. S1–S4. See DOI: 10.1039/c5tc00754a



Journal of
Materials Chemistry A

PAPER

View Article Online
View Journal | View Issue

Cite this: J. Mater. Chem. A, 2015, 3, 3399

The effect of oxygen induced degradation on charge carrier dynamics in P3HT:PCBM and Si-PCPDTBT:PCBM thin films and solar cells†

Safakath Karuthedath,[a] Tobias Sauermann,[b] Hans-Joachim Egelhaaf,*[bc] Reinhold Wannemacher,[a] Christoph J. Brabec[d] and Larry Lüer*[a]

Due to their light weight, transparency and flexibility, organic photovoltaic (OPV) devices are ideal for building integration. As this application requires solar cell life times of more than twenty years and oxygen ingress cannot be avoided at competitive cost on this time scale, OPV modules must be intrinsically stabilized against photo-oxidation. To this end, the mechanism of rapid performance loss of OSCs due to oxygen-induced degradation must be understood. Here, we combine transient absorption experiments with electrical studies in P3HT:PCBM and Si-PCPDTBT:PCBM thin films and solar cells after controlled photo-oxidation, studying charge carrier dynamics on the femtosecond to millisecond time scale. We find that oxygen-induced degradation does not significantly influence charge generation, while its influence on charge recombination is strong in both materials. A dramatic retardation of charge recombination already at low levels of oxygen-induced degradation is attributed to a substantial reduction of charge mobilities. We also observe a significant increase of the background concentration of charge carriers with the level of degradation, which leads to a crossover from second order towards pseudo-first order recombination behaviour. Extraction is shown to be retarded even more strongly than recombination, possibly by a reduction of the extraction field by the background carriers. Overall, the recombination yield is increased with degradation, explaining the strong performance loss already at low degradation levels.

Received 7th December 2014
Accepted 16th December 2014

DOI: 10.1039/c4ta06710e

www.rsc.org/MaterialsA

1. Introduction

Polymer based organic solar cells (OSCs) can be mass-produced by solution-based roll-to-roll printing, which consumes far less energy than needed for the production of silicon based solar cells.[1–3] Further advantages of OSCs are transparency, flexibility and colour tunability, making them apt for new markets like consumer products and architectural integration.[4] For the latter, lifetimes exceeding some 20 years are mandatory. However, the stability of OSCs is compromised by several degradation mechanisms, which occur at different rates, according to packaging and environmental conditions. Humidity is a well-known factor for device degradation by electrode oxidation; it has been shown that the introduction of the inverted architecture led to improvements.[5] Another mechanism affecting mainly the active layer is photo-oxidation.[6–11] Oxygen exclusion by means of high quality encapsulation, which is standard in small area AMOLED displays for example, is not viable for OSCs where the cost of packaging must not exceed 5 € m^{-2}. Therefore, research efforts have to be directed towards intrinsically stabilizing the OSC active layer against photo-oxidation. In poly(3-hexylthiophene) (P3HT) films, it has been shown that irradiation in oxygen atmosphere causes irreversible bleaching of the ground state absorption, attributed to oxygen induced chain scission and formation of stable photoproducts, probably in a radical chain reaction.[6] In OSCs based on P3HT and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM), oxygen-induced degradation causing 2% ground state absorption loss leads to a 70% reduction in the short circuit current.[11] Therefore, the observed strong effect on J_{SC} cannot be attributed to a mere loss of initially excited states due to absorption loss. Considering photoelectric conversion as a sequence of the elementary steps: (i) absorption, (ii) exciton diffusion to the bulk heterojunction, (iii) charge formation by exciton dissociation, and (iv) charge extraction, oxygen-induced degradation is therefore expected to cause a strong reduction in at least one of the latter three processes.

With respect to the second step, it has been shown recently that at elevated levels of degradation (5–20% of optical

---

[a] IMDEA Nanociencia, c/Faraday, 9, 28049 Cantoblanco, Madrid, Spain. E-mail: larry.luer@imdea.org

[b] Belectric OPV GmbH, Landgrabenstr. 94, 90443 Nürnberg, Germany

[c] Bavarian Center for Applied Energy Research, Fürther Str. 250, 90429 Nürnberg, Germany

[d] i-MEET, Friedrich-Alexander University, Martensstr. 7, 91058 Erlangen, Germany

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ta06710e

Real-Time Investigation of Intercalation and Structure Evolution in Printed Polymer:Fullerene Bulk Heterojunction Thin Films

*Thaer Kassar, Nusret S. Güldal, Marvin Berlinghof, Tayebeh Ameri, Andreas Kratzer, Bob C. Schroeder, Giovanni Li Destri, Andreas Hirsch, Martin Heeney, Iain McCulloch, Christoph J. Brabec, and Tobias Unruh**

The complex intermixing morphology is critical for the performance of the nanostructured polymer:fullerene bulk heterojunction (BHJ) solar cells. Time resolved in situ grazing incidence X-ray diffraction and grazing incidence small angle X-ray scattering are used to track the structure formation of BHJ thin films formed from the donor polymer poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene) with different fullerene derivative acceptors. The formation of stable bimolecular crystals through the intercalation of fullerene molecules between the side chains of polymer crystallites is investigated. Such systems exhibit more efficient exciton dissociation but lower photoconductance and faster decay of charges. On the basis of the experimental observations, intercalation obviously takes place before or with the formation of the crystalline polymer domains. It results in more stable structures whose volume remains constant upon further drying. Three distinct periods of drying are observed and the formation of unidimensional fullerene channels along the π-stacking direction of polymer crystallites is confirmed.

1. Introduction

Solution-processable bulk heterojunction (BHJ) organic solar cells exhibit a promising potential as inexpensive alternative to traditional inorganic photovoltaics through "roll-to-roll" printing on flexible materials.[1–7] On a laboratory scale devices with power conversion efficiencies exceeding 11% have been achieved.[4–7] These devices possess an active layer which consists of a blend of an electron-donating conjugated polymer and an electron-accepting fullerene derivative. The polymer is selected to absorb photons in the relevant range of the visible–UV spectrum. In this process, excitons are generated in the polymer. By diffusion, the excitons can reach the donor–acceptor interface at the polymer–fullerene phase boundary where they can dissociate into free charge carriers. Due to the short exciton mean diffusion length of about 5–10 nm in typical conjugated polymers,[8,9] the two phases need to be intermixed on the nanoscale which ensures an effective charge separation in such BHJ systems. Extraction of photo-generated electrons and holes before recombining requires donor/acceptor percolation pathways to facilitate charge carrier transport. From these considerations, it becomes obvious that the performance of a BHJ solar cell strongly depends on the interpenetrating morphology of the nanostructured active layer.[10,11]

BHJs were thought to be separated into domains of relatively pure polymer and pure fullerene phases.[12–15] Later it was found that fullerene derivatives can intercalate between the polymer side chains in some polymer:fullerene blends resulting in bimolecular crystals. Such intercalation affects performance and charge transport of the active layer.[16–20] Fullerenes in blends with intercalation fill all the space between the polymer side chains before forming its pure domains.[21] In this case, high fullerene concentrations are needed to achieve interconnected precipitated fullerene domains[18] which are essential for creating electron percolation paths and thus for device operation.[18] Intercalation increases the blend cohesion and resistance to mechanical failure.[20] The bimolecular

---

T. Kassar, M. Berlinghof, Prof. T. Unruh
Crystallography and Structure Physics
Physics Department
Friedrich-Alexander-Universität
Erlangen-Nürnberg
Staudtstraße 3, 91058 Erlangen, Germany
E-mail: tobias.unruh@fau.de
N. S. Güldal, Dr. T. Ameri, Prof. C. J. Brabec
Materials for Electronics and Energy Technology
Friedrich-Alexander-Universität Erlangen-Nürnberg
Martensstraße 7, 91058 Erlangen, Germany
A. Kratzer, Prof. A. Hirsch
Interdisciplinary Center of
Molecular Materials (ICMM)
Friedrich-Alexander-Universität Erlangen-Nürnberg
Henkestraße 42, 91054 Erlangen, Germany
Dr. B. C. Schroeder, Prof. M. Heeney
Prof. I. McCulloch
Imperial College London
Center for Plastic Electronics
London SW7 2AZ, UK
Dr. G. L. Destri
The European Synchrotron
Radiation Facility (ESRF)
71 Avenue des
Martyrs, 38000 Grenoble, France

DOI: 10.1002/aenm.201502025

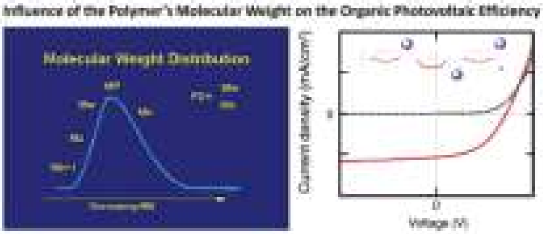
Review

Macromolecular
Rapid Communications

Systematic Analysis of Polymer Molecular Weight Influence on the Organic Photovoltaic Performance

Athanasios Katsouras, Nicola Gasparini, Chrysanthos Koulogiannis,
Michael Spanos, Tayebeh Ameri, Christoph J. Brabec,
Christos L. Chochos,* Apostolos Avgeropoulos

The molecular weight of an electron donor-conjugated polymer is as essential as other well-known parameters in the chemical structure of the polymer, such as length and the nature of any side groups (alkyl chains) positioned on the polymeric backbone, as well as their placement, relative strength, the ratio of the donor and acceptor moieties in the backbone of donor–acceptor (D–A)-conjugated polymers, and the arrangement of their energy levels for organic photovoltaic performance. Finding the "optimal" molecular weight for a specific conjugated polymer is an important aspect for the development of novel photovoltaic polymers. Therefore, it is evident that the chemistry of functional conjugated polymers faces major challenges and materials have to adopt a broad range of specifications in order to be established for high photovoltaic performance. In this review, the approaches followed for enhancing the molecular weight of electron-donor polymers are presented in detail, as well as how this influences the optoelectronic properties, charge transport properties, structural conformation, morphology, and the photovoltaic performance of the active layer.



A. Katsouras, C. Koulogiannis, M. Spanos, Dr. C. L. Chochos, Prof. A. Avgeropoulos
Department of Materials Science Engineering
University of Ioannina
Ioannina 45110, Greece
E-mail: cchochos@cc.uoi.gr
N. Gasparini, Dr. T. Ameri, Prof. C. J. Brabec
Institute of Materials for Electronics and
Energy Technology (i-MEET)
Friedrich-Alexander-University Erlangen-Nuremberg
Martensstraße 7, 91058 Erlangen, Germany
Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Haberstrasse 2a, 91058 Erlangen, Germany

1. Introduction

The certified power conversion efficiencies (PCE) of polymer-fullerene bulk heterojunction (BHJ) solar cells[1] are now above 10 and 11% in single-junction[2] and tandem[3] architectures, respectively. This recent improvement in device performance is due to the design and synthesis of new donor–acceptor (D–A) polymers exhibiting energy levels and band gaps optimized for high PCE.[4] Some of these high-efficiency polymers are now available commercially in small quantities for laboratory-scale research and development. Quite often, these polymers are

Macromol. Rapid Commun. 2015, DOI: 10.1002/marc.201500398

wileyonlinelibrary.com

DOI: 10.1002/marc.201500398

APPLIED PHYSICS LETTERS 107, 103305 (2015)

Low-cost copper complexes as p-dopants in solution processable hole transport layers

Renate Kellermann,[1,2] Dan Taroata,[2] Anna Maltenberger,[2] David Hartmann,[2] Christoph J. Brabec,[1] and Guenter Schmid[2]
[1]*Department for Materials Science and Engineering, Chair for Materials for Electronics and Energy Technology, Friedrich-Alexander-University Erlangen-Nuremberg, Erlangen 91058, Germany*
[2]*Siemens AG – Corporate Technology, Guenther-Scharowsky-Str. 1, Erlangen 91058, Germany*

(Received 24 June 2015; accepted 28 August 2015; published online 11 September 2015)

We demonstrate the usage of the Lewis-acidic copper(II)hexafluoroacetylacetonate (Cu(hfac)$_2$) and copper(II)trifluoroacetylacetonate (Cu(tfac)$_2$) as low-cost p-dopants for conductivity enhancement of solution processable hole transport layers based on small molecules in organic light emitting diodes (OLEDs). The materials were clearly soluble in mixtures of environmentally friendly anisole and xylene and spin-coated under ambient atmosphere. Enhancements of two and four orders of magnitude, reaching 4.0×10^{-11} S/cm with a dopant concentration of only 2 mol% Cu(hfac)$_2$ and 1.5×10^{-9} S/cm with 5 mol% Cu(tfac)$_2$ in 2,2′,7,7′-tetra(N,N-ditolyl)amino-9,9-spiro-bifluorene (spiro-TTB), respectively, were achieved. Red light emitting diodes were fabricated with reduced driving voltages and enhanced current and power efficiencies (8.6 lm/W with Cu(hfac)$_2$ and 5.6 lm/W with Cu(tfac)$_2$) compared to the OLED with undoped spiro-TTB (3.9 lm/W). The OLED with Cu(hfac)$_2$ doped spiro-TTB showed an over 8 times improved LT$_{50}$ lifetime of 70 h at a starting luminance of 5000 cd/m^2. The LT$_{50}$ lifetime of the reference OLED with PEDOT:PSS was only 8 h. Both non-optimized OLEDs were operated at similar driving voltage and power efficiency. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4930237]

Since the first double layer organic light emitting diode (OLED) was presented by Tang and van Slyke in 1987,[1] a lot of efforts have been invested in decreasing the driving voltage and at the same time increasing the efficiency of such devices. Recently, power efficiency of 156 lm/W for a white OLED was presented by NEC Lighting Ltd.[2] These improvements include preparation process, stack layout and materials, e.g., the usage of highly efficient phosphorescent emitting materials[3,4] and electrical doping to improve hole[5] and electron transport.[6] The requirements for the dopants range from enhancement of the electrical conductivity of the host material to electrical and thermal stability during operation and cheap production in large quantities. From the optical point of view, the absorption of the transport layer has to be minimized to enhance the extraction of the generated light in the emitting layer. As host materials, small molecules are promising candidates, because they possess usually a higher electrical conductivity, better reproducibility, and a higher doping potential compared to polymers (e.g., PolyTPD and PVK). A simultaneous solution deposition of small molecule based host materials and dopants is required. First, efforts for solution processing of hole transport layers were made.[7,8] Most of the publications use an additional poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer on the ITO as transport and injection layer. Our focus is therefore towards solution processed doped hole transport layers using small molecules as host materials dissolved in common, environmental and processing friendly solvents like anisole and xylene. The organometallic fluorinated copper(II)β-diketonate complexes were found to be promising candidates to p-dope commonly used hole conductors like NPB or Spiro-TTB. These materials are well known as precursors for copper chemical vapor deposition and, thus well characterized and commercially available.[10–12]

In this paper, we report on p-doping of the small molecule hole transport material 2,2′,7,7′-tetra(N,N-ditolyl)amino-9,9-spiro-bifluorene (spiro-TTB) with copper(II)hexafluoro-acetylacetonate (Cu(hfac)$_2$) and copper(II)trifluoroacetylacetonate (Cu(tfac)$_2$).

The dopants copper(II)hexafluoroacetylacetonate (Cu(hfac)$_2$) and Copper(II)trifluoro-acetylacetonate (Cu(tfac)$_2$) were purchased from Sigma Aldrich, purified by sublimation and stored in an argon filled glove box. The sublimation temperature of Cu(tfac)$_2$ was 100 °C at 10^{-3} mbar and of Cu(hfac)$_2$ 50 °C at 10^{-3} mbar. The host material, 2,2′,7,7′-tetra(N,N-ditolyl)amino-9,9-spiro-bifluorene (spiro-TTB), was used as received from Lumtec Corporation. The solvents, anisole, and xylene (a mixture of isomers) were used after purification. Anisole was dried over sodium and distilled, whereas xylene was dried over molecular sieve. All solutions were filtered through a 0.1 μm syringe before use. All other materials (N,N′-Bis(naphthalene-1-yl)-N,N′-bis(phenyl)-benzidine, 1,3,5-Tris(1-phenyl-1 H-benzimidazol-2-yl)benzene, Iridium(III)bis (2-methyldibenzo[f,h]quinoxaline)-(acetylacetonate), LiF and aluminum) for fabrication of the OLED were purchased from Lumtec Corporation and used as received.

The dopants and the host material were dissolved to yield clear and colorless solutions, unlike the state of the art solution processable suspension PEDOT:PSS. No film forming additives were used. The solutions were spin-coated in a clean-room under ambient atmosphere.

Both, Cu(tfac)$_2$ and Cu(hfac)$_2$ are Lewis acids and therefore supposed to be well suited to dope organic hole transport materials. A higher fluorination of the β-diketonate

NANO FOCUS

Prospects of Nanoscience with Nanocrystals

Maksym V. Kovalenko,* Liberato Manna, Andreu Cabot, Zeger Hens, Dmitri V. Talapin,* Cherie R. Kagan,* Victor I. Klimov, Andrey L. Rogach, Peter Reiss, Delia J. Milliron, Philippe Guyot-Sionnest,* Gerasimos Konstantatos, Wolfgang J. Parak, Taeghwan Hyeon, Brian A. Korgel, Christopher B. Murray, and Wolfgang Heiss*

ABSTRACT Colloidal nanocrystals (NCs, i.e., crystalline nanoparticles) have become an important class of materials with great potential for applications ranging from medicine to electronic and optoelectronic devices. Today's strong research focus on NCs has been prompted by the tremendous progress in their synthesis. Impressively narrow size distributions of just a few percent, rational shape-engineering, compositional modulation, electronic doping, and tailored surface chemistries are now feasible for a broad range of inorganic compounds. The performance of inorganic NC-based photovoltaic and light-emitting devices has become competitive to other state-of-the-art materials. Semiconductor NCs hold unique promise for near- and mid-infrared technologies, where very few semiconductor materials are available. On a purely fundamental side, new insights into NC growth, chemical transformations, and self-organization can be gained from rapidly progressing in situ characterization and direct imaging techniques. New phenomena are constantly being discovered in the photophysics of NCs and in the electronic properties of NC solids. In this Nano Focus, we review the state of the art in research on colloidal NCs focusing on the most recent works published in the last 2 years.

Thermodynamically stable colloidal solutions of nanosized inorganic materials are well-described in colloidal chemistry textbooks as "sols" and have been known in a modern scientific context since the 19th century, with ruby-colored gold sols produced by Michael Faraday as one notable example.[1] The birth of modern nanoscience with nanocrystals (NCs) is, however, attributed to a much later period beginning in the early 1980s and extending to the present. Early photochemistry studies on tailored colloidal CdS and TiO_2 arose from the oil crisis in the late 1970s, and semiconductor NCs with enhanced surface chemistry were considered highly important for efficient harvesting of solar energy by means of photoelectrochemistry (A. Nozik, L. Brus, A. Henglein, and their co-workers).[2−6] Semiconductor NCs were termed quantum dots (QDs) after the discovery and explanation of quantum size effects in the optical spectra of CuCl NCs embedded into glass and alkali-halide matrices (A. Ekimov, A. Onushchenko, A. Efros, T. Itoh, and co-workers)[7−12] and in aqueous solutions of colloidal CdS NCs (L. Brus and co-workers).[6−8] Since the mid-1990s, colloidal QDs have become a masterpiece of NC research and one of the most accomplished building blocks of modern nanoscience due to the emergence of surfactant-assisted

*Address correspondence to mvkovalenko@ethz.ch, wolfgang.heiss@fau.de.

Received for review October 31, 2014

Published online January 23, 2015
10.1021/nn506223h

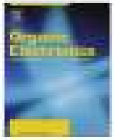
KOVALENKO ET AL.   VOL. 9 ■ NO. 2 ■ 1012–1057 ■ 2015 ACSNANO   1012
www.acsnano.org

Organic Electronics 17 (2015) 334–339

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Printing high performance reflective electrodes for organic solar cells

Johannes Krantz [a,*], Karen Forberich [a], Peter Kubis [a], Florian Machui [a], Jie Min [a], Tobias Stubhan [a], Christoph J. Brabec [a,b]

[a] Department of Materials Science, i-MEET (WW6), Friedrich-Alexander-University of Erlangen-Nuremberg, Martensstraße 7, 91058 Erlangen, Germany
[b] Bavarian Center for Applied Energy Research (ZAE Bayern), Am Weichselgarten 7, 91058 Erlangen, Germany

ARTICLE INFO

Article history:
Received 10 October 2014
Received in revised form 5 December 2014
Accepted 13 December 2014
Available online 24 December 2014

Keywords:
Printed silver precursor ink
Solution processable electrode
Highly reflective electrode
Superstrate architecture
Substrate architecture

ABSTRACT

In this paper we solve a long term material problem of thin film organic electronics, namely the solution processing of an opaque electrode. Solution processing of opaque metallic top electrodes typically leads to severe shunting problems. We solve this issue by reversing the electrode sequence and print a highly conductive but opaque bottom electrode from metallic precursors. Devices based on these printed bottom electrodes are compared to reference stacks based on evaporated silver. The transparent top electrode is solution processed from silver nanowire inks, which results in highly transparent electrodes with excellent conductivity. The optical, mainly reflective properties of the opaque silver electrode are investigated in comparison to screen-printed silver pastes. The outstanding smoothness of the printed Ag electrode results in high reflectivity and poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) based solar cells with $\eta = 2.5\%$ and high fill factors performing on par with reference devices on evaporated silver electrode layers.

1. Introduction

Screen or flexo printable metal pastes are commonly employed for printing an opaque top electrode, for Silicon solar modules [1–3]. Screen printing itself is a rather mechanically violent process, where a heavily particle loaded paste is squeezed through a fine mesh (screen) with a desired pattern [4]. These several micron thick and highly conductive films allow effective charge collection. Highly conductive pastes are required to minimize shading and the aspect ratio of the collection grids (height/width) typically exceeds 20 μm/100 μm or more [5]. Well established pastes employ metals like silver (Ag), copper (Cu) or aluminum (Al) [6].

Organic solar cells on the other hand are prone to shunting due to their extreme small active layer thickness. Screen printing of Ag inks on top of a 100 nm thick active layer is regarded as a high risk process and cells based on screen printed electrodes frequently suffer from shunting. In addition screen printed Ag electrodes are of fairly rough nature due to the rather large size of the metal particles.

Screen-printed bottom electrodes were discussed as a viable alternative, since the very high surface roughness of up to several 100s of nm does not allow deposition of high qualitative and conformal organic semiconductor films [1,3]. In addition, the dominating diffuse reflective properties of screen-printed metal paste based electrode layers cause losses for thin film solar cells which rely on light reflection from the back electrode [7,8]. To employ a screen-printed electrode layer with such a high roughness and undesirable optical properties as a bottom electrode,

---

* Corresponding author.
E-mail address: johannes.krantz@ww.uni-erlangen.de (J. Krantz).

http://dx.doi.org/10.1016/j.orgel.2014.12.015
1566-1199/

Organic Electronics 17 (2015) 334–339

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Printing high performance reflective electrodes for organic solar cells

Johannes Krantz [a,*], Karen Forberich [a], Peter Kubis [a], Florian Machui [a], Jie Min [a], Tobias Stubhan [a], Christoph J. Brabec [a,b]

[a] Department of Materials Science, i-MEET (WW6), Friedrich-Alexander-University of Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany
[b] Bavarian Center for Applied Energy Research (ZAE Bayern), Am Weichselgarten 7, 91058 Erlangen, Germany

ARTICLE INFO

Article history:
Received 10 October 2014
Received in revised form 5 December 2014
Accepted 13 December 2014
Available online 24 December 2014

Keywords:
Printed silver precursor ink
Solution processable electrode
Highly reflective electrode
Superstrate architecture
Substrate architecture

ABSTRACT

In this paper we solve a long term material problem of thin film organic electronics, namely the solution processing of an opaque electrode. Solution processing of opaque metallic top electrodes typically leads to severe shunting problems. We solve this issue by reversing the electrode sequence and print a highly conductive but opaque bottom electrode from metallic precursors. Devices based on these printed bottom electrodes are compared to reference stacks based on evaporated silver. The transparent top electrode is solution processed from silver nanowire inks, which results in highly transparent electrodes with excellent conductivity. The optical, mainly reflective properties of the opaque silver electrode are investigated in comparison to screen-printed silver pastes. The outstanding smoothness of the printed Ag electrode results in high reflectivity and poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) based solar cells with η = 2.5% and high fill factors performing on par with reference devices on evaporated silver electrode layers.

1. Introduction

Screen or flexo printable metal pastes are commonly employed for printing an opaque top electrode, for Silicon solar modules [1–3]. Screen printing itself is a rather mechanically violent process, where a heavily particle loaded paste is squeezed through a fine mesh (screen) with a desired pattern [4]. These several micron thick and highly conductive films allow effective charge collection. Highly conductive pastes are required to minimize shading and the aspect ratio of the collection grids (height/width) typically exceeds 20 μm/100 μm or more [5]. Well established pastes employ metals like silver (Ag), copper (Cu) or aluminum (Al) [6].

Organic solar cells on the other hand are prone to shunting due to their extreme small active layer thickness. Screen printing of Ag inks on top of a 100 nm thick active layer is regarded as a high risk process and cells based on screen printed electrodes frequently suffer from shunting. In addition screen printed Ag electrodes are of fairly rough nature due to the rather large size of the metal particles.

Screen-printed bottom electrodes were discussed as a viable alternative, since the very high surface roughness of up to several 100s of nm does not allow deposition of high qualitative and conformal organic semiconductor films [1,3]. In addition, the dominating diffuse reflective properties of screen-printed metal paste based electrode layers cause losses for thin film solar cells which rely on light reflection from the back electrode [7,8]. To employ a screen-printed electrode layer with such a high roughness and undesirable optical properties as a bottom electrode,

---

* Corresponding author.
E-mail address: johannes.krantz@ww.uni-erlangen.de (J. Krantz).

http://dx.doi.org/10.1016/j.orgel.2014.12.015
1566-1199/

Progress in
PHOTOVOLTAICS

PROGRESS IN PHOTOVOLTAICS: RESEARCH AND APPLICATIONS
Prog. Photovolt: Res. Appl. 2015; **23**:238–246

RESEARCH ARTICLE

Patterning of organic photovoltaic modules by ultrafast laser

Peter Kubis[1,3]*, Ning Li[1], Tobias Stubhan[1], Florian Machui[1], Gebhard J. Matt[1],
Monika M. Voigt[1,2] and Christoph J. Brabec[1,2]

[1] Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany
[2] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstr. 2a, 91058 Erlangen, Germany
[3] Erlangen Graduate School in Advanced Optical Technologies (SAOT), Paul-Gordan-Str. 6, 91052 Erlangen, Germany

ABSTRACT

In this paper, we demonstrate that laser patterning of organic solar cells by ultrafast laser systems (pulse length <350 fs) is an attractive process to produce photovoltaic modules with outstanding high geometric fill factors. Moreover, in terms of precision, registration, and debris generation and in terms of keeping the damage to the underneath layers at a minimum, ultrafast laser patterning with a pulse length of few hundreds of femtoseconds turns out to yield superior results. Ablation of all three different solar cell layers (electrodes (P1 and P3) and interfaces and semiconductor (P2)) is achieved with a single wavelength simply by a precise adjustment of the laser fluence and the patterning overlap. Camera positioning allows a precise registration between the various processing steps and a reduction of the width of the overall interconnection regime to the hundreds of micrometers dimension, resulting in high geometrical fill factors of over 90% for monolithically interconnected organic solar cell modules. Copyright © 2013 John Wiley & Sons, Ltd.

KEYWORDS
femtosecond pulses; laser patterning; PV module; organic solar cells

***Correspondence**
Peter Kubis, Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany.
E-mail: peter.kubis@ww.uni-erlangen.de

Received 2 November 2012; Revised 19 July 2013; Accepted 14 August 2013

1. INTRODUCTION

Recent developments in organic photovoltaics (OPV) showed solar cell efficiencies exceeding 10% [1,2], which is already comparable with the class of amorphous and microcrystalline silicon solar cells. Despite the fact that these achievements were obtained under laboratory conditions, OPV is becoming an attractive technology for the consumer electronics and outdoor photovoltaic (PV) market. The ability of solution processing opens the way for variable production schemes utilizing high throughput roll-to-roll (R2R) or inkjet sheet-to-sheet production of OPV cells [3]. The advantages of the various solution processing methods were already discussed for poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) composites [4]. Besides inkjet printing, slot die and roller coating techniques were the most frequently demonstrated production methods. On the other hand, thin-film PV modules require the sectioning into multiple cells for series interconnection. The P1 line separates the substrate electrode (indium tin oxide (ITO) in our case), the P2 line removes the semiconductor from the ITO to allow the formation of a low ohmic contact between the top and bottom electrodes, and finally, the P3 line separates the top electrode between the single cells (Figure 1). The area between the P1 and P3 lines is PV inactive, or so-called "dead area". Typically, the dead area is accounted for the module efficiency by the geometrical fill factor (GFF), which is the ratio between the PV active area and the total module area. The larger the dead area, the smaller the GFF and the lower the module efficiency. Consequently, high GFF modules require highest resolution of the P1, P2, and P3 lines. This is a clear bottleneck for slot die or roller coating methods. While both methods allow the deposition of stripe patterns in down-web direction, the resolution is rather in the millimeter regime than in the micrometer regime. As a consequence, most coated modules published so far had a GFF ranging from 50% to approximately 70% including contact areas and bus bars [2,3]. To point out the importance of a high GFF: GFF of 50% reduces a 5% cell into a 2.5% module.

Journal of
Materials Chemistry C

COMMUNICATION

View Article Online
View Journal | View Issue

Charge transport in nanoparticular thin films of zinc oxide and aluminum-doped zinc oxide†

Thomas Lenz,‡[a] Moses Richter,[a] Gebhard J. Matt,*[a] Norman A. Luechinger,[b] Samuel C. Halim,[b] Wolfgang Heiss[c] and Christoph J. Brabec[a]

Cite this: J. Mater. Chem. C, 2015, 3, 1468

Received 2nd September 2014
Accepted 22nd December 2014

DOI: 10.1039/c4tc01968e

www.rsc.org/MaterialsC

In this work, we report on the electrical characterization of nanoparticular thin films of zinc oxide (ZnO) and aluminum-doped ZnO (AZO). Temperature-dependent current–voltage measurements revealed that charge transport for both, ZnO and AZO, is well described by the Poole–Frenkel model and excellent agreement between the experimental data and the theoretical predictions is demonstrated. For the first time it is shown that the nature of the charge-transport is not affected by the doping of the nanoparticles and it is proposed that the Poole–Frenkel effect is an intrinsic and universally limiting mechanism for the charge transport in nanoparticular thin films with defect states within the bandgap.

Zinc oxide (ZnO) – a II–VI compound semiconductor with a large band gap (3.37 eV) – exhibits an excitingly widespread range of potential applications,[1] such as lasers,[2] field-effect transistors,[3–5] transducers,[6] varistors,[7] sensors,[8] UV detectors[9] and also thin-film solar cells, where it can serve as an active[10,11] or interfacial[12,13] or electrode material.[14]

Moreover, ZnO is a promising material in the field of transparent[4,5,15] and flexible electronics,[15,16] because large-area solution processing on flexible substrates using techniques like ink-jet printing appears feasible.[17,18] The solutions for film deposition are either based on the sol–gel route or on nanoparticle synthesis. The latter has the advantage that the synthesis and the film deposition can be separated from each other. As pointed out previously,[19,20] this allows cheap and high-throughput synthesis at elevated temperatures, while the film deposition is achieved at lower temperatures, which is a prerequisite for the use of flexible (often polymer-based) substrates.

The problem of nanoparticulate ZnO thin films deposited at low temperatures is that they hardly reach the electric performance of zinc oxide films based on sputtering[21] or spray pyrolysis.[22] Therefore, a better understanding of the electric conduction in these films is desired.

So far, most of the charge transport studies on ZnO nanoparticle films used the transistor device structure: Meulenkamp[23] and Roest *et al.*[24,25] studied ZnO nanoparticles with small sizes (≈5 nm) permeated in electrolyte solutions and it was demonstrated that transport occurs *via* tunnelling between discrete electronic states with or without additional thermal activation depending on the characteristics of the electrolyte.[26] Besides, space-charge limited conduction (SCLC) was shown for ZnO by Babel *et al.*[27] and by Caglar *et al.*[28] (sandwich device geometry). In these two cases,[27,28] the sizes of the nanostructures were larger (above 25 nm) compared to the above-mentioned reports. This might partially explain the different findings.

Discrepancies between various transport investigations were also revealed for other nanoparticular materials, *e.g.* for nanostructured films of silicon. Besides hopping,[29–31] SCLC,[32] the Poole–Frenkel effect,[33,34] and tunnelling[35,36] were reported for nano-Si (porous silicon or nanoparticles). These inconsistent results further emphasize the need for a detailed description of charge transport in nanoparticular films.

In this work, the charge transport of nanoparticulate ZnO and AZO thin films was investigated. A dispersion of ligand-stabilized ZnO or AZO nanoparticles was deposited on top of an ITO substrate *via* multiple doctor blading[37,38] steps. The resulting film thickness is 0.7–1 µm. Afterwards the sample was transferred to a vacuum chamber equipped with a physical vapor deposition (PVD) system for deposition of a 100 nm thick Ag top contact (for further details see ESI†).

---

[a] *Institute Materials for Electronics and Energy Technology (i-MEET), Department of Materials Science, Friedrich-Alexander-Universität (FAU), Martensstraße 7, 91058, Germany. E-mail: gebhard.matt@ww.uni-erlangen.de; Fax: +49 9131 8528495; Tel: +49 9131 8527726*

[b] *Nanograde Ltd, Staefa, Laubisrütistr. 50, CH-8712, Switzerland*

[c] *Institute for Solid-State and Semiconductor Physics, Johannes Kepler University, Linz, Austria*

† Electronic supplementary information (ESI) available: The experimental procedures, the symmetry of the J–V data of AZO and ZnO, the fitting of the AZO J–V plots and tables containing the data related to Fig. 2b and 3b. See DOI: 10.1039/c4tc01968e

‡ Current address: Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany.

EPJ Photovoltaics 6, 60301 (2015)
www.epj-pv.org
DOI: 10.1051/epjpv/2015005

Recrystallized thin-film silicon solar cell on graphite substrate with laser single side contact and hydrogen passivation

Da Li[1,*], Stephan Wittmann[1], Thomas Kunz[1], Taimoor Ahmad[1], Nidia Gawehns[1], Maik T. Hessmann[1], Jan Ebser[2], Barbara Terheiden[2], Richard Auer[1], and Christoph J. Brabec[1,3]

[1] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstr. 2a, 91058 Erlangen, Germany
[2] Department of Physics, University of Konstanz, Box 676, 78457 Konstanz, Germany
[3] Institute of Materials for Electronics and Energy Technology (i-MEET), University of Erlangen-Nuremberg, Martensstr. 7, 91058 Erlangen, Germany

Received: 13 January 2015 / Received in final form: 20 April 2015 / Accepted: 4 May 2015

Abstract Laser single side contact formation (LSSC) and the hydrogen passivation process are studied and developed for crystalline silicon thin film (CSiTF) solar cells on graphite substrates. The results demonstrate that these two methods can improve cell performance by increasing the open circuit voltage and fill factor. In comparison with our previous work, we have achieved an increase of 3.4% absolute cell efficiency for a 40 μm thick 4 cm^2 aperture area silicon thin film solar cell on graphite substrate. Current density-voltage (J-V) measurement, quantum efficiency (QE) and light beam induced current (LBIC) are used as characterization methods.

For crystalline silicon thin film (CSiTF) solar cells on the foreign substrates, a recrystallization process plays an important role in enlarging the size of the silicon grains in order to reduce the density of the electrically active defects and increase the cell efficiencies, and hence the electron-beam recrystallization [1,2], zone melting recrystallization (ZMR) [3,4] and laser recrystallization [5–9] are widely developed [10–13]. Foreign substrate materials, such as ceramics [14–16] and graphite [17], are generally used for CSiTF cell fabrication with the high temperature approach. Schillinger et al. [18] described a CSiTF cell concept on zircon ceramic substrates using ZMR reached 6.1% conversion efficiency. Graphite substrates can be processed at high temperature. Moreover, they are available at high purity and with thermal expansion characteristics similar to silicon. While standard graphite types will not meet the cost requirements, developments for low-cost types such as biogenic substrates are in progress [19].

In previous work, we have reported a best laboratory cell efficiency of 6.8% with the 4 cm^2 aperture area on the graphite substrate [20]. That cell concept is shown in Figure 1a. The laser edge isolation (LEI) technique was applied to avoid the parasitic electrical connection between the front and back contacts. This technique was proved to be a convenient and accurate method instead of the plasma etching process. By using the LEI technique, the best parallel resistance, approximately 1.7 Ω m^2, was achieved.

Much effort has been devoted to the metallization of CSiTF solar cells on foreign substrates. Stocks et al. [21] presented the concept of CSiTF solar cells with base front-contacts. Hebling et al. [22] realized the concept by using photolithography. Meanwhile, Lüdemann et al. [23] realized base front-contacts silicon solar cells on a SiC intermediate layer with a graphite substrate. Furthermore, Rachow et al. [24] named the concept as single side contact formation. Different microstructures of single side concepts can be formed using photolithography [21] or reactive ion etching (RIE) [25]. However, the photolithography is an expensive technology, whereas a typical RIE system consists of a vacuum chamber and a plasma generation system. Due to the development of laser techniques, laser processes are nowadays widely used in thin film solar cell fabric processing. Such techniques can now be used to complete a solar cell with single side contact formation in fewer steps.

In this paper, we developed the cell concept on graphite substrates as shown in Figure 1b. The current density-voltage (J-V) curves and quantum efficiency (QE) measurements show the improvements of open circuit voltage (V_{oc}), fill factor (FF), cell efficiency (η), and quantum efficiency due to the hydrogen bulk passivation process [26,27] and laser single side contact (LSSC) formation.

---

[*] e-mail: da.li@zae-bayern.de

Thin Solid Films 583 (2015) 25–33

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Silicon nitride and intrinsic amorphous silicon double antireflection coatings for thin-film solar cells on foreign substrates

Da Li [a,*], Thomas Kunz [a], Nadine Wolf [b], Jan Philipp Liebig [c], Stephan Wittmann [a], Taimoor Ahmad [a], Maik T. Hessmann [a], Richard Auer [a], Mathias Göken [c], Christoph J. Brabec [a,d]

[a] Bavarian Center for Applied Energy Research (ZAE Bayern), Division: Photovoltaics and Thermosensorics, Haberstr. 2a, 91058 Erlangen, Germany
[b] Bavarian Center for Applied Energy Research (ZAE Bayern), Division: Energy Efficiency, Am Galgenberg 87, 97074 Würzburg, Germany
[c] Materials Science and Engineering, Institute I, University of Erlangen-Nürnberg, Martensstr. 5, 91058 Erlangen, Germany
[d] Institute of Materials for Electronics and Energy Technology, University of Erlangen-Nürnberg, Martensstr. 7, 91058 Erlangen, Germany

ARTICLE INFO

Article history:
Received 9 October 2014
Received in revised form 17 February 2015
Accepted 20 March 2015
Available online 28 March 2015

Keywords:
Amorphous silicon
Crystalline silicon thin film
Double layer antireflection coating
Surface passivation
Graphite substrate
Focus ion beam
Scanning transmission electron microscopy

ABSTRACT

Hydrogenated intrinsic amorphous silicon (a-Si:H) was investigated as a surface passivation method for crystalline silicon thin film solar cells on graphite substrates. The results of the experiments, including quantum efficiency and current density–voltage measurements, show improvements in cell performance. This improvement is due to surface passivation by an a-Si:H(i) layer, which increases the open circuit voltage and the fill factor. In comparison with our previous work, we have achieved an increase of 0.6% absolute cell efficiency for a 40 μm thick 4 cm^2 aperture area on the graphite substrate. The optical properties of the SiN$_x$/a-Si:H(i) stack were studied using spectroscopic ellipsometer techniques. Scanning transmission electron microscopy inside a scanning electron microscope was applied to characterize the cross section of the SiN$_x$/a-Si:H(i) stack using focus ion beam preparation.

1. Introduction

Graphite is a high thermal stability material and available at high purity. Consequently, several cell concepts have been developed for solar cells on graphite substrates, i.e., zone melting recrystallization (ZMR) [1,2], laser edge isolation (LEI) [3], hydrogen passivation [4] and laser single side contact (LSSC) [5]. In our previous work, we reported our 10.2% cell efficiency for a 40 μm thick and 4 cm^2 aperture area on graphite substrate [5].

In order to improve the thin film cell concept further, the surface recombination must be suppressed using a surface passivation process. Several dielectric materials are widely applied as surface passivation coatings, including aluminum oxide (Al$_2$O$_3$) [6,7], hydrogenated amorphous silicon (a-Si:H) [8–11], amorphous silicon carbide (a-SiC$_x$:H) [12,13], silicon nitride (SiN$_x$) [14,15] and thermal silicon oxide (SiO$_2$) [16–18]. When considering passivation of the sunside surface in particular, not only the passivation quality but also optical properties such as antireflection must also be taken into account [19], such as, SiN$_x$/SiO$_2$ [20–23], SiN$_x$/SiN$_x$ [24,25] SiN$_x$/a-Si:H [26–28] and SiO$_x$/indium tin oxide [29] stacks. Among these various concepts, the a-Si:H(i)/c-Si(n) hetero-interface has a high passivation quality and can be fabricated at low temperature (~250 °C). It is used e.g. in heterojunction with intrinsic thin (HIT) layer cell concept [30–32].

In this paper, we combine our cell concept on graphite substrates with surface passivation, using an SiN$_x$/a-Si:H(i) stack on a phosphorus-doped c-Si(n$^+$) emitter. The a-Si:H(i) passivation has the advantages of high surface passivation quality and short process times at low temperature. We observed improved cell performance, i.e., an increase in short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and cell efficiency due to the SiN$_x$/a-Si:H(i) stack. We report a laboratory cell efficiency of 10.8% on the same aperture area and the graphite substrate.

2. Experimental

2.1. Solar cell design and processing

Our cell concepts are based on high purity graphite substrates ("FP479", Schunk Kohlenstofftechnik GmbH) with a size of 10 cm × 10 cm × 2 mm. In order to prevent impurity diffusion from the foreign substrate, a SiC layer was deposited as an intermediate layer on both sides of the substrate using a hot wall chemical vapor deposition (HWCVD). Afterwards, a c-Si(p$^+$) layer, which served as a seed and back surface field layer (approximately 20 μm thick and with an acceptor concentration of 4 × 10^{18} cm^{-3}), was deposited on top of the SiC

---

[*] Corresponding author at: ZAE Bayern, Haberstr. 2a, 91058 Erlangen, Germany.

http://dx.doi.org/10.1016/j.tsf.2015.03.051

Energy &
Environmental
Science

COMMUNICATION

View Article Online
View Journal | View Issue

Air-processed polymer tandem solar cells with power conversion efficiency exceeding 10%†

Ning Li*[a] and Christoph J. Brabec[ab]

Cite this: Energy Environ. Sci., 2015, 8, 2902

Received 12th July 2015,
Accepted 10th August 2015

DOI: 10.1039/c5ee02145f

www.rsc.org/ees

The power conversion efficiencies (PCEs) of the state-of-the-art organic tandem solar cells are steadily improved in the range of 10–12%, which can be mainly attributed to the design and development of highly efficient absorbers with complementary absorption spectra. However, the impressive recorded efficiencies are only achieved for devices spin-coated in an inert atmosphere, which does not directly contribute to the commercialization of the organic photovoltaic technology. Herein, we perform a systematic study of PTB7-Th-based single-junction solar cells fabricated under various conditions. The relatively low photovoltaic performance and poor environmental stability of the air-processed devices are successfully improved by a post-treatment with alcohol-based solvents. The effect of solvent treatment is valid for both regular and inverted device architecture. Tandem devices fabricated by doctor-blading in air achieve a high PCE of 10.03% along with an unprecedentedly high FF of 76.6%.

Broader context

All the attraction and advantages of organic photovoltaic (OPV) technology as compared to other material systems are due to their easy processing by printing or coating under environmental conditions. This is the promise for this technology. Although the power conversion efficiencies (PCEs) of the state-of-the-art OPV devices are steadily improved in the range of 10–12%, the impressive record efficiencies are mainly achieved for devices spin-coated in an inert atmosphere, which does not directly contribute to the commercialization of OPV technology. Compared to the record efficiencies reported for lab-processed OPV devices with various architectures, the performance of devices produced on a large scale is still at very low levels, which can be mainly attributed to the air-sensitive donor materials as well as the non-optimized large-scale deposition techniques. The benzodithiophene (BDT)-based building blocks have been successfully developed in recent years for constructing high performance polymer donors. Owing to their great photovoltaic properties along with easy processibility, the BDT polymers are very promising candidates for large-scale production. However, the high-performance BDT-polymers are normally air-unstable and degrade very quickly in the presence of oxygen and light. Thus, the air-instability of the BDT-polymers limits the performance of the air-processed devices and hinders their application under large-scale production. Herein, we demonstrate that a simple treatment with alcohol solvents can significantly improve the relatively low performance and poor environmental stability of the air-processed OPV devices based on BDT-polymers. Organic tandem solar cells based on a BDT-polymer fabricated by doctor-blading in air achieve high PCEs of > 10% and FFs of > 76%.

Introduction

Organic photovoltaics (OPVs) have attracted tremendous attention from researchers in the last decade, owing to their novel properties, practical applicability and low-cost large-scale manufacturing process.[1–12] The power conversion efficiencies (PCEs) of single-junction OPV devices have been continuously improved to ~11%[13] and are expected to approach 15% theoretical limit as a result of designing and developing novel absorbing materials with reduced bandgap-voltage offset along with high fill factor (FF) and external quantum efficiency (EQE).[3] Compared to their inorganic counterparts, the relatively narrow absorption windows of the organic absorbers inevitably restrict the utilization of photons, thus limiting their performances.

The tandem architecture, in which two or more sub-cells with complementary absorption spectra are monolithically stacked together and connected in series, has been proven to be one of the most promising concepts to address the losses related to the narrow absorption of organic absorbers.[13–17] The loss due to thermalization of the excess energy photons can also be simultaneously minimized by combining absorbers possessing different bandgaps in a tandem architecture. The high-energy photons can be absorbed in a front-placed wide bandgap donor to deliver a high open circuit voltage (V_{OC}), whereas the photons with energies lower than the bandgap of the front donor can be

---

[a] *Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander University Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany. E-mail: Ning.Li@fau.de; Fax: +49 (0)9131-8528495; Tel: +49 (0)9131-8527634*

[b] *Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a, 91058 Erlangen, Germany*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ee02145f

Optical model for simulation and optimization of luminescent down-shifting layers filled with phosphor particles for photovoltaics

Benjamin Lipovšek,[1,*] Anastasiia Solodovnyk,[2,3,4] Karen Forberich,[3] Edda Stern,[2] Janez Krč,[1] Christoph J. Brabec,[2,3,4] and Marko Topič[1]

[1] *University of Ljubljana, Faculty of Electrical Engineering, Tržaška 25, 1000 Ljubljana, Slovenia*
[2] *Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstr. 2a, 91058 Erlangen, Germany*
[3] *Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Martensstr. 7, 91058 Erlangen, Germany*
[4] *Erlangen Graduate School in Advanced Optical Technologies (SAOT), FAU, Paul-Gordan-Str. 6, 91052 Erlangen, Germany*
[*] *benjamin.lipovsek@fe.uni-lj.si*

Abstract: We developed an optical model for simulation and optimization of luminescent down-shifting (LDS) layers for photovoltaics. These layers consist of micron-sized phosphor particles embedded in a polymer binder. The model is based on ray tracing and employs an effective approach to scattering and photoluminescence modelling. Experimental verification of the model shows that the model accurately takes all the structural parameters and material properties of the LDS layers into account, including the layer thickness, phosphor particle volume concentration, and phosphor particle size distribution. Finally, using the verified model, complete organic solar cells on glass substrate covered with the LDS layers are simulated. Simulations reveal that an optimized LDS layer can result in more than 6% larger short-circuit current of the solar cell.

OCIS codes: (230.7405) Wavelength conversion devices; (160.2540) Fluorescent and luminescent materials; (290.5850) Scattering, particles; (350.6050) Solar energy.

References and links

1. C. H. Henry, "Limiting efficiencies of ideal single and multiple energy gap terrestrial solar cells," J. Appl. Phys. **51**(8), 4494 (1980).
2. M. Topič, R. M. Geisthardt, and J. R. Sites, "Performance limits and status of single-junction solar cells with emphasis on CIGS," IEEE J. Photovoltaics **5**(1), 360–365 (2015).
3. B. S. Richards, "Enhancing the performance of silicon solar cells via the application of passive luminescence conversion layers," Sol. Energy Mater. Sol. Cells **90**(15), 2329–2337 (2006).
4. A. Marti and G. L. Araujo, "Limiting efficiencies for photovoltaic energy conversion in multigap systems," Sol. Energy Mater. Sol. Cells **43**(2), 203–222 (1996).
5. D. Fischer, S. Dubail, J. A. A. Selvan, N. P. Vaucher, R. Platz, C. Hof, U. Kroll, J. Meier, P. Torres, H. Keppner, N. Wyrsch, M. Goetz, A. Shah, and K.-D. Ufert, "The 'micromorph' solar cell: extending a-Si:H technology towards thin film crystalline silicon," in Conference Record of the 25th IEEE Photovoltaic Specialists Conference (IEEE 1996), pp. 1053–1056.
6. W. G. Goetzberger, "Solar energy conversion with fluorescent collectors," Appl. Phys., A Mater. Sci. Process. **14**(2), 123–139 (1977).
7. H. J. Hovel, R. T. Hodgson, and J. M. Woodall, "The effect of fluorescent wavelength shifting on solar cell spectral response," Sol. Energy Mater. **2**(1), 19–29 (1979).
8. E. Klampaftis, D. Ross, K. R. McIntosh, and B. S. Richards, "Enhancing the performance of solar cells via luminescent down-shifting of the incident spectrum: a review," Sol. Energy Mater. Sol. Cells **93**(8), 1182–1194 (2009).
9. E. Klampaftis and B. S. Richards, "Improvement in multi-crystalline silicon solar cell efficiency via addition of luminescent material to EVA encapsulation layer," Prog. Photovolt. Res. Appl. **19**(3), 345–351 (2011).
10. E. Klampaftis, D. Ross, S. Seyrling, A. N. Tiwari, and B. S. Richards, "Increase in short-wavelength response of encapsulated CIGS devices by doping the encapsulation layer with luminescent material," Sol. Energy Mater. Sol. Cells **101**, 62–67 (2012).
11. X. Pi, Q. Li, D. Li, and D. Yang, "Spin-coating silicon-quantum-dot ink to improve solar cell efficiency," Sol. Energy Mater. Sol. Cells **95**(10), 2941–2945 (2011).

#238062
© 2015 OSA
Received 15 Apr 2015; revised 12 Jun 2015; accepted 12 Jun 2015; published 1 Jul 2015
27 Jul 2015 | Vol. 23, No. 15 | DOI:10.1364/OE.23.00A882 | OPTICS EXPRESS A882

NANO LETTERS
Letter
pubs.acs.org/NanoLett

"Black" TiO_2 Nanotubes Formed by High-Energy Proton Implantation Show Noble-Metal-co-Catalyst Free Photocatalytic H_2-Evolution

Ning Liu,[†] Volker Häublein,[‡] Xuemei Zhou,[†] Umamaheswari Venkatesan,[§] Martin Hartmann,[§] Mirza Mačković,[∥] Tomohiko Nakajima,[⊥] Erdmann Spiecker,[∥] Andres Osvet,[#] Lothar Frey,[‡] and Patrik Schmuki[*,†]

[†]Department of Materials Science WW-4, LKO, University of Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany
[‡]Fraunhofer Institute for Integrated Systems and Device Technology IISB, Schottkystrasse 10, 91058 Erlangen, Germany
[§]ECRC - Erlangen Catalysis Resource Center, University of Erlangen-Nuremberg, Egerlandstrasse 3, 91058 Erlangen, Germany
[∥]Institute of Micro- and Nanostructure Research (WW9) & Center for Nanoanalysis and Electron Microscopy (CENEM), University of Erlangen-Nuremberg, Cauerstrasse 6, 91058 Erlangen, Germany
[⊥]National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
[#]Department of Materials Science 6, iMEET, University of Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany

Supporting Information

ABSTRACT: We apply high-energy proton ion-implantation to modify TiO_2 nanotubes selectively at their tops. In the proton-implanted region, we observe the creation of intrinsic cocatalytic centers for photocatalytic H_2-evolution. We find proton implantation to induce specific defects and a characteristic modification of the electronic properties not only in nanotubes but also on anatase single crystal (001) surfaces. Nevertheless, for TiO_2 nanotubes a strong synergetic effect between implanted region (*catalyst*) and implant-free tube segment (*absorber*) can be obtained.

KEYWORDS: *Nanotubes, photocatalysis, water-splitting, titania, self-organization, ion-implantation*

Ever since 1972 when Honda and Fujishima introduced photolysis of water using a single crystal of TiO_2 photocatalytic water splitting has become one of the most investigated scientific topics of our century.[1] The concept is strikingly simple: light (preferably sun-light) is absorbed in a suitable semiconductor and thereby generates electron−hole pairs. These charge carriers migrate in valence and conduction bands to the semiconductor surface where they react with water to form O_2 and H_2, respectively. Thus, hydrogen, the energy carrier of the future, could be produced using just water and sunlight.

Key factors for an optimized conversion of water to H_2 are (i) as complete as possible absorption of solar light (small band gap) while (ii) still maintaining the thermodynamic driving force for water splitting (sufficiently large band gap), including suitable band-edge positions relative to the water red-ox potentials, and (iii), possibly the most challenging, a sufficiently fast carrier transfer from semiconductor to water to obtain a reasonable reaction kinetics as opposed to carrier recombination or photocorrosion.[2−7]

Despite virtually countless investigations on a wide range of semiconductor materials that in many respects are superior to titania (mostly in view of solar light absorption and carrier transport), TiO_2 still remains one of the most investigated photocatalysts. This is only partially due to suitable energetics but more so because of its outstanding (photocorrosion) stability.[2−7]

In general, the main drawbacks of TiO_2 are on the one hand its too large band gap of 3−3.2 eV that allows only for about 7% of solar light absorption and on the other hand although a charge transfer to aqueous electrolytes is thermodynamically possible, the kinetics of these processes at the TiO_2/water interface are extremely slow if no suitable cocatalysts such as Pt, Au, Pd, or similar are used.[8−10]

However, in view of the first challenge (the "too" large optical band gap for efficient sunlight absorption), the recent finding of "black" TiO_2 by Chen and Mao[11] seems to partially overcome this issue and has thus attracted accordingly wide scientific interest. The authors produced this modified form of TiO_2 (that showed strong visible absorption) by exposing anatase TiO_2 nanoparticles to a high pressure/high temperature treatment in H_2. This material was found to show a range of outstanding functional features. In the original work, Chen and Mao demonstrated a significantly increased photocatalytic activity for water splitting when black TiO_2 was loaded with a Pt cocatalyst and used under bias-free conditions (i.e., used

Received: July 6, 2015
Revised: August 27, 2015

DOI: 10.1021/acs.nanolett.5b02663
Nano Lett. XXXX, XXX, XXX−XXX

DOI: 10.1002/ente.201402095

Round-Robin Studies on Roll-Processed ITO-free Organic Tandem Solar Cells Combined with Inter-Laboratory Stability Studies

Francesco Livi,[a] Roar R. Søndergaard,[a] Thomas R. Andersen,[a] Bérenger Roth,[a] Suren Gevorgyan,[a] Henrik F. Dam,[a] Jon E. Carlé,[a] Martin Helgesen,[a] George D. Spyropoulos,[b] Jens Adams,[c] Tayebeh Ameri,[b] Christoph J. Brabec,[b, c] Mathilde Legros,[d] Noella Lemaître,[d] Stephane Berny,[e] Owen R. Lozman,[e] Stefan Schumann,[f] Arnulf Scheel,[f] Pälvi Apilo,[g] Marja Vilkman,[h] Eva Bundgaard,[a] and Frederik C. Krebs*[a]

Roll-processed, indium tin oxide (ITO)-free, flexible, organic tandem solar cells and modules have been realized and used in round-robin studies as well as in parallel inter-laboratory stability studies. The tandem cells/modules show no significant difference in comparison to their single-junction counterparts and the use of round-robin studies as a consensus tool for evaluation of organic solar cell parameters is judged just as viable for the tandem solar cells as for single-junction devices. The inter-laboratory stability studies were conducted according to testing protocols ISOS-D-2, ISOS-D-3, and ISOS-L-2, and in spite of a much more complicated architecture the organic tandem solar cells show no significant differences in stability in comparison to their single-junction counterparts.

Research on organic solar cells is thriving, but with the increasing number of publications comes the problem of consensus. The reported results come from a large variety of groups with different types of measuring equipment at their disposal, which can lead to ambiguous results. The organic solar cell community thus needs an approach to certify the obtained results in order to reach a common agreement on the status of the field. Very few laboratories have the capability to certify efficiency data for solar cells, and, although it is possible to acquire certification from them, this is not a viable approach as these laboratories would simply not have capacity to deal with such large volumes of certification. In addition, certification is a rather costly affair for many groups. As alternatives to certification, round-robin studies (in which the same solar cell sample is characterized by independent participants) and inter-laboratory studies (in which the same type of cell is studied by independent participants) are powerful tools to reach a consensus, and both methods have been used successfully as evaluation tools on several occasions for inorganic solar cells[1] and polymer solar cells/modules.[2]

Organic tandem solar cells have recently received increased attention because of the prospects of harvesting a larger portion of the solar spectrum and which would bring about a corresponding increase in efficiency.[3] The tandem solar cell employs complementary polymers that absorb light in different wavelength regions to increase the total absorption band, and this is typically achieved by stacking the two junctions on top of each other with a recombination layer between the two to ensure effective charge flow through the device.

An important question to be answered with respect to the tandem cell is whether such a new cell design comprising a broader total absorption spectrum will impose larger (or lesser) discrepancies to the efficiency data between laboratories as compared to single-junction solar cells. The tandem cell contains a significantly increased number of processed layers in the solar cell stack (typically 10–14) compared to its single-junction counterparts, which of course renders the finished device more susceptible to defects. This is probably the

---

[a] F. Livi, Dr. R. R. Søndergaard, Dr. T. R. Andersen, B. Roth, Dr. S. Gevorgyan, Dr. H. F. Dam, Dr. J. E. Carlé, Dr. M. Helgesen, Dr. E. Bundgaard,
Prof. F. C. Krebs
Dept. of Energy Conversion and Storage
Technical University of Denmark
Frederiksborgvej 399, DK-4000 Roskilde (Denmark)
E-mail: frkr@dtu.dk

[b] G. D. Spyropoulos, Dr. T. Ameri, Prof. C. J. Brabec
Institute of Materials for Electronics and Energy Technology (I-MEET)
Department of Materials Science and Engineering
Friedrich-Alexander University Erlangen-Nuremberg
Martensstraße 7, 91058 Erlangen (Germany)

[c] J. Adams, Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern e.V.)
Renewable Energies
Haberstraße 2a, 91058 Erlangen (Germany)

[d] Dr. M. Legros, Dr. N. Lemaître
CEA, LITEN, Department of Solar Technologies
F-73375 Le Bourget du Lac (France)

[e] Dr. S. Berny, Dr. O. R. Lozman
Merck Chemicals Ltd., Chilworth Technical Centre
University Parkway, Southampton SO16 7QD (UK)

[f] Dr. S. Schumann, Dr. A. Scheel
Heraeus Precious Metals GmbH & Co. KG
Electronic Materials Division
Chempark Leverkusen/Gebäude B 202, D-51368 Leverkusen (Germany)

[g] P. Apilo
VTT Technical Research Centre of Finland, Printed Functional Solutions
Kaitoväylä 1, FI-90571 Oulu (Finland)

[h] Dr. M. Vilkman
VTT Technical Research Centre of Finland, Printed Functional Solutions
Tietotie 3, FI-02150 Espoo (Finland)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ente.201402095.

Part of a Special Issue on "Printed Energy Technologies". To view the complete issue, visit:
http://onlinelibrary.wiley.com/doi/10.1002/ente.v3.4/issuetoc

Energy &
Environmental
Science

COMMUNICATION

View Article Online

Cite this: DOI: 10.1039/c5ee03315b

Received 30th October 2015,
Accepted 13th November 2015

DOI: 10.1039/c5ee03315b

www.rsc.org/ees

Highly efficient, large area, roll coated flexible and rigid OPV modules with geometric fill factors up to 98.5% processed with commercially available materials†

L. Lucera,*[a] F. Machui,[a] P. Kubis,[a] H. D. Schmidt,[a] J. Adams,[a] S. Strohm,[a] T. Ahmad,[a] K. Forberich,[b] H.-J. Egelhaaf*[a] and C. J. Brabec[ab]

Highly efficient, large area OPV modules achieving full area efficiencies of up to 93% of the reference small area cells are reported. The way to a no-loss up-scaling process is highlighted: photoelectrical conversion efficiencies of 5.3% are achieved on rigid modules and of 4.2% on flexible, roll coated ones, employing a commercially available photoactive material. Exceptionally high geometric fill factors (98.5%), achieved via structuring by ultrashort laser pulses, with interconnection widths below 100 µm are demonstrated.

Broader context

The achievement of high performances for solar modules can be considered one of the biggest challenges to be tackled in order to scale printed photovoltaics suitable for industrial production and commercialisation. Often the scientific community is solely focused on achieving the highest record performances on small scale devices, disregarding the development of suitable up-scaling strategies to minimize the performance drop between single cells and modules. In this contribution the key factors for an ideal large area processing are addressed: optical and electrical simulations for the design of the geometry of the modules and the choice of the electrode materials, roll-to-roll printing and laser structuring, demonstrating that losses between cells and modules can be as low as 7%. The use of halogen-free formulations and materials available in large quantities constitute as well an important step towards industrially sustainable processes.

1. Introduction

In recent years, printable photovoltaic technologies have been attracting the attention of the scientific community, due to their potentialities; in fact, solution processability constitutes a major advantage towards large scale, cheap, industrial production of solar cells. Furthermore, the rapid energy payback time of these technologies makes them of particular interest.[1] Despite the high efficiencies reported on lab scale devices, which recently surpassed 10% power conversion efficiency (PCE) for organic photovoltaics (OPV)[2] and 20%[3] for perovskite based ones, very little progress is shown towards upscaling processing of solar cells.[4–6] Large area, roll-to-roll (R2R) processed solar cells and modules usually show a quite remarkable drop in efficiencies compared to small area, lab-produced hero cells,[7] highlighting the importance of the development of a stable, reliable production process which should allow a minimization of the performance losses. Recently we showed what are the guidelines for an optimal upscaling route for large area modules,[8,9] using a combination of optical simulations (transfer matrix formalism – TMF) and electrical simulations (finite element simulations – FEM): a loss in PCE of less than 10% should be achievable for opaque devices under optimized conditions. Generally this involves (i) a careful choice and optimization of the printing techniques, (ii) the development of halogen-free formulations allowing the achievement of the right morphology for the active layers, (iii) the development of a reliable, fast, high resolution patterning method for the monolithical interconnection of the cells in a module, the latest being of particular importance to minimize the size of the interconnection area which is not photoactive and thus is accountable as a loss. The ratio between the photoactive area and the total area of the module is usually referred to as the geometric fill factor (GFF).

In this report we performed optical simulations to quantify the losses induced by the change of electrode materials when going to up-scaled modules and compared them with experimental results. Then electrical simulations are carried out to assess the losses due to the monolithic interconnection of the cells in a module and are able to minimize them by choosing the appropriate layout. We will show how theoretical calculations can be matched with experimental results, yielding large area modules with PCEs of up to 93% of the reference hero cells by choosing high precision slot-die coating on a fully R2R compatible printing setup in combination with high precision,

---

[a] ZAE Bayern – Solar Factory of the Future, Energy Campus Nürnberg, Fürther Strasse 250, 90429 Nürnberg, Germany. E-mail: luca.lucera@zae-bayern.de, hans-joachim.egelhaaf@zae-bayern.de

[b] Institute of Materials for Electronics and Energy Technology, Friedrich-Alexander University Erlangen-Nürnberg, 91058 Erlangen, Germany

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ee03315b

DOI: 10.1002/ente.201402195

Guidelines for Closing the Efficiency Gap between Hero Solar Cells and Roll-To-Roll Printed Modules

Luca Lucera,*[a] Peter Kubis,[a] Frank W. Fecher,[a] Carina Bronnbauer,[b, c]
Mathieu Turbiez,[d] Karen Forberich,[b] Tayebeh Ameri,[b] Hans-Joachim Egelhaaf,[a] and
Christoph J. Brabec*[a, b]

One of the biggest challenges for the commercialization of polymer-based and other printed photovoltaic (PV) technologies is to establish reliable up-scaling processes that minimize the efficiency losses occurring during the transition from record laboratory cells to roll-to-roll (R2R) printed PV modules. This article reviews the latest advances in reducing the efficiency gap between record solar cells and large-area organic PV modules. The major loss sources are identified for the most popular cell architectures and categorized into optical, electrical, and processing-related contributions. Their relative share in the overall efficiency drop are quantified through optical and electrical simulations. Further potential sources of efficiency loss, such as the replacement of halogenated by green solvents for active layer processing, are also addressed. Finally, the effect of reduced efficiency gaps on the production costs of R2R printed modules is discussed, demonstrating that values as low as 0.1 € Wp⁻¹ (the nominal power of a solar module/cell) can be achieved.

1. Introduction

Organic photovoltaics (OPV) have experienced a huge increase in development in the past few years, with major efficiencies reported regularly both for multi-junction devices[1–3] and single-junction devices.[4] The appeal of this technology lies at the intersection between the potential low-cost materials used for this technology[5] and the high throughput obtainable using roll-based production, together with appealing applications as semitransparent modules.[6]

New solution-processable photovoltaic technologies, such as those employing organometal halide perovskites, have experienced an exponential increase in the number of scientific reports during recent months, due to the higher efficiencies of the single-junction devices, which allow, for example, for the same advantages of organic photovoltaics (roll-to-roll production compatibility, low-cost technology, semitransparency), but with a considerably higher power conversion efficiency.

However, independent of the technology, it appears clear that very little is reported on the technological challenges upon upscaling of record cells towards efficient modules, with only a few groups showing progress.[7–11] It is further well known and recognized that a successful technology must quickly bridge the large gap between the "hero" lab scale (record) cells and large-area modules.[12] Different PV technologies suffer from different losses upon scaling from lab-scale to the production levels (lab-to-fab). On the one hand, the typical module [illegible] losses are inherent to any type of PV technology. Beyond that, specific PV technologies have individual losses, which either originate from (i) nonhomogeneous processing, (ii) limited temperature windows, (iii) [illegible] leading to a larger or smaller cell width, (iv) various and charge-connection layers with distinct absorption features or (v) inhomogeneities and varying film quality upon scaling to large areas. The list of roll-to-module losses given here is certainly not exhaustive and could be easily continued. For any PV technology aiming to reach the market, this gap has to be considerably reduced and pushed to its limits. In this study we perform an in-depth analysis of the various loss mechanisms involved when scaling towards large-area organic PV modules, and we outline potential concepts for how to overcome them. The focus will be on organic photovoltaics for this survey, and the conclusions will be valid for all printed PV technologies. Finally, the conclusion section will

---

[a] L. Lucera, Dr. P. Kubis, F. W. Fecher, Dr. H.-J. Egelhaaf, Prof. Dr. C. J. Brabec
ZAE Bayern – Solar Factory of the Future
Energy Campus Nürnberg
Fürther Straße 250
90429 Nürnberg (Germany)
E-mail: [illegible]
[illegible]

[b] C. Bronnbauer, Dr. K. Forberich, Dr. T. Ameri, Prof. Dr. C. J. Brabec
Institute of Materials for Electronics and Energy Technology (i-MEET)
Friedrich-Alexander-University Erlangen-Nürnberg
91058 Erlangen (Germany)

[c] C. Bronnbauer
Erlangen Graduate School in Advanced Optical Technologies (SAOT)
Paul-Gordan-Strasse 6
91052 Erlangen (Germany)

[d] M. Turbiez
BASF Schweiz AG
Schwarzwaldallee 215
CH-4002 Basel (Switzerland)

Part of a Special Issue on "Printed Energy Technologies". To view the complete issue, visit:
http://onlinelibrary.wiley.com/doi/10.1002/ente.v3.4/issuetoc

Synthesis and photovoltaic effect in red/near-infrared absorbing A-D-A-D-A-type oligothiophenes containing benzothiadiazole and thienothiadiazole central units

Yuriy N. Luponosov,[a,*,†] Jie Min,[b,*,†] Dmitry A. Khanin,[a] Derya Baran,[b] Sergey A. Pisarev,[a,c] Svetlana M. Peregudova,[d] Petr V. Dmitryakov,[e] Sergei N. Chvalun,[a,e] Georgiy V. Cherkaev,[a] Evgeniya A. Svidchenko,[a] Tayebeh Ameri,[b] Christoph J. Brabec,[b,f] and Sergei A. Ponomarenko[a,g]

[a]Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences,
Profsoyuznaya Street 70, Moscow 117393, Russia
[b]Friedrich-Alexander University Erlangen-Nuremberg, Institute of Materials for Electronics and Energy Technology (I-MEET), Martensstraße 7, 91058 Erlangen, Germany
[c]Russian Academy of Sciences, Institute of Physiologically Active Compounds,
Severny Proezd 1, Chernogolovka 142432, Russia
[d]Russian Academy of Sciences, Nesmeyanov Institute of Organoelement Compounds,
Vavilova Street 28, Moscow 119991, Russia
[e]Scientific and Research Centre Kurchatov Institute, 1 Kurchatov Square,
Moscow 123182, Russia
[f]Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a,
91058 Erlangen, Germany
[g]Moscow State University, Chemistry Department, Leninskie Gory 1-3, Moscow 119991, Russia

Abstract. Two π-conjugated acceptor-donor-acceptor-donor-acceptor-type (A-D-A-D-A) oligothiophenes, TT-(2T-DCV-Hex)$_2$ and BT-(2T-DCV-Hex)$_2$ were designed and synthesized with thienothiadiazole (TT) or benzothiadiazole (BT) as the core and dicyanovinyl (DCV) as the terminal acceptor groups for comprehensively investigating and understanding structure–property relationships. The resulting oligomers were first characterized by thermal analysis, UV-Vis spectroscopy, and cyclic voltammetry. By simply changing the BT to TT core in these two oligothiophenes, the highest occupied molecular orbital levels were varied from −5.55 eV for BT-(2T-DCV-Hex)$_2$ to −5.11 eV for TT-(2T-DCV-Hex)$_2$, and the optical band gaps were varied from 1.72 eV for BT-(2T-DCV-Hex)$_2$ to 1.25 eV for TT-(2T-DCV-Hex)$_2$, ascribed to the stronger electron accepting character of the TT core. However, the power conversion efficiency of bulk heterojunction organic solar cells (OSCs) with TT-(2T-DCV-Hex)$_2$ as donor and [6,6]-phenyl C_{70}-butyric acid methyl ester ($PC_{71}BM$) as acceptor was measured to be 0.04% only, which is much lower than that of BT-(2T-DCV-Hex)$_2$:$PC_{71}BM$ (1.54%). Compared to the TT-(2T-DCV-Hex)$_2$ system, the BT-(2T-DCV-Hex)$_2$ based device shows smoother film surface morphology, and superior charge generation and charge carrier mobilities. Therefore, the results clearly demonstrate that in addition to modifying the alkyl side chains and π-bridge lengths, the design of new small molecules for high-performance OSCs should also aim to choose suitable acceptor units. *© 2015 Society of Photo-Optical Instrumentation Engineers (SPIE)* [DOI: 10.1117/1.JPE.5.057213]

Keywords: donor-acceptor oligomer; charge generation; dicyanovinyl group; thienothiadiazole; benzothiadiazole; organic solar cell; charge carrier mobility.

Paper 14076SS received Oct. 7, 2014; accepted for publication Jan. 7, 2015; published online Feb. 16, 2015.

---

*Address all correspondence to: Yuriy N. Luponosov and Jie Min, E-mail: luponosov@ispm.ru and Min.Jie@ww.uni-erlangen.de

†Yuriy N. Luponosov and Jie Min contributed equally.

Dyes and Pigments 122 (2015) 213–223

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Effects of bridging atom and π-bridge length on physical and photovoltaic properties of A–π-D–π-A oligomers for solution-processed organic solar cells

Yuriy N. Luponosov [a,*,1], Jie Min [b,*,1], Artem V. Bakirov [a,c], Petr V. Dmitryakov [c], Sergei N. Chvalun [a,c], Svetlana M. Peregudova [d], Tayebeh Ameri [b], Christoph J. Brabec [b,e], Sergei A. Ponomarenko [a,f]

[a] Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences, Profsoyuznaya st. 70, Moscow 117393, Russia
[b] Institute of Materials for Electronics and Energy Technology (I-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstraße 7, 91058 Erlangen, Germany
[c] National Research Centre "Kurchatov Institute", 1, Akademika Kurchatova pl., Moscow 123182, Russia
[d] Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova St. 28, Moscow 119991, Russia
[e] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a, 91058 Erlangen, Germany
[f] Chemistry Department, Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russia

A R T I C L E I N F O

Article history:
Received 18 May 2015
Received in revised form
30 June 2015
Accepted 30 June 2015
Available online 2 July 2015

Keywords:
Donor–acceptor oligomers
Oligothiophenes
Organic solar cells
Alkyldicyanovinyl groups
Dithienosilole
Effect of heteroatom substitution

A B S T R A C T

Synthesis of novel acceptor–donor–acceptor oligomers with electron-withdrawing alkyldicyanovinyl groups linked through an oligothiophene π-bridge with either dithienosilole or cyclopentadithiophene electron donor units is described. Changing the bridgehead atom from carbon to silicon in the central donor unit leads to a significant change in optical, thermal and structural properties of the oligomers. In addition, elongation of the oligothiophene π-bridge in the oligomers increases energies of HOMO and LUMO levels and leads to an unexpected hypsochromic shift of their absorption spectrum, because extension of the conjugation length cannot compensate a decrease of the intramolecular charge transfer between the dithienosilole and dicyanovinyl units. Although these minor changes in the chemical structures have a pronounced impact on the morphologies of their blends with $PC_{71}BM$, the optimized solution-processed organic solar cells based on these small molecules demonstrate similar power conversion efficiencies.

1. Introduction

Organic solar cells (OSCs) based on small molecules possess several potential advantages over the polymeric systems [1,2]. Compared to their polymeric counterparts, small molecules do not suffer from the effects of polydispersity, tend to have less batch-to-batch variation, and are easily functionalized and purified via standard techniques. The linear [3,4] or branched [5,6] derivatives of oligothiophenes are among the most investigated classes of materials for small molecules OSCs, since they may exhibit a combination of high-charge carrier mobility, good solubility in organic solvents, efficient light absorption as well as high stability. Nowadays the most successful design of oligothiophenes for OSCs was found to be when additional electron donor (D) and acceptor (A) units are introduced into the oligothiophene structure, which leads to the appearance of internal charge transfer (ICT) [7] between the donor and the acceptor units and significantly reduces the bandgap of the compounds [3,8]. Along this theme, a large number of D–A molecules have been extensively investigated as donor materials for OSCs. Examples of D–A oligothiophenes have been reported that include the following acceptor and donor units: dicyanovinyl (DCV) [7], alkyl cyanoacetate [9], rhodanine [10], isoindigo [11], tetracyanobutadiene [12], arylamines [13,14], dithienosilole [15], benzodithiophene [16], and dithienopyrrole [17] etc. Although optimized OSCs based on small-molecule donor materials blended with fullerene acceptors achieved the efficiencies approaching 10% [18], development of the photoactive

---

* Corresponding authors.
E-mail addresses: luponosov@ispm.ru (Y.N. Luponosov), jie.min@ww.uni-erlangen.de (J. Min).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.dyepig.2015.06.026

ChemPubSoc Europe
DOI: 10.1002/cphc.201402734
CHEMPHYSCHEM
Articles

Classification of Additives for Organic Photovoltaic Devices

Florian Machui,*[a] Philipp Maisch,[a] Ignasi Burgués-Ceballos,[b] Stefan Langner,[c] Johannes Krantz,[c] Tayebeh Ameri,[c] and Christoph J. Brabec[a, c]

The use of additives to improve the performance of organic photovoltaic cells has been intensely researched in recent years. However, so far, no system has been reported for the classification of additives and their functions. In this report, a system for classifying additives according to the fundamental mechanism by which they influence microstructure formation for P3HT:PCBM is suggested. The major parameters used for their classification are solubility and drying kinetics. Both are discussed in detail and their consequences on processing are analyzed. Furthermore, a general mechanism to classify the impact of additives on structure formation is suggested and discussed for different materials relevant to organic photovoltaic devices.

1. Introduction

The growing interest in energy supply has stimulated interest in new approaches for the development of renewable, efficient, and inexpensive photovoltaic devices. In recent years, organic semiconductors have attracted increasing attention in academia and industry. Solution-processed organic photovoltaics (OPV) have attracted a lot of interest during the last few years. Compared to their inorganic counterparts they offer various advantages such as ease of processing, mechanical flexibility, and potential low-cost fabrication on larger scales.[1] Furthermore, modification of the chemical structure allows the properties of the materials to be tailored, and thus, enhancement of their applicability to photovoltaics.[2] The main advantage of organic semiconductors is the possibility to process from solution and at low temperatures, which enables their manufacture by using standard printing and coating processes. The most used concept for the active layer is the bulk heterojunction, which consists of an interpenetrating network of a hole-donating and an electron-accepting semiconductor couple. Upon spontaneous phase separation during film formation an intimate mixture of two nanostructures is formed, which is crucial for charge-carrier generation, as well as for charge transport. The key for high OPV performance is to control the morphology of the polymer:fullerene blend.[3] Poly(3-hexylthiophene-2,5-diyl) (P3HT), a conjugated semicrystalline organic semiconductor, and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), a fullerene derivative, comprise the most representative material composite from the second generation of OPV semiconductors.[4–6] Further approaches to control the bulk heterojunction (BHJ) composite microstructure have been reported; in addition to the choice of processing solvent and thermal- or solvent-activated annealing, different solvent mixtures have been used to influence the domain size.[7–9] The solvent blend has been suggested to adjust microstructure through differences in solubility and drying behavior. Chlorobenzene (CB), ortho-dichlorobenzene (DCB), xylene, and chloroform are commonly used in combination with each other, frequently resulting in enhanced device performance, owing to slower or faster drying.[10–12] For P3HT:PCBM, this has frequently resulted in higher device performance through the promotion of P3HT aggregates, owing to enhanced crystallinity, and therefore, higher mobility.[13]

Another approach to control morphology is the addition of additives into a host solvent. Advantages of this method are the easy application to polymers with higher and lower solubility without additional processing.[14] Various groups have already reported the effect of additives.[15–19] Most commonly used additives for this approach are materials that have a higher boiling point compared to the host and in which PCBM is selectively soluble. But until now a systematic classification of additives according to their working principle is still missing.

In this article, we suggest a system to classify additives. Furthermore, their influence on the drying behavior and morphological formation mechanisms are analyzed. Two essential parameters highlighted for microstructure modifications are identified: solubility and evaporation kinetics. Herein, the analysis is

---

[a] Dr. F. Machui, P. Maisch, Prof. C. J. Brabec
Sol. Fab. of the Future
Bavarian Center for Applied Energy Research (ZAE Bayern)
Haberstr. 2a, 91058 Erlangen (Germany)
E-mail: Florian.Machui@zae-bayern.de

[b] Dr. I. Burgués-Ceballos
Catalonia Technological Centre
Av. Ernest Lluch 36, 08302, Mataró, Spain

[c] S. Langner, J. Krantz, Dr. T. Ameri, Prof. C. J. Brabec
Materials for Electronics and Energy Technology (i-MEET)
University Erlangen-Nuremberg
Martensstrasse 7, 91058 Erlangen (Germany)

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cphc.201402734.

An invited contribution to a Special Issue on Organic Electronics

CHEMISTRY OF MATERIALS

Interface Engineering of Perovskite Hybrid Solar Cells with Solution-Processed Perylene–Diimide Heterojunctions toward High Performance

Jie Min,[†] Zhi-Guo Zhang,[*,‡] Yi Hou,[†,§] Cesar Omar Ramirez Quiroz,[†] Thomas Przybilla,[∥] Carina Bronnbauer,[†,§] Fei Guo,[†] Karen Forberich,[†] Hamed Azimi,[*,†] Tayebeh Ameri,[†] Erdmann Spiecker,[∥] Yongfang Li,[‡] and Christoph J. Brabec[†,⊥]

[†]Institute of Materials for Electronics and Energy Technology (I-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstraße 7, 91058 Erlangen, Germany

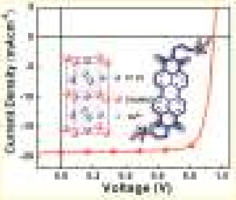
[‡]CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[§]Erlangen Graduate School in Advanced Optical Technologies (SAOT), Paul-Gordan-Str. 6, 91052 Erlangen, Germany

[∥]Center for Nanoanalysis and Electron Microscopy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Cauerstraße 6, 91058 Erlangen, Germany

[⊥]Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a, 91058 Erlangen, Germany

Supporting Information



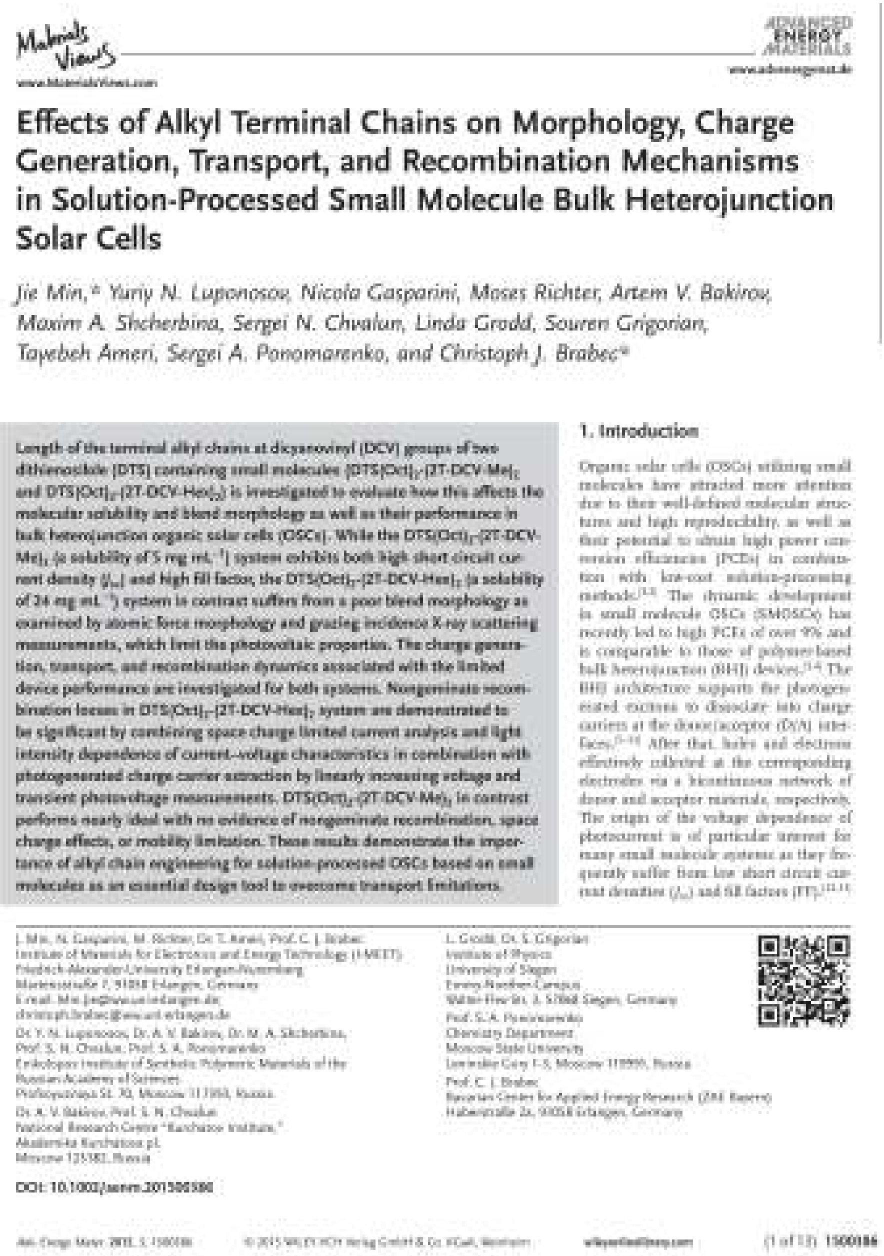
ABSTRACT: Perovskite hybrid solar cells (pero-HSCs) were demonstrated to be among the most promising candidates within the emerging photovoltaic materials with respect to their power conversion efficiency (PCE) and inexpensive fabrication. Further PCE enhancement mainly relies on minimizing the interface losses via interface engineering and the quality of the perovskite film. Here, we demonstrate that the PCEs of pero-HSCs are significantly increased to 14.0% by incorporation of a solution-processed perylene–diimide (PDINO) as cathode interface layer between the [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) layer and the top Ag electrode. Notably, for PDINO-based devices, prominent PCEs over 13% are achieved within a wide range of the PDINO thicknesses (5−24 nm). Without the PDINO layer, the best PCE of the reference PCBM/Ag device was only 10.0%. The PCBM/PDINO/Ag devices also outperformed the PCBM/ZnO/Ag devices (11.3%) with the well-established zinc oxide (ZnO) cathode interface layer. This enhanced performance is due to the formation of a highly qualitative contact between PDINO and the top Ag electrode, leading to reduced series resistance (R_s) and enhanced shunt resistance (R_{sh}) values. This study opens the door for the integration of a new class of easily-accessible, solution-processed high-performance interfacial materials for pero-HSCs.

1. INTRODUCTION

Hybrid solar cells (HSCs) using organometal halide perovskites as light absorbers have been intensively studied in the recent 4 years as a next-generation photovoltaic technology that can address the scalability changes in combination with low-cost solution processing.[1−3] Organolead halide perovskite materials, ABX_3 ($A = CH_3NH_3$ or NH_2CHNH_2, $B = Pb$, and $X = Br$, Cl, or I), are the subject of extensive investigations. This kind of perovskite absorbers possess several attractive features including broad light absorption from the visible to the near-infrared region, a high extinction coefficient, large charge carrier diffusion lengths, low-temperature solution-processability, and tunable optical and electronic properties via compositional changes.[1,4−8] Recently, perovskite-based HSCs (pero-HSCs) from the $CH_3NH_3PbI_{3-x}Cl_x$ sensitizer family have reached power conversion efficiencies (PCEs) of >15%,[9,21] for both device architectures of a mesoscopic bulk heterojunction[1,9] and a planar heterojunction one.[10] These attract tremendous attention in the photovoltaic industry. Efficiencies exceeding 20% might be realized by further optimization of the perovskite film quality and the interface engineering, or by introducing tandem architectures with multiple-junction solar cells.[3,11]

Normally, pero-HSC architectures can be classified according to their heterojunction sequence as a conventional (compact TiO_2 (n)/Perovskite (i)/organic semiconductors (p))[10,12,14] or inverted (poly(3,4-ethylenedioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) (p) /Perovskite (i) /fullerene derivatives (n))[15−17] structure. In these heterojunctions, the main challenges encountered in perovskite devices are the control of the perovskite crystallization process and the interface engineering preventing recombination defects between the different interface layers. On the one hand, a poor perovskite film morphology has been cited as very detrimental to the device performance.[13,14,18] On the other hand, since this

Received: October 15, 2014
Revised: December 1, 2014
Published: December 8, 2014



Effects of Alkyl Terminal Chains on Morphology, Charge Generation, Transport, and Recombination Mechanisms in Solution-Processed Small Molecule Bulk Heterojunction Solar Cells

Jie Min, Yuriy N. Luponosov, Nicola Gasparini, Moses Richter, Artem V. Bakirov, Maxim A. Shcherbina, Sergei N. Chvalun, Linda Grodd, Souren Grigorian, Tayebeh Ameri, Sergei A. Ponomarenko, and Christoph J. Brabec**

Length of the terminal alkyl chains at dicyanovinyl (DCV) groups of two dithienosilole (DTS) containing small molecules {$DTS(Oct)_2$-$(2T\text{-}DCV\text{-}Me)_2$ and $DTS(Oct)_2$-$(2T\text{-}DCV\text{-}Hex)_2$} is investigated to evaluate how this affects the molecular solubility and blend morphology as well as their performance in bulk heterojunction organic solar cells (OSCs). While the $DTS(Oct)_2$-$(2T\text{-}DCV\text{-}Me)_2$ (a solubility of 5 mg mL^{-1}) system exhibits both high short circuit current density (J_{sc}) and high fill factor, the $DTS(Oct)_2$-$(2T\text{-}DCV\text{-}Hex)_2$ (a solubility of 24 mg mL^{-1}) system in contrast suffers from a poor blend morphology as examined by atomic force morphology and grazing incidence X-ray scattering measurements, which limit the photovoltaic properties. The charge generation, transport, and recombination dynamics associated with the limited device performance are investigated for both systems. Nongeminate recombination losses in $DTS(Oct)_2$-$(2T\text{-}DCV\text{-}Hex)_2$ system are demonstrated to be significant by combining space charge limited current analysis and light intensity dependence of current–voltage characteristics in combination with photogenerated charge carrier extraction by linearly increasing voltage and transient photovoltage measurements. $DTS(Oct)_2$-$(2T\text{-}DCV\text{-}Me)_2$ in contrast performs nearly ideal with no evidence of nongeminate recombination, space charge effects, or mobility limitation. These results demonstrate the importance of alkyl chain engineering for solution-processed OSCs based on small molecules as an essential design tool to overcome transport limitations.

1. Introduction

Organic solar cells (OSCs) utilizing small molecules have attracted more attention due to their well-defined molecular structures and high reproducibility, as well as their potential to obtain high power conversion efficiencies (PCEs) in combination with low-cost solution-processing methods.[1,2] The dynamic development in small molecule OSCs (SMOSCs) has recently led to high PCEs of over 9% and is comparable to those of polymer-based bulk heterojunction (BHJ) devices.[3,4] The BHJ architecture supports the photogenerated excitons to dissociate into charge carriers at the donor/acceptor (D/A) interfaces.[5–10] After that, holes and electrons effectively collected at the corresponding electrodes via a bicontinuous network of donor and acceptor materials, respectively. The origin of the voltage dependence of photocurrent is of particular interest for many small molecule systems as they frequently suffer from low short circuit current densities (J_{sc}) and fill factors (FF).[11,12]

J. Min, N. Gasparini, M. Richter, Dr. T. Ameri, Prof. C. J. Brabec
Institute of Materials for Electronics and Energy Technology (i-MEET)
Friedrich-Alexander-University Erlangen-Nürnberg
Martensstraße 7, 91058 Erlangen, Germany
E-mail: min.jie@ww.uni-erlangen.de;
christoph.brabec@ww.uni-erlangen.de
Dr. Y. N. Luponosov, Dr. A. V. Bakirov, Dr. M. A. Shcherbina,
Prof. S. N. Chvalun, Prof. S. A. Ponomarenko
Enikolopov Institute of Synthetic Polymeric Materials of the
Russian Academy of Sciences
Profsoyuznaya St. 70, Moscow 117393, Russia
Dr. A. V. Bakirov, Prof. S. N. Chvalun
National Research Centre "Kurchatov Institute,"
Akademika Kurchatova pl. 1
Moscow 123182, Russia
L. Grodd, Dr. S. Grigorian
Institute of Physics
University of Siegen
Emmy-Noether-Campus
Walter-Flex-Str. 3, 57068 Siegen, Germany
Prof. S. A. Ponomarenko
Chemistry Department
Moscow State University
Leninskie Gory 1-3, Moscow 119991, Russia
Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Haberstraße 2a, 91058 Erlangen, Germany

DOI: 10.1002/aenm.201500386

Journal of
Materials Chemistry A

PAPER

View Article Online
View Journal | View Issue

Cite this: J. Mater. Chem. A, 2015, 3, 22695

Integrated molecular, morphological and interfacial engineering towards highly efficient and stable solution-processed small molecule solar cells†

Jie Min,‡*[a] Yuriy N. Luponosov,‡*[b] Nicola Gasparini,[a] Lingwei Xue,[c]
Fedor V. Drozdov,[b] Svetlana M. Peregudova,[d] Petr V. Dmitryakov,[e] Kirill L. Gerasimov,[f]
Denis V. Anokhin,[fg] Zhi-Guo Zhang,[c] Tayebeh Ameri,[a] Sergei N. Chvalun,[be]
Dimitri A. Ivanov,[fh] Yongfang Li,[c] Sergei A. Ponomarenko*[bi] and Christoph J. Brabec*[aj]

The synthesis of a series of A–π–D–π–A oligomers bearing coplanar electron-donating dithieno[3,2-b:2′,3′-d]silole (DTS) unit linked through bithiophene π-bridges with the electron-withdrawing alkyldicyanovinyl (alkyl-DCV) groups is described. This study demonstrates a systematic investigation of structure–property relationships in this type of oligomer and shows obvious benefits of alkyl-DCV groups as compared to the commonly used DCV ones, in terms of elaboration of high performance organic solar cells (OSCs). Considerable efforts have been made to improve the power conversion efficiency (PCE) of oligomer-based OSCs by diverse strategies including fine-tuning of the oligomer properties via variation of their terminal and central alkyl chains, blend morphology control via solvent vapor annealing (SVA) treatment, and surface modification via interfacial engineering. These efforts allowed achieving PCEs of up to 6.4% for DTS(Oct)$_2$-(2T-DCV-Me)$_2$ blended with PC$_{71}$BM. Further morphological investigations demonstrated that the usage of SVA treatment indeed effectively results in increased absorption and ordering of the BHJ composite, with the only exception for the most soluble oligomer DTS(Oct)$_2$-(2T-DCV-Hex)$_2$. Besides, a detailed study analyzed the charge transport properties and recombination loss mechanisms for these oligomers. This study not only revealed the importance of integrated alkyl chain engineering on gaining morphological control for high performance OSCs but also exhibited a clear correlation between molecular ordering and charge carrier mobility respective to carrier dynamics. These results outline a detailed strategy towards a rather complete characterization and optimization methodology for organic photovoltaic devices, thereby paving the way for researchers to easily find the performance parameters adapted for widespread applications.

Received 25th August 2015
Accepted 23rd September 2015

DOI: 10.1039/c5ta06706e

www.rsc.org/MaterialsA

1. Introduction

Organic photovoltaic (OPV) devices utilizing small molecules attract the attention of researchers due to their well-defined molecular structures and high reproducibility in combination with their potential to obtain high power conversion efficiencies (PCEs) as well as low fabrication costs achievable via solution-processing methods.[1] The dynamic development in small molecule organic solar cells (SMOSCs) has recently led to PCEs

---

[a] Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany. E-mail: Min.Jie@ww.uni-erlangen.de

[b] Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences, Profsoyuznaya St. 70, Moscow 117393, Russia. E-mail: luponosov@ispm.ru

[c] CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[d] Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova St. 28, Moscow, 119991, Russia

[e] National Research Centre "Kurchatov Institute", 1, Akademika Kurchatova pl., Moscow, 123182, Russia

[f] Moscow State University, Faculty of Fundamental Physical and Chemical Engineering, GSP-1, 1-51 Leninskie Gory, Moscow, 119991, Russia

[g] Institute for Problems of Chemical Physics, Russian Academy of Sciences, Semenov Prospect 1, Chernogolovka, Moscow Region, 142432, Russia

[h] Institut de Sciences des Matériaux de Mulhouse (CNRS UMR7361), 15 rue Jean Starcky, B.P 2488, Mulhouse, 68057, France

[i] Chemistry Department, Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russia

[j] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstrasse 2a, 91058 Erlangen, Germany

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ta06706e

‡ These two first authors contributed equally.

Materials Views
www.MaterialsViews.com

ADVANCED MATERIALS
www.advmat.de

High Mobility and Low Density of Trap States in Dual-Solid-Gated PbS Nanocrystal Field-Effect Transistors

Mohamad Insan Nugraha, Roger Häusermann, Satria Zulkarnaen Bisri, Hiroyuki Matsui, Mykhailo Sytnyk, Wolfgang Heiss, Jun Takeya, and Maria Antonietta Loi**

Semiconducting colloidal nanocrystals (CNCs) are of remarkable research interest due to their prospects for a wide range of optoelectronic devices, including solar cells,[1–3] photodetectors,[4–6] photoelectrochemical hydrogen production,[7] and light-emitting devices.[8,9] The quantum confinement of carrier wavefunctions in the NCs leads to the formation of discrete electronic energy levels and a tunability of their electronic band gaps by NC size.[10] Among a broad variety of NCs, lead sulfide (PbS) is one of the most interesting because of a well-developed synthetic control leading to their high quality, high absorbance, and optimal band gap tunability for solar cell applications.[10,11] While PbS NC assemblies have demonstrated a promising breakthrough for efficient solar cells[1–3,12] and highly sensitive photodetectors,[4–6] a main obstacle for further improvements is given by the low carrier mobility due to carrier traps, and the lack of understanding charge carrier transport processes in NC solids. Moreover, there is strong disagreement in literature whether this material behaves as hole transporting,[13] as electron transporting material or as both[14–16] as is observed in its bulk form.[17] This large variability is determined by fabrication conditions,[16,18,19] chemical nature of the ligands,[18] and stoichiometric variations obtained during or post synthesis.[20]

To assemble CNCs into arrays able to transport carriers, the about 2 nm long molecular ligands, which stabilize the NCs and provide their solubility, have to be exchanged to shorter ones. These shorter ligands can be organic molecules (e.g., benzenedithiol, ethanedithiol, 3-mercaptopropionic acid, etc.)[1,15,18,19] or inorganic ones (e.g., AsS_3^-, S^{2-}, etc.).[1,14,20–22] The ligands have an influence on the electronic states of the NC assembly, they can shift the energy levels,[23] can passivate dangling bonds and therefore fill trap states, or even provide additional carrier traps.[18]

The fabrication of field-effect transistors (FETs) is one of the best methods to evaluate charge carrier transport properties in semiconductors, including CNC assemblies.[13,24] Since FETs are interface-based devices, charge trapping is not only influenced by the properties of the active layer (the NCs assembly in this case) but also by the nature of the gate dielectric and its surface. Many efforts have been made to enhance the charge carrier mobility in PbS NC transistors. These attempts include variation of cross-linked ligands,[14–16,25] chemical post-deposition treatments to vary doping levels or to fill carrier traps,[1,20,22] increasing of the chemical purity,[1] and controlling the effect of oxygen/moisture during fabrication.[13,26] Nevertheless, the typical mobility values are still only up to 10^{-2} cm^2 V^{-1} s^{-1}, with the exception of sintered PbS NCs, which however often give rise to unipolar devices with limited on/off ratio,[18,27] and the devices which utilize ionic-liquid gating that allow to accumulate a higher carrier density than trap density.[15,28,29] In devices using conventional oxide dielectrics such as SiO_2, the transport characteristics are still trap dominated.[15,16]

In this communication, we demonstrate high electron mobility and a very low trap density in ambipolar PbS NC-FETs through the improvement of the NC assembly and the utilization of an amorphous fluoropolymer (Cytop) thin film as gate dielectric. Cytop is a hydroxyl-free and transparent polymer dielectric which has a dielectric constant of 2–2.5. We first improve the assembly organization of the 3-mercapto propionic acid (3MPA) cross-linked PbS nanocrystals on the SiO_2 surface through the utilization of hexamethyldisilazane self-assembled monolayers (HMDS-SAMs). This SAM treatment passivates the silanol on the SiO_2 surface that may act as electron trapping site. Cytop was deposited on top of the PbS nanocrystal assembly as second gate structure. The dual-gated FET structures using Cytop as a top gate and SiO_2 as bottom gate dielectric (**Figure** 1a), are utilized to compare the influence of the two different dielectrics on the same PbS nanocrystal assembly. Finally, from the obtained transport characteristics, and the simulation and numerical fitting to quantify the trap density of states (trap DOS), we observe for both holes and electrons in the FETs a sheet trap density lower than 10^{12} cm^{-2}, which explains the very high electron mobility of 0.2 cm^2 V^{-1} s^{-1}.

M. I. Nugraha, Dr. S. Z. Bisri,[+] Prof. M. A. Loi
Zernike Institute for Advanced Materials
University of Groningen
Nijenborgh 4, Groningen 9747AG, The Netherlands
E-mail: m.a.loi@rug.nl
M. I. Nugraha, Dr. R. Häusermann,
Dr. H. Matsui, Prof. J. Takeya
Department of Advanced Materials Science
School of Frontier Sciences
The University of Tokyo
5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan
E-mail: takeya@k.u-tokyo.ac.jp
M. Sytnyk, Prof. W. Heiss[++]
Institute for Semiconductor and Solid State Physics
University of Linz
Altenbergerstr. 69, Linz 4040, Austria
[+]Present address: RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
[++]Present address: Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-Universität, Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany and Energie Campus Nürnberg (EnCN), Fürther Straße 250, 90429 Nürnberg, Germany

DOI: 10.1002/adma.201404495

Journal of
Materials Chemistry A

PAPER

View Article Online
View Journal | View Issue

Pushing efficiency limits for semitransparent perovskite solar cells†

Cite this: J. Mater. Chem. A, 2015, 3, 24071

César Omar Ramírez Quiroz,*ab Ievgen Levchuk,a Carina Bronnbauer,ab
Michael Salvador,ac Karen Forberich,a Thomas Heumüller,a Yi Hou,ab
Peter Schweizer,d Erdmann Spiecker d and Christoph J. Brabec ae

While perovskite-based semitransparent solar cells deliver competitive levels of transparency and efficiency to be envisioned for urban infrastructures, the complexity and sensitivity of their processing conditions remain challenging. Here, we introduce two robust protocols for the processing of sub-100 nm perovskite films, allowing fine-tuning of the active layer without compromising the crystallinity and quality of the semiconductor. Specifically, we demonstrate that a method based on solvent-induced crystallization with a rapid drying step affords perovskite solar cells with 37% average visible transmittance (AVT) and 7.8% PCE. This process enhances crystallization with a preferential phase orientation presumably at the interface, yielding a high fill factor of 72.5%. The second method is based on a solvent–solvent extraction protocol, enabling active layer films as thin as 40 nm and featuring room-temperature crystallization in an ambient environment on a few second time span. As a result, we demonstrate a maximum AVT of 46% with an efficiency of 3.6%, which is the highest combination of efficiency and transparency for a full device stack to date. By combining the two methods presented here we cover a broad range of thicknesses vs. transparency values and confirm that solvent-induced crystallization represents a powerful processing strategy toward high-efficiency semitransparent solar cells. Optical simulations support our experimental findings and provide a global perspective of the opportunities and limitations of semitransparent perovskite photovoltaic devices.

Received 21st October 2015
Accepted 21st October 2015

DOI: 10.1039/c5ta08450d

www.rsc.org/MaterialsA

1. Introduction

The development of innovative technologies with improved levels of sustainability that are capable to compete with today's state of the art photovoltaic devices is challenging, given their widely established deployment methods. Silicon technologies, nowadays leading the market, still have several advantages over second and third generation solar cells for conventional applications. One application with promising potential on getting into the fast track of becoming a realistic contender for silicon technologies is semitransparent photovoltaics. The ability to implement semitransparent solar panels into consumer products such as building integrated elements, *e.g.* windows, or portable electronic devices relying on existing infrastructure could potentially lead to an economic boost in the field of photovoltaics. In this regard, organic photovoltaic (OPV) devices offer a unique potential given their characteristics including low manufacturing cost, lightweight, flexibility, intrinsic transparency and, most importantly, solution processability, desirable properties in "roll-to-roll" scalable protocols. Despite their strategic advantages, recent progress in up-and-coming new technologies such as perovskites has shown significant potential outshining OPV established technologies in terms of efficiency. The latest findings demonstrated efficiencies as high as 10.8% for single-junction opaque OPV devices.[1,2] In contrast, perovskite photovoltaic devices have shown certified efficiencies up to 20.1% within their short time of development since their emergence.[3–7] In the case of semitransparent photovoltaic devices, three main areas of focus are recognized in the literature for advancing transparency and performance. First, the strategic selection or design of the absorber material;[8,9] second, the realization of light management approaches through device engineering or nanostructured materials and architectures;[10] and third, the development of

---

[a] Institute of Materials for Electronics and Energy Technology (i-MEET), Department of Materials Science and Engineering, Friedrich-Alexander University Erlangen-Nürnberg, Martensstrasse 7, 91058 Erlangen, Germany. E-mail: cesar.quiroz@fau.de

[b] Erlangen Graduate School in Advanced Optical Technologies (SAOT), Paul-Gordan-Str. 6, 91052 Erlangen, Germany

[c] Instituto de Telecomunicações, Instituto Superior Técnico, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal

[d] Center for Nanoanalysis and Electron Microscopy (CENEM), Department Werkstoffwissenschaften, Friedrich-Alexander University Erlangen-Nürnberg, Cauerstraße 6, 91058 Erlangen, Germany

[e] Bavarian Center for Applied Energy Research (ZAE Bayern), Am Weichselgarten 7, 91058 Erlangen, Germany

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ta08450d

Journal of Crystal Growth 418 (2015) 64–69

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Determination of GaN solubility in supercritical ammonia with NH_4F and NH_4Cl mineralizer by *in situ* x-ray imaging of crystal dissolution

Saskia Schimmel[a,*], Michael Lindner[a], Thomas G. Steigerwald[b,c], Benjamin Hertweck[b], Theresia M.M. Richter[d], Ulrike Künecke[a], Nicolas S.A. Alt[b], Rainer Niewa[d], Eberhard Schlücker[b], Peter J. Wellmann[a]

[a] Materials Department 6, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Martensstraße 7, 91058 Erlangen, Germany
[b] Institute of Process Machinery and Systems Engineering, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Cauerstraße 4, 91058 Erlangen, Germany
[c] Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Cauerstraße 4, 91058 Erlangen, Germany
[d] Institute of Inorganic Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

A R T I C L E I N F O

Article history:
Received 16 December 2014
Received in revised form
2 February 2015
Accepted 8 February 2015
Communicated by: Pierre Müller
Available online 14 February 2015

Keywords:
A1. Solubility
A1. Solvents
A1. Mineralizers
A2. Growth from solutions
A2. Ammonothermal crystal growth
B1. Nitrides

A B S T R A C T

Quantitative data on the solubility of GaN in supercritical ammonia using NH_4F as mineralizer are reported. The solubility is determined by *in situ* x-ray imaging of the dissolution of GaN single crystals. First, solubility values obtained by this method with NH_4Cl as mineralizer are presented and discussed with respect to existing literature data. Monitoring the dissolution process in situ reveals the time when the solubility limit is reached. Thus, it allows to distinguish the saturation of the solution from dissolution based on mass transport and deposition. This is a key advantage of solubility measurements by in situ x-ray imaging compared to gravimetric methods. Our results indicate that the solubility limit is reached much faster than usually assumed in gravimetric solubility studies and the solubility of GaN in ammonothermal media is significantly lower than reported so far.

1. Introduction

The availability of native GaN substrates of very low defect density is essential for improving the performance, yield and lifetime of optoelectronic and electronic GaN-based devices [1,2], in particular reliability of high-power laser diodes [3]. A promising method for obtaining high-quality GaN bulk single crystals is solution growth using supercritical ammonia as a solvent, i.e., the ammonothermal method. Despite impressive progress in the ammonothermal growth of bulk GaN crystals was achieved during the last years [4–6], further development is still hindered by the lack of fundamental data such as the solubility of GaN, the chemical nature and stability of solved and transported species and the viscosity of the fluid [7–9]. These parameters are difficult to investigate due to the challenging process conditions, namely high pressure, high temperature and highly corrosive reaction medium.

One of the key parameters to understand and further develop ammonothermal crystal growth of nitrides is the solubility of the nitride [8] under varying process conditions such as temperature, pressure, mineralizer and molar ratio of the reactants. To date, only few quantitative data on the solubility of GaN have been reported for selective process conditions [4,10–12]. Additionally, all of the reported quantitative data (for ammonoacidic mineralizers: NH_4Cl [10–12], NH_4Br [12] and NH_4I [12]) have been obtained by gravimetric investigation of residual reactants after dissolution experiments, i.e., by ex situ methods. No investigations of GaN solubility with NH_4F as mineralizer have so far been reported although it shows promising properties: NH_4F offers a negative temperature gradient of solubility observed at temperatures of 550–650 °C [13], growth in polar, semipolar as well as nonpolar directions [13,14], high growth rates and good crystal quality [13,14].

We have developed a method for investigating the solubility of nitrides in ammonothermal reaction media which is capable of monitoring the dissolution process in situ. Hereby, reaching of the solubility limit can be observed. Experimental details of our method as well as first solubility data using NH_4F as a mineralizer

---

[*] Corresponding author. Tel.: +49 9131 85 27718.
E-mail address: Saskia.schimmel@fau.de (S. Schimmel).

http://dx.doi.org/10.1016/j.jcrysgro.2015.02.021

THE JOURNAL OF
PHYSICAL CHEMISTRY
Letters

Letter

pubs.acs.org/JPCL

Quantifying the Extent of Contact Doping at the Interface between High Work Function Electrical Contacts and Poly(3-hexylthiophene) (P3HT)

R. Clayton Shallcross,*[†] Tobias Stubhan,[‡] Erin L. Ratcliff,[§] Antoine Kahn,[∥] Christoph J. Brabec,[‡] and Neal R. Armstrong*[†]

[†]Department of Chemistry and Biochemistry, University of Arizona, 1306 East University Boulevard, Tucson, Arizona 85721, United States

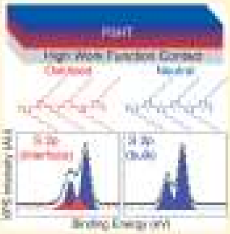
[‡]Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstrasse 7, Erlangen 91058, Germany

[§]Department of Materials Science and Engineering, University of Arizona, 1235 East James E. Rogers Way, Tucson, Arizona 85721, United States

[∥]Department of Electrical Engineering, Princeton University, Olden Street, Princeton, New Jersey 08544, United States

Supporting Information

ABSTRACT: We demonstrate new approaches to the characterization of oxidized regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) that results from electronic equilibration with device-relevant high work function electrical contacts using high-resolution X-ray (XPS) and ultraviolet (UPS) photoelectron spectroscopy (PES). Careful interpretation of photoemission signals from thiophene sulfur atoms in thin (ca. 20 nm or less) P3HT films provides the ability to uniquely elucidate the products of charge transfer between the polymer and the electrical contact, which is a result of Fermi-level equilibration between the two materials. By comparing high-resolution S 2p core-level spectra to electrochemically oxidized P3HT standards, the extent of the contact doping reaction is quantified, where one in every six thiophene units (ca. 20%) in the first monolayer is oxidized. Finally, angle-resolved XPS of both pure P3HT and its blends with phenyl-C_{61}-butyric acid methyl ester (PCBM) confirms that oxidized P3HT species exist near contacts with work functions greater than ca. 4 eV, providing a means to characterize the interface and "bulk" region of the organic semiconductor in a single film.



The interface region between electrical contacts and organic semiconductors is critical to the overall performance of organic electronic devices, especially as these regions control charge injection in organic light-emitting diodes (OLEDs) and organic field effect transistors (OFETs), charge extraction/surface recombination in organic photovoltaics (OPVs), and device lifetime/degradation in all of these technologies.[1−3] Interlayer materials are often used to tune the contact work function (Φ), ultimately controlling the energetic barrier for charge injection/extraction and turn-on/open-circuit voltage of OLEDs and OPVs, respectively.[3] Understanding the energetics and the relationship between energetics and interfacial structure and the possible chemical reactions between electrical contacts and the active semiconducting materials are important issues when designing and optimizing optoelectronic devices.

Energy level alignment at the contact/organic semiconductor interface is dependent on the work function of the contact relative to the frontier orbital energies (i.e., HOMO and LUMO) of the semiconductor.[4] Different scenarios are possible for weak interactions (e.g., no chemical bonding) between an organic semiconductor and a contact: Fermi-level pinning near the organic semiconductor frontier orbitals for both high and low work function contacts (relative to the oxidation and reduction potential of the organic semiconductor, respectively) and vacuum level alignment when the contact work function is between the organic semiconductor HOMO and LUMO energy.[5] In the pinning regimes, interfacial charge transfer or "contact doping" has been posited; however, the extent of doping has rarely been quantified.[6] Doping of the organic semiconductor may be significantly enhanced by the addition of strongly electron-donating (n-type) or -accepting (p-type) dopants,[7] and while both forms of doping influence electrical properties, the molecular components (i.e., radical cations/anions) resulting from the charge-transfer process can be difficult to both identify and quantify spectroscopically, especially for ultrathin films. These charge-transfer processes with organic semiconductors are not only dependent on the work function of the neighboring contact and the presence of molecular dopants but also are thought to depend strongly on

Received: March 3, 2015
Accepted: March 24, 2015
Published: March 24, 2015

ACS Publications

DOI: 10.1021/acs.jpclett.5b00444
J. Phys. Chem. Lett. 2015, 6, 1303−1309

Highly transmissive luminescent down-shifting layers filled with phosphor particles for photovoltaics

Anastasiia Solodovnyk,[1,2,3,*] **Karen Forberich,**[2] **Edda Stern,**[1] **Janez Krč,**[4] **Marko Topič,**[4]
Miroslaw Batentschuk,[2] **Benjamin Lipovšek**[4] **and Christoph J. Brabec**[1,2,3]
[1]*Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstr. 2a, 91058 Erlangen, Germany*
[2]*Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Martensstr. 7, 91058 Erlangen, Germany*
[3]*Erlangen Graduate School in Advanced Optical Technologies (SAOT), FAU, Paul-Gordan-Str. 6, 91052 Erlangen, Germany*
[4]*Laboratory of Photovoltaics and Optoelectronics (LPVO), Faculty of Electrical Engineering, University of Ljubljana, Tržaška cesta 25, SI-1000 Ljubljana, Slovenia*
*anastasiia.solodovnyk@zae-bayern.de

Abstract: We study the optical properties of polymer layers filled with phosphor particles in two aspects. First, we used two different polymer binders with refractive indices $n = 1.46$ and $n = 1.61$ ($\lambda = 600$ nm) to study the influence of Δn with the phosphor particles ($n = 1.81$). Second, we prepared two particle size distributions $D_{50} = 12$ μm and $D_{50} = 19$ μm. The particles were dispersed in both polymer binders in several volume concentrations and coated with thicknesses of 150-600 μm onto glass substrates. Experimental results and numerical simulations show that the layers of the higher refractive index binder with larger particles result in the highest optical transmittance in the visible light spectrum. Finally, we used numerical simulations to determine optimal layer composition for application in realistic photovoltaic devices.

OCIS codes: (230.7405) Wavelength conversion devices; (160.5690) Rare-earth-doped materials; (290.5850) Scattering, particles; (160.2540) Fluorescent and luminescent materials.

References and links

1. EUPVSEC, 2014, Press Release, "The European Photovoltaic Solar Energy Conference and Exhibition 2014 Confirms the Future of PV as a Major Electricity Source," *https://www.photovoltaic-conference.com/pressroom/press-releases/english/2014-pr-e-26sept2014.html*.
2. B. S. Richards, "Enhancing the performance of silicon solar cells via the application of passive luminescence conversion layers," Sol. Energy Mater. Sol. Cells 90(15), 2329–2337 (2006).
3. W. H. Weber and J. Lambe, "Luminescent greenhouse collector for solar radiation," Appl. Opt. 15(10), 2299–2300 (1976).
4. A. Goetzberger and W. Greube, "Solar energy conversion with fluorescent collectors," Appl. Phys. (Berl.) 14(2), 123–139 (1977).
5. E. Klampaftis and B. S. Richards, "Improvement in multi-crystalline silicon solar cell efficiency via addition of luminescent material to EVA encapsulation layer," Prog. Photovolt. Res. Appl. 19(3), 345–351 (2011).
6. E. Klampaftis, D. Ross, S. Seyrling, A. N. Tiwari, and B. S. Richards, "Increase in short-wavelength response of encapsulated CIGS devices by doping the encapsulation layer with luminescent material," Sol. Energy Mater. Sol. Cells 101, 62–67 (2012).
7. W. G. van Sark, K. W. J. Barnham, L. H. Slooff, A. J. Chatten, A. Büchtemann, A. Meyer, S. J. McCormack, R. Koole, D. J. Farrell, R. Bose, E. E. Bende, A. R. Burgers, T. Budel, J. Quilitz, M. Kennedy, T. Meyer, C. M. Donegá, A. Meijerink, and D. Vanmaekelbergh, "Luminescent Solar Concentrators - A review of recent results," Opt. Express 16(26), 21773–21792 (2008).
8. E. Klampaftis, D. Ross, K. R. McIntosh, and B. S. Richards, "Enhancing the performance of solar cells via luminescent down-shifting of the incident spectrum: A review," Sol. Energy Mater. Sol. Cells 93(8), 1182–1194 (2009).
9. X. Pi, Q. Li, D. Li, and D. Yang, "Spin-coating silicon-quantum-dot ink to improve solar cell efficiency," Sol. Energy Mater. Sol. Cells 95(10), 2941–2945 (2011).
10. S. Kalytchuk, S. Gupta, O. Zhovtiuk, A. Vaneski, S. V. Kershaw, H. Fu, Z. Fan, E. C. H. Kwok, C.-F. Wang, W. Y. Teoh, and A. L. Rogach, "Semiconductor Nanocrystals as Luminescent Down-Shifting Layers To Enhance

#235055 - $15.00 USD Received 23 Feb 2015; revised 10 Apr 2015; accepted 11 Apr 2015; published 6 May 2015
(C) 2015 OSA 1 Jun 2015 | Vol. 5, No. 6 | DOI:10.1364/OME.5.001296 | OPTICAL MATERIALS EXPRESS 1296

Journal of
Materials Chemistry A

PAPER

View Article Online
View Journal | View Issue

Cite this: J. Mater. Chem. A, 2015, 3, 16279

Ultra low band gap α,β-unsubstituted BODIPY-based copolymer synthesized by palladium catalyzed cross-coupling polymerization for near infrared organic photovoltaics†

Benedetta M. Squeo,[a] Nicola Gasparini,[b] Tayebeh Ameri,[b] Alex Palma-Cando,[c] Sybille Allard,[c] Vasilis G. Gregoriou,[ad] Christoph J. Brabec,[be] Ullrich Scherf[c] and Christos L. Chochos*[ad]

A new ultra low band gap (LBG) α,β-unsubstituted BODIPY-based conjugated polymer has been synthesized by conventional cross coupling polymerization techniques (Stille cross coupling) for the first time. The polymer exhibits a panchromatic absorption spectrum ranging from 300 nm to 1100 nm and an optical band gap (E_g^{opt}) of 1.15 eV, suitable for near infrared (NIR) organic photovoltaic applications as electron donor. Preliminary power conversion efficiency (PCE) of 1.1% in polymer : [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) 1 : 3 weight ratio bulk heterojunction (BHJ) solar cells has been achieved, demonstrating very interesting and promising photovoltaic characteristics, such as good fill factor (FF) and open circuit voltage (V_{oc}). These results showing that by the proper chemical design, new α,β-unsubstituted BODIPY-based NIR copolymers can be developed in the future with suitable energy levels matching those of $PC_{71}BM$ towards more efficient NIR organic photovoltaics (OPVs).

Received 10th June 2015
Accepted 13th July 2015

DOI: 10.1039/c5ta04229a

www.rsc.org/MaterialsA

1. Introduction

Low band gap (LBG) organic materials that absorb into the near-infrared (NIR) are of great interest in the recent years for a number of potential applications.[1] For example, the use of NIR-absorbing or NIR photovoltaic organic materials (small molecules or polymers) could extend the material's absorption into the NIR spectral region and even beyond 1000 nm wavelength, which in principle could enhance the current power conversion efficiency (PCE) of organic photovoltaics (OPVs).[2]

Even though semiconducting polymers with ultra LBGs have been synthesized before,[3–19] the challenge in designing and synthesizing materials that have a good photoresponse beyond 900 nm and an appreciable PCE in polymer : fullerene solar cells lies (among others) in the precise energy level control that is required. Two major methodologies are employed to fine tune the band gap and energy level alignment of conjugated polymers. One methodology relies on the donor–acceptor (D–A) approach and the other on the stabilization of the quinoid structure.[20] D–A approach is the most common tool to synthesize NIR conjugated polymers due to the plethora of functional electron rich and electron deficient building blocks. In order to develop ultra LBG D–A polymers, usually strong electron rich units and strong electron deficient building blocks are used. Common monomer units function as strong electron donors include pyrrole, thiophene, ethylenedioxythiophene (EDOT), bridged bithiophenes derivatives etc.[20] Moreover, the most well-known strong electron deficient units used to construct NIR D–A polymers are diketopyrrolopyrrole dyes,[4,7,9,11,18] benzobisthiadiazole,[3,5,8] pyrazinoquinoxaline derivatives,[10,12–14] thiadiazoloquinoxaline derivatives,[7,12,13–15] annelated benzotriazole,[16] thienoisoindigo,[10,17,18] cinnolinone,[19] cyclopentadithiophenone,[20] tetraazabenzodifluoranthene diimides,[20,21] etc.[21,22]

One of the least explored electron deficient monomers for the synthesis of NIR conjugated polymers is the so-called, 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, commonly known as BODIPY (Scheme 1).[23] BODIPY dyes were first discovered in 1968 by Treibs and Kreuzer[24] and exhibit unique properties such as large absorption coefficients, high fluorescence quantum yields, and remarkable photostability.[25] In addition,

---

[a] Advent Technologies SA, Patras Science Park, Stadiou Street, Platani-Rio, 26504 Patra, Greece. E-mail: cchochos@advent-energy.com

[b] Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstraße 7, 91058 Erlangen, Germany

[c] Macromolecular Chemistry Group (buwmakro) and Institute for Polymer Technology, Bergische Universität Wuppertal, Gaußstraße 20, D-42119 Wuppertal, Germany

[d] National Hellenic Research Foundation (NHRF), 48 Vassileos Constantinou Avenue, 11635, Athens, Greece

[e] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstrasse 2a, 91058 Erlangen, Germany

† Electronic supplementary information (ESI) available: Gel Permeation Chromatography (GPC), 1H-NMR spectra, atmospheric pressure photoelectron spectroscopy graph of the studied material and external quantum efficiency graph. See DOI: 10.1039/c5ta04229a

Journal of
Materials Chemistry A

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: J. Mater. Chem. A, 2015, 3, 14116

Received 4th June 2015
Accepted 5th June 2015

DOI: 10.1039/c5ta04053a

www.rsc.org/MaterialsA

A facile one-step method to reduce surface impurities in solution-processed $CuInS_2$ nanocrystal solar cells†

Melissa S. Stahl,‡[a] Hamed Azimi‡*[a] and Christoph J. Brabec[ab]

The presence of impurities and disorders presents a potential barrier for the success of solution processed inorganic nanocrystalline devices. The removal of impurities typically requires harsh conditions and complex procedures that limit utility. This paper demonstrates the successful use of a set of solvents, which can efficaciously remove the surface impurities formed during *in situ* deposition of $CuInS_2$ nanocrystals. These impurities include a hard-to-remove byproduct melamine that is formed by the decomposition of thiourea at elevated temperatures, and other organic residues like amines, conjugated organic systems, as well as ketones, aldehydes or esters. This work provides some design rules for the selection of solvents for removal purposes that could potentially be used for other absorber materials as well.

Introduction

The use of photovoltaic devices as an energy resource has become increasingly important due to increasing energy demand and climate change. Thin film solar cells contain inorganic absorber materials that could break into the roof top application market by allowing production on a greater scale due to lower material cost or roll to roll techniques, while at the same time enabling efficiencies of over 20% already demonstrated.[1,2] These high efficiencies have been attained by vacuum deposition of CIGSSe solar cells, which is not a technique well suited for large throughput roll-to-roll processes.[3,4] In the literature, various solution-processing methods have already been demonstrated for gallium and selenium free [$CuInS_2$] absorber materials,[5–7] and this gives hope for the future of roll-to-roll processes being envisaged for $CuInS_2$ solar cells, pending the breakthrough of problems that are associated with the film quality of these materials.

Solution processing of $CuInS_2$ can proceed through several methods and through the use of various precursors. Spray pyrolysis and chemical bath deposition methods[8–12] have previously been demonstrated, though this paper works on the laboratory-scale spin coating method for a proof of concept. It is known that during the crystal growth of $CuInS_2$ with molecular precursors, unwanted Cu rich phases like CuS can form at the top of the absorber film, which are detrimental to the device performance; highly reactive medium like a potassium cyanide bath is used to remove the segregated CuS. In other solution mixtures, a long reaction time is sometimes required, together with the use of reflux at elevated temperatures.[13] In another case, highly efficient $CuInS_2$ has been formed with the use of hydrazine that is highly reactive and toxic.[14,15] In various nanoparticle (NP) systems, the method of Layer-by-Layer (LbL) solvent treatment has been used to remove the organic ligands from the surface and to alleviate the adverse influence of disorders, reconstructions, and uncoordinated atoms on the performance of NP devices.[16–19] In this communication, we demonstrate that impurities formed on the $CuInS_2$ film surface can be removed to a large extent through the use of a simple one-step washing technique. The nature of solution processed layers results in there being a large amount of organic components remaining on the solid film, and this is not easily removed. Indeed, this has been documented elsewhere that there is a build-up of C, O and Cl elements still found on the absorber film,[20–24] which causes the formation of an absorber film that is less efficient as its vacuum deposited counterpart. This problem has also encouraged an effort to change the solvent system for some chalcogenide absorber materials in order to circumvent the problem of organic residuals in the thin film.

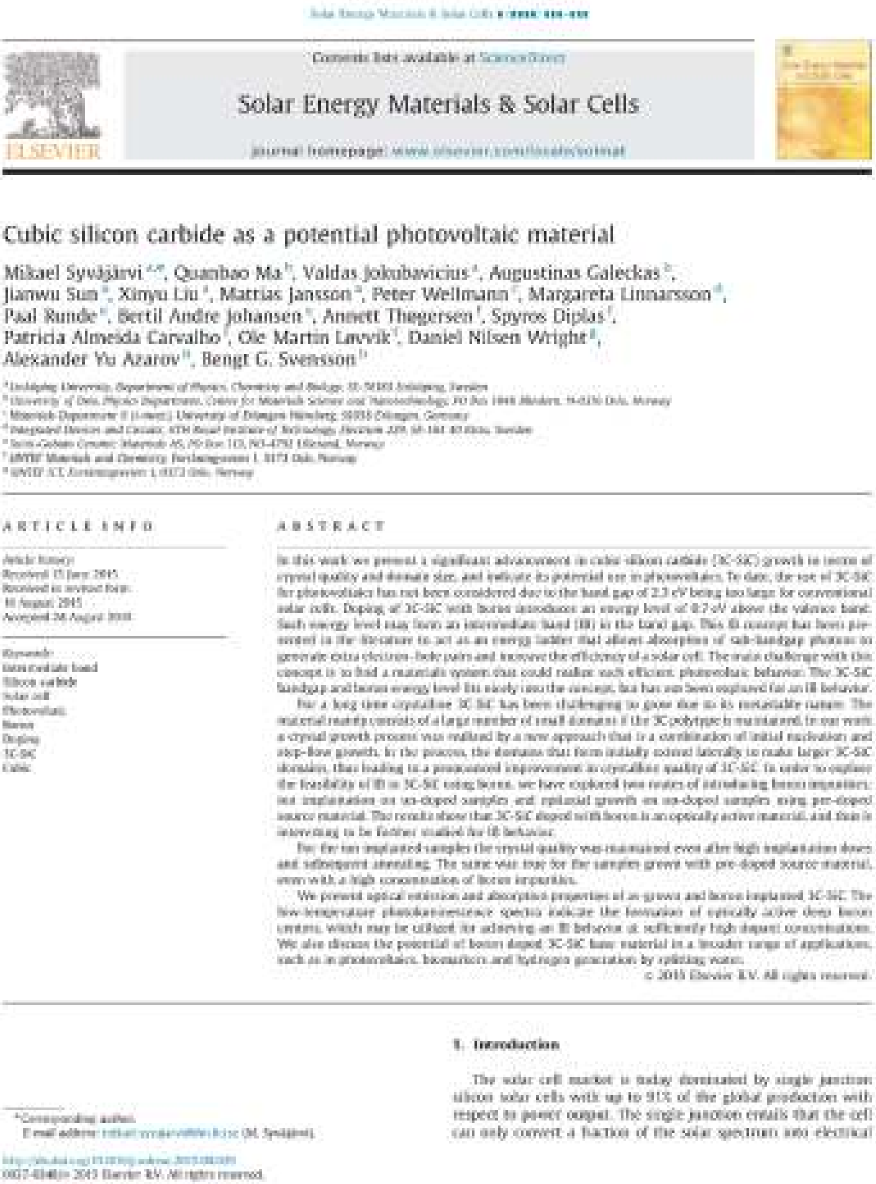
---

[a] Institute of Materials for Electronics and Energy Technology (i-MEET), Department of Materials Science and Engineering, Friedrich-Alexander University Erlangen-Nuremberg, Martensstr. 7, 91058 Erlangen, Germany. E-mail: hamed.azimi@fau.de

[b] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstr. 2a, 91058 Erlangen, Germany

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ta04053a

‡ These authors contributed equally to this work.



Solar Energy Materials & Solar Cells ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Cubic silicon carbide as a potential photovoltaic material

Mikael Syväjärvi[a,*], Quanbao Ma[b], Valdas Jokubavicius[a], Augustinas Galeckas[b], Jianwu Sun[a], Xinyu Liu[a], Mattias Jansson[a], Peter Wellmann[c], Margareta Linnarsson[d], Paal Runde[e], Bertil Andre Johansen[e], Annett Thøgersen[f], Spyros Diplas[f], Patricia Almeida Carvalho[f], Ole Martin Løvvik[f], Daniel Nilsen Wright[g], Alexander Yu Azarov[b], Bengt G. Svensson[b]

[a] Linköping University, Department of Physics, Chemistry and Biology, SE-58183 Linköping, Sweden
[b] University of Oslo, Physics Department, Centre for Materials Science and Nanotechnology, PO Box 1048 Blindern, N-0316 Oslo, Norway
[c] Materials Department 6 (i-meet), University of Erlangen-Nürnberg, 91058 Erlangen, Germany
[d] Integrated Devices and Circuits, KTH Royal Institute of Technology, Electrum 229, SE-164 40 Kista, Sweden
[e] Saint-Gobain Ceramic Materials AS, PO Box 113, NO-4792 Lillesand, Norway
[f] SINTEF Materials and Chemistry, Forskningsveien 1, 0373 Oslo, Norway
[g] SINTEF ICT, Forskningsveien 1, 0373 Oslo, Norway

A R T I C L E I N F O

Article history:
Received 15 June 2015
Received in revised form
10 August 2015
Accepted 26 August 2015

Keywords:
Intermediate band
Silicon carbide
Solar cell
Photovoltaic
Boron
Doping
3C-SiC
Cubic

A B S T R A C T

In this work we present a significant advancement in cubic silicon carbide (3C-SiC) growth in terms of crystal quality and domain size, and indicate its potential use in photovoltaics. To date, the use of 3C-SiC for photovoltaics has not been considered due to the band gap of 2.3 eV being too large for conventional solar cells. Doping of 3C-SiC with boron introduces an energy level of 0.7 eV above the valence band. Such energy level may form an intermediate band (IB) in the band gap. This IB concept has been presented in the literature to act as an energy ladder that allows absorption of sub-bandgap photons to generate extra electron–hole pairs and increase the efficiency of a solar cell. The main challenge with this concept is to find a materials system that could realize such efficient photovoltaic behavior. The 3C-SiC bandgap and boron energy level fits nicely into the concept, but has not been explored for an IB behavior.

For a long time crystalline 3C-SiC has been challenging to grow due to its metastable nature. The material mainly consists of a large number of small domains if the 3C polytype is maintained. In our work a crystal growth process was realized by a new approach that is a combination of initial nucleation and step-flow growth. In the process, the domains that form initially extend laterally to make larger 3C-SiC domains, thus leading to a pronounced improvement in crystalline quality of 3C-SiC. In order to explore the feasibility of IB in 3C-SiC using boron, we have explored two routes of introducing boron impurities: ion implantation on un-doped samples and epitaxial growth on un-doped samples using pre-doped source material. The results show that 3C-SiC doped with boron is an optically active material, and thus is interesting to be further studied for IB behavior.

For the ion implanted samples the crystal quality was maintained even after high implantation doses and subsequent annealing. The same was true for the samples grown with pre-doped source material, even with a high concentration of boron impurities.

We present optical emission and absorption properties of as-grown and boron implanted 3C-SiC. The low-temperature photoluminescence spectra indicate the formation of optically active deep boron centers, which may be utilized for achieving an IB behavior at sufficiently high dopant concentrations. We also discuss the potential of boron doped 3C-SiC base material in a broader range of applications, such as in photovoltaics, biomarkers and hydrogen generation by splitting water.

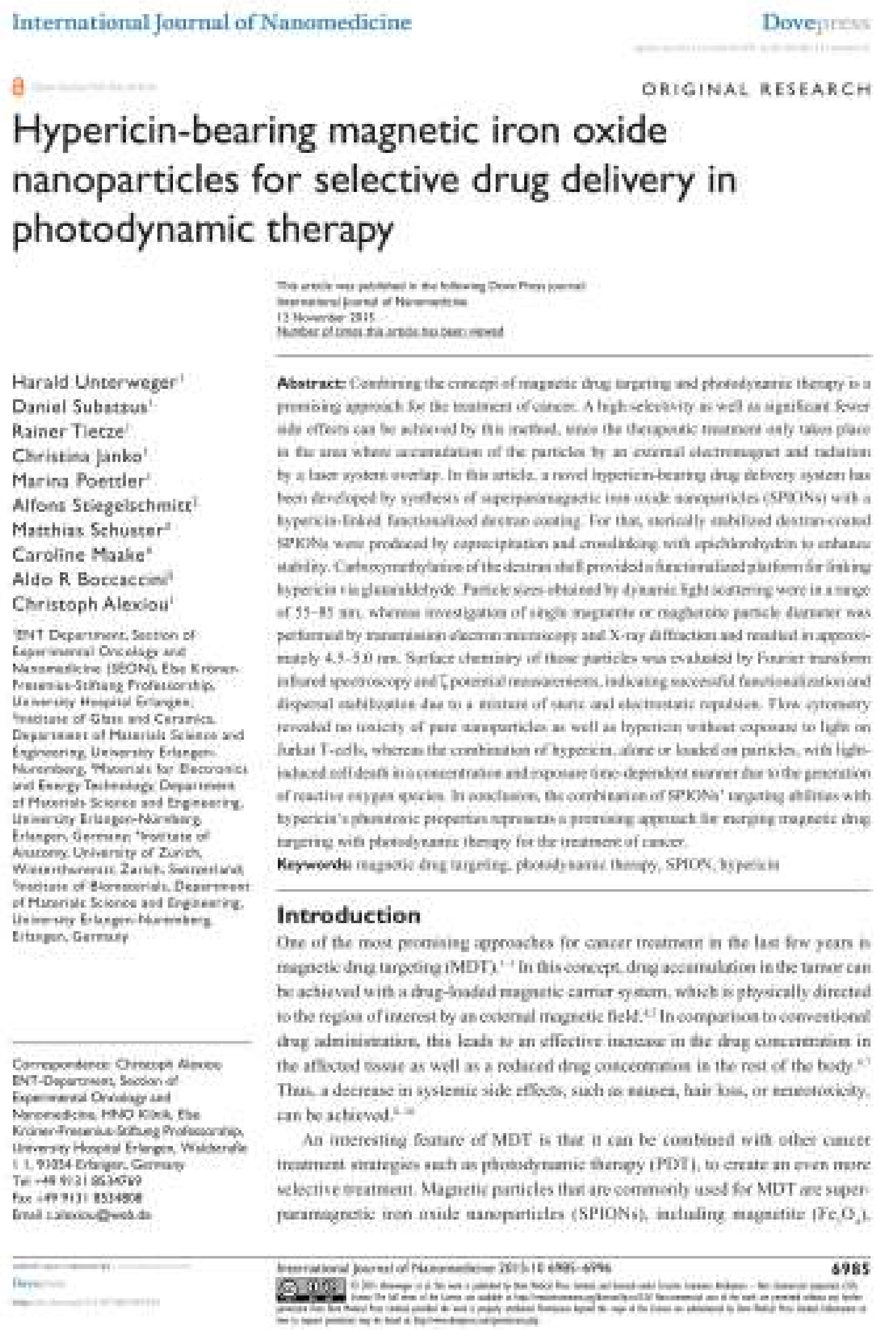
1. Introduction

The solar cell market is today dominated by single junction silicon solar cells with up to 91% of the global production with respect to power output. The single junction entails that the cell can only convert a fraction of the solar spectrum into electrical

---

[*] Corresponding author.
E-mail address: mikael.syvajarvi@liu.se (M. Syväjärvi).

[illegible]



International Journal of Nanomedicine

Dovepress

ORIGINAL RESEARCH

Hypericin-bearing magnetic iron oxide nanoparticles for selective drug delivery in photodynamic therapy

This article was published in the following Dove Press journal:
International Journal of Nanomedicine
12 November 2015
Number of times this article has been viewed

Harald Unterweger[1]
Daniel Subatzus[1]
Rainer Tietze[1]
Christina Janko[1]
Marina Poettler[1]
Alfons Stiegelschmitt[2]
Matthias Schuster[3]
Caroline Maake[4]
Aldo R Boccaccini[5]
Christoph Alexiou[1]

[1]ENT Department, Section of Experimental Oncology and Nanomedicine (SEON), Else Kröner-Fresenius-Stiftung Professorship, University Hospital Erlangen; [2]Institute of Glass and Ceramics, Department of Materials Science and Engineering, University Erlangen-Nuremberg; [3]Materials for Electronics and Energy Technology, Department of Materials Science and Engineering, University Erlangen-Nürnberg, Erlangen, Germany; [4]Institute of Anatomy, University of Zurich, Winterthurerstr, Zurich, Switzerland; [5]Institute of Biomaterials, Department of Materials Science and Engineering, University Erlangen-Nuremberg, Erlangen, Germany

Abstract: Combining the concept of magnetic drug targeting and photodynamic therapy is a promising approach for the treatment of cancer. A high selectivity as well as significant fewer side effects can be achieved by this method, since the therapeutic treatment only takes place in the area where accumulation of the particles by an external electromagnet and radiation by a laser system overlap. In this article, a novel hypericin-bearing drug delivery system has been developed by synthesis of superparamagnetic iron oxide nanoparticles (SPIONs) with a hypericin-linked functionalized dextran coating. For that, sterically stabilized dextran-coated SPIONs were produced by coprecipitation and crosslinking with epichlorohydrin to enhance stability. Carboxymethylation of the dextran shell provided a functionalized platform for linking hypericin via glutaraldehyde. Particle sizes obtained by dynamic light scattering were in a range of 55–85 nm, whereas investigation of single magnetite or maghemite particle diameter was performed by transmission electron microscopy and X-ray diffraction and resulted in approximately 4.5–5.0 nm. Surface chemistry of those particles was evaluated by Fourier transform infrared spectroscopy and ζ potential measurements, indicating successful functionalization and dispersal stabilization due to a mixture of steric and electrostatic repulsion. Flow cytometry revealed no toxicity of pure nanoparticles as well as hypericin without exposure to light on Jurkat T-cells, whereas the combination of hypericin, alone or loaded on particles, with light-induced cell death in a concentration and exposure time-dependent manner due to the generation of reactive oxygen species. In conclusion, the combination of SPIONs' targeting abilities with hypericin's phototoxic properties represents a promising approach for merging magnetic drug targeting with photodynamic therapy for the treatment of cancer.

Keywords: magnetic drug targeting, photodynamic therapy, SPION, hypericin

Introduction

One of the most promising approaches for cancer treatment in the last few years is magnetic drug targeting (MDT).[1–3] In this concept, drug accumulation in the tumor can be achieved with a drug-loaded magnetic carrier system, which is physically directed to the region of interest by an external magnetic field.[4,5] In comparison to conventional drug administration, this leads to an effective increase in the drug concentration in the affected tissue as well as a reduced drug concentration in the rest of the body.[6,7] Thus, a decrease in systemic side effects, such as nausea, hair loss, or neurotoxicity, can be achieved.[8–10]

An interesting feature of MDT is that it can be combined with other cancer treatment strategies such as photodynamic therapy (PDT), to create an even more selective treatment. Magnetic particles that are commonly used for MDT are superparamagnetic iron oxide nanoparticles (SPIONs), including magnetite (Fe_3O_4),

Correspondence: Christoph Alexiou
ENT-Department, Section of Experimental Oncology and Nanomedicine, HNO Klinik, Else Kröner-Fresenius-Stiftung Professorship, University Hospital Erlangen, Waldstraße 1, 91054 Erlangen, Germany
Tel +49 9131 8534769
Fax +49 9131 8534808
Email c.alexiou@web.de

International Journal of Nanomedicine 2015:10 6985–6996

Progress in
PHOTOVOLTAICS

PROGRESS IN PHOTOVOLTAICS: RESEARCH AND APPLICATIONS
Prog. Photovolt: Res. Appl. 2015; **23**:124–130

APPLICATIONS

Defect recognition in crystalline silicon solar cells by X-ray tomosynthesis with layer resolution

Virginia Voland[1], Ulrich Hoyer[2]*, Richard Auer[2], Michael Salamon[1], Norman Uhlmann[1]
and Christoph J. Brabec[2,3]

[1] Fraunhofer Institute for Integrated Circuits Division, Development Center X-Ray Technology EZRT, Fürth, Germany
[2] Bavarian Center for Applied Energy Research (ZAE Bayern e.V.), Erlangen, Germany
[3] Friedrich Alexander University Erlangen, i-MEET, Erlangen, Germany

ABSTRACT

The increasing demand for higher quality in solar cell production led to the development of several inline control methods. Beneath the image-guided methods, X-ray is not yet very well investigated for the application in photovoltaic research but shows high potential. In contrast to the ordinary X-ray radioscopic method, the tomosynthesis technique exhibits additional depth information of the solar cells and modules. In this article, several applications of tomosynthesis for the investigation of solar cells and modules are studied. It will be shown what potential the application of X-ray and especially tomosynthesis has as quality control tool for photovoltaics.

KEYWORDS

metrology; X-ray; tomosynthesis; defect recognition

***Correspondence**

Ulrich Hoyer, ZAE Bayern, III, Erlangen, Germany.
E-mail: hoyer@zae.uni-erlangen.de

Received 7 March 2012; Revised 20 December 2012; Accepted 3 July 2013

1. INTRODUCTION

The main degradation mechanisms of crystalline silicon PV modules are inadequate encapsulation foils [1], cell breakage [2], shunts [3], insufficient soldering and others. To detect these defects, several methods are already available and in use: The I–V curve under illumination [4], [5] determines the cell and module power and allows for quantitative values of the parallel and series resistance. Microcracks and cell breakage can be detected, for example, by the fast and easy to use technique electroluminescence [2, 6] and by transillumination with infrared light. Lock-in thermography is used for the detection of shunts [7, 8], the quantitative two-dimensional mapping of series resistance [9], saturation current and diode ideality factor [10]. Transmission electron microscopy, for example, facilitates the investigation of solder joints, while electroluminescence is also used for the search for silver paste and screen printing defects. Defect bypass diodes on the other hand can be found using thermography under sun illumination [11].

Because many of the contemporary methods are slow and expensive, there is still a high demand for new quality control techniques that are fast and reliable and, therefore, suitable for the use as inline methods. One method that is scarcely used in PV is X-ray imaging. Its simplest application, the radioscopic method, yields integrated information over the entire depth of the device, which is sufficient for the detection of cracks and others. A more advanced X-ray method, the so-called tomosynthesis, facilitates the resolution of several layers in wide-stretched thin objects such as solar cells and modules. In the following, several possible applications of this measurement technique in the field of PV are shown and interpretation ways of the images are given.

2. X-RAY IMAGING AND THE PRINCIPLES OF X-RAY TOMOSYNTHESIS

X-rays in contrast to visible light are able to penetrate most materials and interact with them. Depending on the material, its density and the energy spectrum of the radiation, the X-rays are attenuated by the object. This fact in

A New Crystal Phase Molybdate $Yb_2Mo_4O_{15}$: The Synthesis and Upconversion Properties

Hai-Qiao Wang, Mirza Mačković, Andres Osvet, Ivan Litzov, Elena Epelbaum, Alfons Stiegelschmitt, Miroslaw Batentschuk, Erdmann Spiecker, and Christoph J. Brabec**

A new upconversion nanocrystal phase $Yb_2Mo_4O_{15}$:Er is developed by using a facile aqueous-precipitation procedure combined with thermal annealing. Nanocrystals of $Yb_2Mo_4O_{15}$ are exclusively synthesized, with particle sizes ranging from 1 to 20 nm. The optical properties are characterized and a high upconversion quantum yield is determined to be ~1.3% at room temperature, under excitation of ~500 mW cm^{-2} IR (975 nm). To the best of our knowledge, this is the first work concerning the synthesis of nanocrystalline $Yb_2Mo_4O_{15}$ and the characterization of its upconversion properties, which possesses the potential to be utilized in bio-probing and thin-film optoelectronic device applications.

1. Introduction

Molybdenum oxides (MoO_x), especially nanocrystalline MoO_3, exhibit attractive catalytic, photochromic and electronic properties, as well as a great potential for various applications. MoO_3 has attracted considerable attention from researchers in the field of catalysts,[1,2] chemical sensors,[3] solid lubricants,[4] thermoelectric materials,[5] bioscience,[6] and especially in the recent years in electronic device applications such as field emitters,[7] light-emitting diodes,[8] and photovoltaics.[9,10] As a hole-extracting layer, MoO_3 was demonstrated to improve device performance in solar cells due to its favorable electronic and optical properties.[11] Not only thermally evaporated,[12] but also solution deposited MoO_3 layers from both precursor solution[13] and nanocrystal dispersion,[14,15] has been reported with the purpose to develop a low temperature and full solution fabrication technique for stable and large-scale thin-film organic solar cells. Solution deposited MoO_3 films, especially deposited from crystalline MoO_3 dispersion,[15,16] offer electronic properties comparable to thermally evaporated MoO_3 film, while keeping the advantage of low temperature deposition.

Oxide materials are usually chemically, mechanically, and thermally stable. In addition, MoO_x has relatively low maximum optical phonon energy,[16–18] suppressing the non-radiative multi-phonon relaxation processes, which can be responsible for a considerable reduction of the emission intensity.[19] MoO_x could therefore be promising as a host for light upconversion applications. This promising upconversion property could provide the rare-earth ion-doped molybdate nanocrystals with great potential for biological and energy conversion applications (i.e., photovoltaics).

It is well known that the use of upconversion phosphor as probe in biological labeling, imaging, and therapy has remarkable advantages over traditional organic dyes and quantum dots, such as low noise and large detection depth.[20] The upconversion concept is also considered as a practical technique to harvest infrared solar photons in photovoltaic application,[21] especially in combination with other engineering techniques, such as solar concentrators.[22] In the past, a lot of efforts have been put into these topics.[20,21,23–27]

Up to now various upconversion phosphors have been reported.[28–30] However, rare-earth ion-doped phosphor crystals, especially metal oxides host upconversion phosphors, are usually formed in the sub-micrometer or micrometer size range,[31,32] which usually challenges their application as a labeling probe in bioresearch and the formation of high-quality interfacial films in photovoltaic devices. In our previous work, we have reported the use of MoO_3 as hole-extracting interfacial

Dr. H.-Q. Wang
Institute of Functional Nano and
Soft Materials (FUNSOM)
Soochow University
199 Ren-Ai Road, Suzhou Industrial Park, Suzhou,
Jiangsu 215123, P. R. China
E-mail: hqwang@suda.edu.cn
Dr. M. Mačković, Prof. E. Spiecker
Department of Materials Science and Engineering
Center for Nanoanalysis and Electron Microscopy (CENEM)
University Erlangen-Nuremberg
Cauerstr. 6, 91058, Erlangen, Germany
Dr. A. Osvet, Dr. I. Litzov, Dr. E. Epelbaum, Dr. M. Batentschuk,
Prof. C. J. Brabec
Institute Materials for Electronics and Energy Technology (I-MEET)
University Erlangen-Nuremberg
Martensstraße 7, D-91058, Erlangen, Germany
E-mail: christoph.brabec@ww.uni-erlangen.de
Dr. A. Stiegelschmitt
Institute of Glass and Ceramics
Department of Materials Science
University Erlangen-Nuremberg
Martensstraße 5, 91058, Erlangen, Germany
Prof. C. J. Brabec
Bavarian Center for Applied Energy Research (ZAE Bayern)
Am Weichselgarten 7, 91058, Erlangen, Germany

DOI: 10.1002/ppsc.201400137

CRYSTAL
Research & Technology

Cryst. Res. Technol. **50**, No. 1, 2–9 (2015) / DOI 10.1002/crat.201400216

Review Article

Growth of SiC bulk crystals for application in power electronic devices – process design, 2D and 3D X-ray in situ visualization and advanced doping

Peter Wellmann[1,*], *Georg Neubauer*[1], *Lars Fahlbusch*[1], *Michael Salamon*[2], *and Norman Uhlmann*[2]

Received 30 June 2014, revised 26 August 2014, accepted 27 August 2014

Silicon carbide single crystals have become widely used as substrates for power electronic devices like diodes and electronic switches. Today, 4 inch and 6 inch wafer diameters are commercially available which are processed from vapor grown crystals. The state of the art physical vapor transport method may be called mature. Nevertheless, low defect density and uniform doping are still topics which can be further improved by current research and development of more sophisticated processes and process control. The aim of the paper is to review the physical vapor transport growth method as applied today. Special emphasis will be put on currently less advanced in situ growth monitoring tools based on 2D and 3D X-ray imaging that could be a tool for production monitoring. These techniques allow a precise determination of the crystal and source material evolution. Another topic will be the processing of highly conductive p-type 4 H-SiC which is of particular interest for power electronic switches.

1 Introduction

Since the commercialization of silicon carbide (SiC) for power electronic applications, bulk crystal growth is mainly performed using the PVT (physical vapor transport) method at elevated temperatures above 2000 °C. Today, mainly the 4 H-SiC polytype is applied in electronic switching devices. The cubic 3C-SiC polytype would be of particular interest. Among the various SiC polytypes, 3C-SiC exhibits the greatest electron mobility and lowest defect density at the native oxide interface. However, process control is far from being stable. In the case of 4H-SiC, 4 inch single crystal diameter can be viewed state of the art while 6 inch diameter has been successfully demonstrated and is expected to replace the current standard within the next years. Besides a number of news announcements, so far only few scientific publications have been released on bulk growth of 150 mm 4H-SiC (see e.g. [1]). The state-of-the-art PVT method may be called mature. Nevertheless, low defect density and uniform doping are still topics which can be further improved by current research and development of more sophisticated processes and process control.

The aim of the paper is to review the PVT growth method as it is applied today. Special emphasis is put on the discussion of (i) process variations that may improve the standard PVT capabilities in terms of polytype stability and doping (section 2), (ii) in-situ growth monitoring tools based on 2D and 3D X-ray imaging to visualize the crystal growth interface and its shape during growth (section 3), as well as on (iii) the technological implementation of p-type doping using aluminum which is the most common acceptor in SiC exhibiting the lowest activation energy (section 4). The latter requires special process treatment during aluminum doping like gas feeding in order to grow highly conductive p-type 4H-SiC. This is of particular interest for power electronic switches like insulated gate barrier transistors (IGBT) and related devices.

2 Bulk growth methods

The phase diagram of SiC (figure 1) exhibits a peritectic point at ca. 2840 °C for stoichiometric composition (see

---

[*] Corresponding author: e-mail: peter.wellmann@fau.de

[1] Crystal Growth Lab, Materials Department 6 (i-meet), University of Erlangen-Nürnberg, Erlangen, Germany

[2] Fraunhofer Institute for Integrated Circuits, Development Center for X-Ray Technology (EZRT), Fürth, 90768, Germany

Thin Solid Films 577 (2015) 88–93

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Optimization of growth parameters for growth of high quality heteroepitaxial 3C–SiC films at 1200 °C

Martin Wilhelm [a,*], Marcel Rieth [a], Marco Brandl [b], Rachmat Adhi Wibowo [b], Rainer Hock [b], Peter Wellmann [a]

[a] University of Erlangen, Materials Department 6, Martensstr. 7, 91058 Erlangen, Germany
[b] University of Erlangen, Chair for Crystallography and Structural Physics, Staudtstr. 3, 91058 Erlangen, Germany

ARTICLE INFO

Article history:
Received 17 March 2014
Received in revised form 13 January 2015
Accepted 22 January 2015
Available online 30 January 2015

Keywords:
Cubic silicon carbide
Heteroepitaxy
X-ray diffraction
Raman spectroscopy

ABSTRACT

In order to reduce the residual stress caused by the mismatch of thermal expansion coefficients of 3C–SiC layers grown on Si after cooling down to room temperature, the growth temperature was reduced from usually above 1300 °C to 1200 °C. Epitaxial layers with high crystalline quality were grown on 1 × 1 cm² (100) Si substrates. The layers were evaluated by means of x-ray diffraction (XRD), Raman measurements, scanning electron microscopy and atomic force microscopy. Full width at half maximum values of 0.15° for XRD rocking curve measurements of the (200) 3C–SiC peak were achieved, indicating high crystalline quality of the layers and epitaxial growth. For optimized growth at 1200 °C a high C/Si-ratio, on-axis substrates and a layer thickness of over 1 μm are necessary.

1. Introduction

Silicon carbide is one of the most promising materials for applications in high power and high temperature electronics. Its high bandgap, high thermal conductivity and high electrical breakdown field qualify it for use in inverters for solar energy applications or engine control systems where high power density can reduce cost and weight [1]. The high electron mobility of the cubic polytype is beneficial for switching devices like metal-oxide-semiconductor field-effect transistors where high channel mobility is needed [2]. Because of its good mechanical properties, especially its high hardness and high Young's modulus [3], it is also suitable for micro-electro-mechanical systems. Since 3C–SiC bulk material is not available today and most devices only use the top part of a wafer, heteroepitaxy is the only way to compensate this deficiency. To lower the price of components, large area substrates are required and a lot of obstacles need to be overcome. In this work we focus on the improvement of crystalline quality on small area substrates. The most important issue of 3C–SiC heteroepitaxy on Si, the high lattice mismatch of about 20%, has been overcome by adding a carbonization step before growth [4]. Probably the most severe remaining problem is the large difference in thermal expansion coefficient between SiC and Si of ca. 8% at room temperature [5] which leads to massive wafer bow after cooling down from growth temperature. A reasonable approach to diminish this obstacle is to reduce the growth temperature. Most 3C–SiC/Si layers are grown at temperatures exceeding 1300 °C and often the growth temperature is near the melting point of silicon. The reports at 1350 °C by Chung and Kim [6] and by Portail et al. [7] and at 1370 °C by Anzalone et al. [8] are just a few examples for high temperature grown 3C–SiC materials on Si. There are many attempts to grow at low temperatures e.g. via alternating supply epitaxy [9] or with germanium modified Si substrates [10] which both enable the growth around 1000 °C. Though the quality of the achieved layers is worse than that of their high temperature counterparts, they can be used for applications with low requirements. By the addition of chlorine into the gas phase, the growth temperature can also be reduced. The latter can be done either by adding HCl [11] or by the use of chlorine based precursors like methyl-trichlor-silane [12,13] at growth temperatures of 1000 °C and 1200 °C, respectively.

Besides the temperature reduction another way to reduce the wafer bow is by compensating the thermoelastic strain by properly adjusting the mismatch strain through the growth conditions [14]. Zielinski et al. [14] investigated the influence of C/Si-ratio, the growth rate and the layer thickness on the wafer curvature. Growth at the optimized C/Si-ratio nearly eliminated the bow but at the same time reduced the layer quality. Good layers with low bow were achieved by adjusting the growth rate while keeping the C/Si-ratio at the value for best quality.

In this work we present the growth of high crystalline quality epitaxial 3C–SiC layers on Si at a growth temperature of 1200 °C.

2. Experimental details

3C–SiC layers were grown on 1 × 1 cm² pieces of (100) Si wafers. In order to optimize the growth process at 1200 °C we varied the substrate orientation, the C/Si-ratio and the growth time. The experiments were carried out in an Aixtron AIX 200/4HT inductively heated cold-wall

---

* Corresponding author. Tel.: +49 9131 85 27719; fax: +49 9131 85 28495.
E-mail address: martin.wilhelm@fau.de (M. Wilhelm).

http://dx.doi.org/10.1016/j.tsf.2015.01.038

nature photonics
ARTICLES
PUBLISHED ONLINE: 25 MAY 2015 | DOI: 10.1038/NPHOTON.2015.82

Detection of X-ray photons by solution-processed lead halide perovskites

Sergii Yakunin[1,2], Mykhailo Sytnyk[1], Dominik Kriegner[1], Shreetu Shrestha[3], Moses Richter[3], Gebhard J. Matt[3], Hamed Azimi[3], Christoph J. Brabec[3,4], Julian Stangl[1], Maksym V. Kovalenko[2,5] and Wolfgang Heiss[1,3,4*]

The evolution of real-time medical diagnostic tools such as angiography and computer tomography from radiography based on photographic plates was enabled by the development of integrated solid-state X-ray photon detectors made from conventional solid-state semiconductors. Recently, for optoelectronic devices operating in the visible and near-infrared spectral regions, solution-processed organic and inorganic semiconductors have also attracted a great deal of attention. Here, we demonstrate a possibility to use such inexpensive semiconductors for the sensitive detection of X-ray photons by direct photon-to-current conversion. In particular, methylammonium lead iodide perovskite ($CH_3NH_3PbI_3$) offers a compelling combination of fast photoresponse and a high absorption cross-section for X-rays, owing to the heavy Pb and I atoms. Solution-processed photodiodes as well as photoconductors are presented, exhibiting high values of X-ray sensitivity (up to 25 μC mGy_{air}^{-1} cm^{-3}) and responsivity (1.9×10^4 carriers/photon), which are commensurate with those obtained by the current solid-state technology.

The detection of X-ray photons is of utmost importance for a wide range of applications, from specific crystal structure determinations[1] to radio astronomy[2]. The largest demand for X-ray detectors comes from medical radiography, where pixel-array detectors based on solid-state semiconductors are under development as a replacement for radiographic films[3–5]. Of the two currently available approaches to X-ray imaging—indirect conversion by the use of scintillators and direct conversion of X-ray photons into electrical current (for example, by photoconductivity)—the latter approach is reported to provide higher resolution[6]. Sensitive photoconduction is observable in various crystalline inorganic semiconductors under X-ray illumination, including amorphous Se[3,4], crystalline Si[7] and CdTe[5,7], but very few of these materials can be deposited uniformly onto the thin-film-transistor active-matrix arrays needed for readout of the electronic signals in pixel-array detectors[4,5,8] below the temperatures at which deterioration of the active matrix occurs. In this respect, solution-processed semiconductors such as those applied in photovoltaic and photoconducting devices operating in the visible or infrared spectral region[9–12] may represent an appealing alternative, owing to their low-temperature, non-vacuum and large-scale deposition in the form of homogeneous films by inexpensive techniques such as ink-jet, slit and screen printing, spin-coating and spray-coating. Finding such solution-processable semiconductors with high photoconductivity under X-ray illumination is therefore a key prerequisite. Here, we report that methylammonium lead triiodide ($MAPbI_3$, where MA is CH_3NH_3), a solution-processable organic–inorganic direct-gap semiconductor, can be used as a highly sensitive photoconductor for the direct conversion of X-ray photons into electrical current. Although solution processing at lower temperatures is generally thought to reduce the electronic quality of semiconductors due to structural imperfections, numerous reports providing evidence of the very high suitability of such lead halide perovskites for optoelectronic applications have recently been presented. In particular, perovskite-based solar cells have rapidly progressed to certified power conversion efficiencies of up to 20%[13–18]. Thin films of $MAPbI_3$ have also been used in bright light-emitting diodes[19], as a lasing medium[20] and in highly sensitive detectors operating in the visible spectral region[21].

For X-ray detection, not only are the semiconducting properties of the active material important, but so is the nature of its atomic constituents. This is because X-ray absorption scales with atomic number Z as Z^4/AE^3, where A is the atomic mass and E is the X-ray photon energy. Thus, the absorption at photon energies of ~10 keV to 1 MeV (plotted in Fig. 1a based on the atomic absorption coefficients[22] of the individual constituents of $MAPbI_3$) is dominated by the contribution of the Pb ions. At these high energies, the absorption length is more than two orders of magnitude larger than in the visible range, even though Pb is the second heaviest, after Bi, stable element in the periodic table. Thus, the ability to fabricate uniform semiconducting films with unusually large thicknesses, on the order of 10–100 μm, is also a prerequisite for the optimization of X-ray detectors. In this study, such thicknesses are readily obtained by spray-coating solutions of $MAPbI_3$ dissolved in common polar solvents such as dimethylformamide (DMF, Supplementary Fig. 1).

In this proof-of-concept study, we successfully test two main device architectures: photovoltaic and photoconductive. Thin-film photovoltaic cells (photodiodes), in which charge separation is achieved by the built-in potential of a p–i–n junction, exhibit a specific X-ray sensitivity of 25 μC mGy_{air}^{-1} cm^{-3}, which is commensurate with the performance of conventional solid-state

---

[1]Institute of Semiconductor and Solid State Physics, University Linz, Altenbergerstraße 69, Linz 4040, Austria. [2]Department of Chemistry and Applied Biosciences, Institute of Inorganic Chemistry, ETH Zürich, Zürich CH-8093, Switzerland. [3]Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstraße 7, Erlangen 91058, Germany. [4]Energie Campus Nürnberg (EnCN), Fürther Straße 250, Nürnberg 90429, Germany. [5]Empa - Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, Dübendorf 8600, Switzerland. *e-mail: wolfgang.heiss@jku.at

nature COMMUNICATIONS

ARTICLE

Received 21 Apr 2015 | Accepted 13 Jul 2015 | Published 20 Aug 2015 DOI: 10.1038/ncomms9056 OPEN

Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites

Sergii Yakunin[1,2], Loredana Protesescu[1,2], Franziska Krieg[1,2], Maryna I. Bodnarchuk[1,2], Georgian Nedelcu[1,2], Markus Humer[3], Gabriele De Luca[4], Manfred Fiebig[4], Wolfgang Heiss[3,5,6] & Maksym V. Kovalenko[1,2]

Metal halide semiconductors with perovskite crystal structures have recently emerged as highly promising optoelectronic materials. Despite the recent surge of reports on microcrystalline, thin-film and bulk single-crystalline metal halides, very little is known about the photophysics of metal halides in the form of uniform, size-tunable nanocrystals. Here we report low-threshold amplified spontaneous emission and lasing from ~10 nm monodisperse colloidal nanocrystals of caesium lead halide perovskites CsPbX$_3$ (X = Cl, Br or I, or mixed Cl/Br and Br/I systems). We find that room-temperature optical amplification can be obtained in the entire visible spectral range (440–700 nm) with low pump thresholds down to 5 ± 1 μJ cm^{-2} and high values of modal net gain of at least 450 ± 30 cm^{-1}. Two kinds of lasing modes are successfully observed: whispering-gallery-mode lasing using silica microspheres as high-finesse resonators, conformally coated with CsPbX$_3$ nanocrystals and random lasing in films of CsPbX$_3$ nanocrystals.

---

[1] Department of Chemistry and Applied Biosciences, Laboratory of Inorganic Chemistry, ETH Zürich, Vladimir-Prelog-Weg 1, CH-8093 Zürich, Switzerland. [2] Laboratory for Thin Films and Photovoltaics, Empa—Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland. [3] Institute of Semiconductor and Solid State Physics, University Linz, Altenbergerstraße 69, 4040 Linz, Austria. [4] Department of Materials, Laboratory for Multifunctional Ferroic Materials, ETH Zürich, Vladimir-Prelog-Weg 4, CH-8093 Zürich, Switzerland. [5] Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany. [6] Energie Campus Nürnberg (EnCN), Fürther Straße 250, 90429 Nürnberg, Germany. Correspondence and requests for materials should be addressed to M.V.K. (email: mvkovalenko@ethz.ch).

J. Am. Ceram. Soc., 98 [1] 30–38 (2015)
DOI: 10.1111/jace.13258

Aging Time and Temperature Effects on the Structure and Bioactivity of Gel-Derived 45S5 Glass-Ceramics

Kai Zheng,[‡] Anastasia Solodovnyk,[§] Wei Li,[‡] Ourania-Menti Goudouri,[‡] Christoph Stähli,[¶] Showan N. Nazhat,[¶] and Aldo R. Boccaccini[‡,†]

[‡]Institute of Biomaterials, Department of Materials Science and Engineering, University of Erlangen-Nuremberg, 91058 Erlangen, Germany

[§]Bavarian Center for Applied Energy Research (ZAE Bayern), Erlangen 91058, Germany

[¶]Department of Mining and Materials Engineering, McGill University, Montreal H3A 0C5, Canada

Porous bioactive glass-ceramics based on the 45S5 Bioglass® composition were fabricated by an acid-catalyzed sol–gel method. The effects of aging time and temperature on the structure and *in vitro* bioactivity were investigated. Fourier-transform infrared spectroscopy (FTIR) was carried out on the samples to understand the structure and to monitor the formation of hydroxyapatite (HA) after immersion in simulated body fluid (SBF). The bioactivity of gel-derived 45S5 glass-ceramic and amorphous 45S5 Bioglass® was compared. The results showed that an increase in both aging time and temperature can enhance crystallization, whereas bioactivity is reduced with increasing aging time but not significantly influenced by aging temperature. Compared with amorphous 45S5 Bioglass®, gel-derived glass-ceramic aged for 3 d at 60°C exhibited a more rapid rate of HA formation after immersion for less than 7 d. Amorphous 45S5 Bioglass® showed higher HA formation rate after immersion in SBF for more than 7 d, whereas the quantity of formed HA on gel-derived 45S5 glass-ceramic was still comparable to that of amorphous 45S5 Bioglass® after immersion for 14 d. It is suggested that the lower bioactivity of 45S5 glass-ceramics could be outweighed by the higher surface area and higher content of Si–NBO groups in gel-derived glass-ceramics. The results thus confirm that gel-derived 45S5 glass-ceramic exhibiting bioactivity comparable to that of amorphous 45S5 Bioglass® can be fabricated by sol–gel method under suitable aging conditions.

I. Introduction

Bioactive silicate glasses can be used as bone substitutes in orthopedic and dental applications as well as in the field of bone tissue engineering, in the form of granules, scaffolds, porous or dense powders, and coatings.[1–4] Silicate 45S5 Bioglass® (45 SiO_2–24.5 CaO–24.5 Na_2O–6 P_2O_5) is the most widely investigated bioactive glass, which was discovered by Hench *et al.* in the late 1960s.[5] This glass possesses excellent bioactivity and biocompatibility, osteoconductivity, and even osteoinductivity.[6,7] The ability of bioactive glass to enhance angiogenesis *in vitro* and *in vivo* has been also reported.[8,9] In addition, the ability of the dissolved products of bioactive glass (e.g., metallic ions) to promote stem cell differentiation into osteoblasts has been also reported.[4,10–12]

The production of 45S5 bioactive glass has traditionally been carried out through melting technology. In the melting process, precursors are mixed homogeneously and melted at a high temperature (>1300°C). The product is then quenched to form amorphous glass. However, the high temperature can induce the volatilization of phosphate components, which may change the composition of the glass. As an alternative, the sol–gel method is a wet-chemical technique that can be used for the fabrication of both glassy and ceramic materials.[13,14] The primary advantage of the sol–gel technique is the potential of gaining high purity and homogeneity materials. Moreover, lower processing temperatures are required compared with the traditional melting method, being thus energy-efficient and environmentally friendly. Another advantage of the sol–gel technique is the possibility to incorporate functional metal elements (such as Ag^+ and Zn^{2+}) into glasses or ceramics to improve specific properties.[15–17]

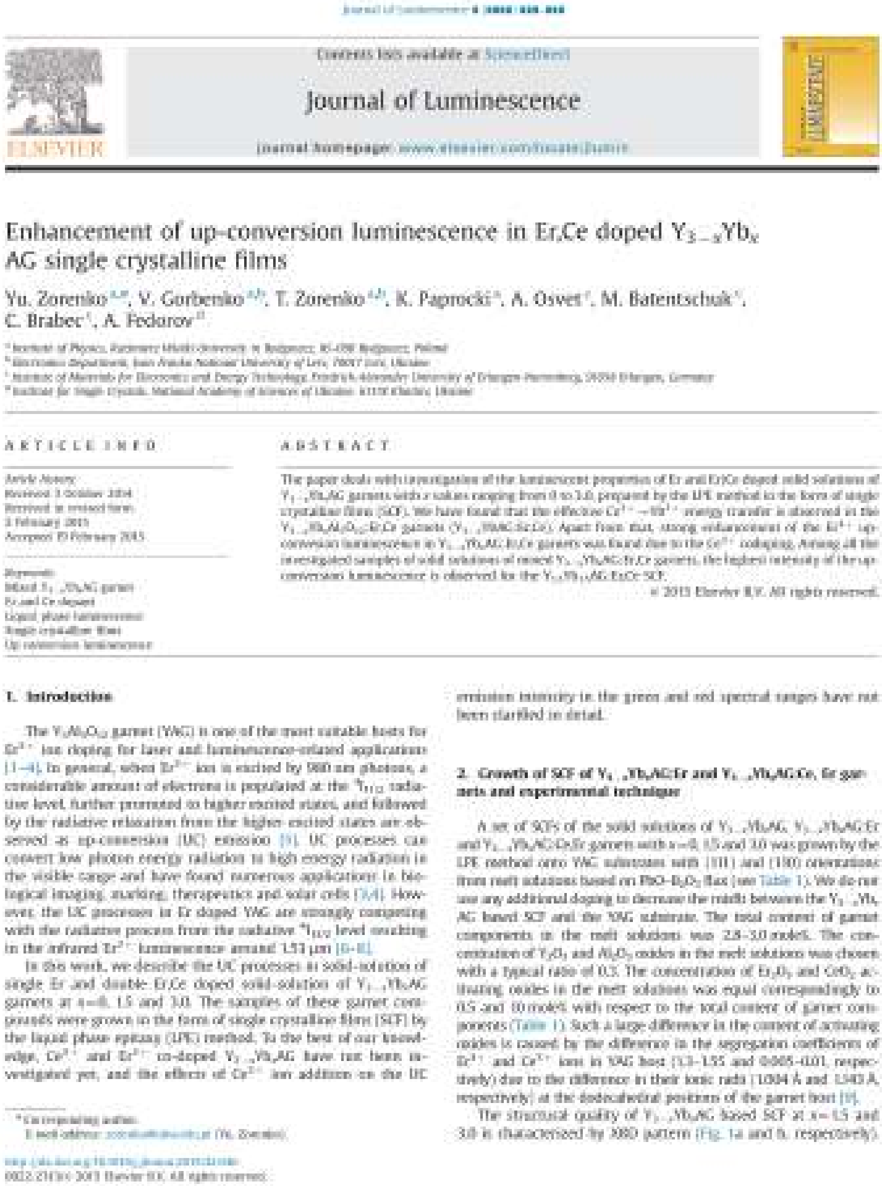
In the sol–gel processes, the precursors are catalyzed and dissolved in the solvent to form a sol. The sol gradually becomes a gel-like diphasic system containing both a liquid and a solid phase. The morphology ranges from dispersed particles to continuous polymer-like networks, which mainly depends on the pH and solvent. Generally, the sol–gel processes include hydrolysis, polycondensation, gelation, aging, drying, and stabilization. To strengthen the network, an aging process is necessary. Removal of the remaining liquid (solvent) phase requires a drying process. Finally, a thermal treatment (stabilization) is often carried out to enhance the mechanical properties and to improve the structural stability.[13,14]

Compared to melt-derived bioactive glasses, gel-derived bioactive glasses are highly porous and have higher surface area, consequently facilitating the degradation on the surface and leading to higher bioactivity.[18,19] Hence, glass-ceramics based on the 45S5 composition prepared by sol–gel method might overcome the relatively reduced rates of degradation and apatite formation on melt-derived 45S5 bioactive glass-ceramics.[1] Recently, Cacciotti *et al.*[20] studied the effect of different stabilization conditions on the microstructure and crystalline phase of gel-derived 45S5 glass. According to their study, sodium–calcium silicates were the main constituents of the crystalline phase stabilized at 900°C and 1000°C, whereas wollastonite was the major crystalline phase stabilized at 1100°C. Bahniuk *et al.*[1] compared the surface chemistry and crystallinity of melt-derived and gel-derived 45S5 Bioglass®. It was confirmed that gel-derived 45S5 glass exhibited higher surface area and submicrometer porosity, which led to increased plasma protein adsorption both in terms of quantity and variety. Pirayesh *et al.*[21] investigated the *in vitro* dissolution and mineralization behavior of gel-derived 45S5 glass. They found that 80% of the gel-derived 45S5 glass

---

S. Bose—contributing editor

Manuscript No. 35350. Received March 19, 2014; approved September 3, 2014.
[†] Author to whom correspondence should be addressed. e-mail: aldo.boccaccini@ww.uni-erlangen.de



Journal of Luminescence ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Enhancement of up-conversion luminescence in Er,Ce doped $Y_{3-x}Yb_x$AG single crystalline films

Yu. Zorenko[a,*], V. Gorbenko[a,b], T. Zorenko[a,b], K. Paprocki[a], A. Osvet[c], M. Batentschuk[c], C. Brabec[c], A. Fedorov[d]

[a] Institute of Physics, Kazimierz Wielki University in Bydgoszcz, 85-090 Bydgoszcz, Poland
[b] Electronics Department, Ivan Franko National University of Lviv, 79017 Lviv, Ukraine
[c] Institute of Materials for Electronics and Energy Technology, Friedrich-Alexander University of Erlangen-Nürnberg, 91058 Erlangen, Germany
[d] Institute for Single Crystals, National Academy of Sciences of Ukraine, 61178 Kharkiv, Ukraine

ARTICLE INFO

Article history:
Received 3 October 2014
Received in revised form
3 February 2015
Accepted 10 February 2015

Keywords:
Mixed $Y_{3-x}Yb_x$AG garnet
Er and Ce dopant
Liquid phase luminescence
Single crystalline films
Up-conversion luminescence

ABSTRACT

The paper deals with investigation of the luminescent properties of Er and Er,Ce doped solid solutions of $Y_{3-x}Yb_x$AG garnets with *x* values ranging from 0 to 3.0, prepared by the LPE method in the form of single crystalline films (SCF). We have found that the effective $Ce^{3+} \rightarrow Yb^{3+}$ energy transfer is observed in the $Y_{3-x}Yb_xAl_5O_{12}$:Er,Ce garnets ($Y_{3-x}Yb_x$AG:Er,Ce). Apart from that, strong enhancement of the Er^{3+} up-conversion luminescence in $Y_{3-x}Yb_x$AG:Er,Ce garnets was found due to the Ce^{3+} codoping. Among all the investigated samples of solid solutions of mixed $Y_{3-x}Yb_x$AG:Er,Ce garnets, the highest intensity of the up-conversion luminescence is observed for the $Y_{1.5}Yb_{1.5}$AG:Er,Ce SCF.

1. Introduction

The $Y_3Al_5O_{12}$ garnet (YAG) is one of the most suitable hosts for Er^{3+} ion doping for laser and luminescence-related applications [1–4]. In general, when Er^{3+} ion is excited by 980 nm photons, a considerable amount of electrons is populated at the $^4I_{11/2}$ radiative level, further promoted to higher excited states, and followed by the radiative relaxation from the higher excited states are observed as up-conversion (UC) emission [5]. UC processes can convert low photon energy radiation to high energy radiation in the visible range and have found numerous applications in biological imaging, marking, therapeutics and solar cells [3,4]. However, the UC processes in Er doped YAG are strongly competing with the radiative process from the radiative $^4I_{13/2}$ level resulting in the infrared Er^{3+} luminescence around 1.53 µm [6–8].

In this work, we describe the UC processes in solid-solution of single Er and double Er,Ce doped solid-solution of $Y_{3-x}Yb_x$AG garnets at x=0, 1.5 and 3.0. The samples of these garnet compounds were grown in the form of single crystalline films (SCF) by the liquid phase epitaxy (LPE) method. To the best of our knowledge, Ce^{3+} and Er^{3+} co-doped $Y_{3-x}Yb_x$AG have not been investigated yet, and the effects of Ce^{3+} ion addition on the UC emission intensity in the green and red spectral ranges have not been clarified in detail.

2. Growth of SCF of $Y_{3-x}Yb_x$AG:Er and $Y_{3-x}Yb_x$AG:Ce, Er garnets and experimental technique

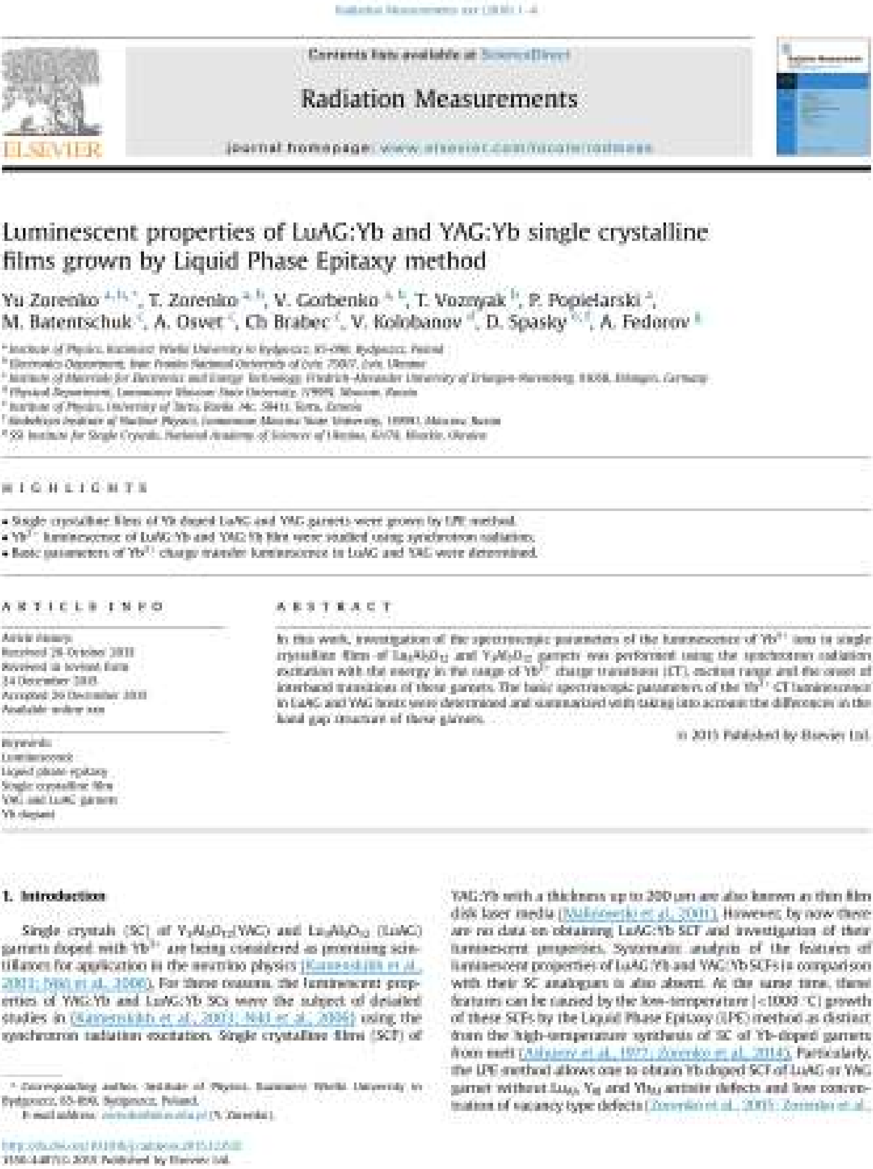
A set of SCFs of the solid solutions of $Y_{3-x}Yb_x$AG, $Y_{3-x}Yb_x$AG:Er and $Y_{3-x}Yb_x$AG:Ce,Er garnets with x=0, 1.5 and 3.0 was grown by the LPE method onto YAG substrates with (111) and (100) orientations from melt solutions based on PbO–B_2O_3 flux (see Table 1). We do not use any additional doping to decrease the misfit between the $Y_{3-x}Yb_x$AG based SCF and the YAG substrate. The total content of garnet components in the melt solutions was 2.8–3.0 mole%. The concentration of Y_2O_3 and Al_2O_3 oxides in the melt solutions was chosen with a typical ratio of 0.3. The concentration of Er_2O_3 and CeO_2 activating oxides in the melt solutions was equal correspondingly to 0.5 and 10 mole% with respect to the total content of garnet components (Table 1). Such a large difference in the content of activating oxides is caused by the difference in the segregation coefficients of Er^{3+} and Ce^{3+} ions in YAG host (1.3–1.55 and 0.005–0.01, respectively) due to the difference in their ionic radii (1.004 Å and 1.143 Å, respectively) at the dodecahedral positions of the garnet host [9].

The structural quality of $Y_{3-x}Yb_x$AG based SCF at x=1.5 and 3.0 is characterized by XRD pattern (Fig. 1a and b, respectively).

---

* Corresponding author.
E-mail address: [illegible] (Yu. Zorenko).

http://dx.doi.org/10.1016/j.jlumin.2015.02.[illegible]


Radiation Measurements xxx (2016) 1–4

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Luminescent properties of LuAG:Yb and YAG:Yb single crystalline films grown by Liquid Phase Epitaxy method

Yu Zorenko [a, b, *], T. Zorenko [a, b], V. Gorbenko [a, b], T. Voznyak [b], P. Popielarski [a], M. Batentschuk [c], A. Osvet [c], Ch Brabec [c], V. Kolobanov [d], D. Spassky [e, f], A. Fedorov [g]

[a] Institute of Physics, Kazimierz Wielki University in Bydgoszcz, 85-090, Bydgoszcz, Poland
[b] Electronics Department, Ivan Franko National University of Lviv, 79017, Lviv, Ukraine
[c] Institute of Materials for Electronics and Energy Technology, Friedrich-Alexander University of Erlangen-Nürnberg, 91058, Erlangen, Germany
[d] Physical Department, Lomonosov Moscow State University, 119991, Moscow, Russia
[e] Institute of Physics, University of Tartu, Ravila 14c, 50411, Tartu, Estonia
[f] Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University, 119991, Moscow, Russia
[g] SSI Institute for Single Crystals, National Academy of Sciences of Ukraine, 61178, Kharkiv, Ukraine

HIGHLIGHTS

- Single crystalline films of Yb doped LuAG and YAG garnets were grown by LPE method.
- Yb^{3+} luminescence of LuAG:Yb and YAG:Yb film were studied using synchrotron radiation.
- Basic parameters of Yb^{3+} charge transfer luminescence in LuAG and YAG were determined.

ARTICLE INFO

Article history:
Received 28 October 2015
Received in revised form
14 December 2015
Accepted 30 December 2015
Available online xxx

Keywords:
Luminescence
Liquid phase epitaxy
Single crystalline film
YAG and LuAG garnets
Yb dopant

ABSTRACT

In this work, investigation of the spectroscopic parameters of the luminescence of Yb^{3+} ions in single crystalline films of $Lu_3Al_5O_{12}$ and $Y_3Al_5O_{12}$ garnets was performed using the synchrotron radiation excitation with the energy in the range of Yb^{3+} charge transitions (CT), exciton range and the onset of interband transitions of these garnets. The basic spectroscopic parameters of the Yb^{3+} CT luminescence in LuAG and YAG hosts were determined and summarized with taking into account the differences in the band gap structure of these garnets.

1. Introduction

Single crystals (SC) of $Y_3Al_5O_{12}$ (YAG) and $Lu_3Al_5O_{12}$ (LuAG) garnets doped with Yb^{3+} are being considered as promising scintillators for application in the neutrino physics [Kamenskikh et al., 2003; Nikl et al., 2006]. For these reasons, the luminescent properties of YAG:Yb and LuAG:Yb SCs were the subject of detailed studies in [Kamenskikh et al., 2003; Nikl et al., 2006] using the synchrotron radiation excitation. Single crystalline films (SCF) of YAG:Yb with a thickness up to 200 μm are also known as thin film disk laser media [Malinowski et al., 2001]. However, by now there are no data on obtaining LuAG:Yb SCF and investigation of their luminescent properties. Systematic analysis of the features of luminescent properties of LuAG:Yb and YAG:Yb SCFs in comparison with their SC analogues is also absent. At the same time, these features can be caused by the low-temperature (<1000 °C) growth of these SCFs by the Liquid Phase Epitaxy (LPE) method as distinct from the high-temperature synthesis of SC of Yb-doped garnets from melt [Ashurov et al., 1977; Zorenko et al., 2014]. Particularly, the LPE method allows one to obtain Yb doped SCF of LuAG or YAG garnet without Lu_{Al}, Y_{Al} and Yb_{Al} antisite defects and low concentration of vacancy type defects [Zorenko et al., 2005; Zorenko et al.,

---

[*] Corresponding author. Institute of Physics, Kazimierz Wielki University in Bydgoszcz, 85-090, Bydgoszcz, Poland.
E-mail address: zorenko@ukw.edu.pl (Yu. Zorenko).

http://dx.doi.org/10.1016/j.radmeas.2015.12.[illegible]
1350-4487/© 2015 Published by Elsevier Ltd.

Conference Proceedings

Ulrike Künecke, Christina Hetzner, Stefan Möckel, Hyesun Yoo, Rainer Hock, Peter Wellmann
Characterization of kesterite thin films fabricated by rapid thermal processing of stacked elemental layers using spatially resolved cathodoluminescence
Thin Solid Films ***582****, pp. 387-391, 2015*

Benjamin Lipovšek,1 Anastasiia Solodovnyk, Karen Forberich, Edda Stern, Janez Krč, Christoph J. Brabec, and Marko Topič
Optical model for simulation and optimization of luminescent down-shifting layers in photovoltaics
Energy Procedia ***84****, pp. 3-7, 2015*

Yuriy N. Luponosov, Jie Min, Alexander N. Solodukhin, Sergey N. Chvaluna, Tayebeh Ameri, Christoph J. Brabec, Sergey A. Ponomarenko
Design of low band gap small molecules with alkyldicyanovinyl acceptor and different donor groups for efficient bulk heterojunction organic solar cells
Proceedings of SPIE, Organic Photovoltaics XVI ***9567****, pp. 1-13, 2015*

Stefan A. Möckel, Tobias Wernicke, Matthias Arzig, Philipp Köder, Marco Brandl, Rameez Ahmad, Monica Distaso,Wolfgang Peukert, Rainer Hock, Peter J. Wellmann
Low temperature formation of $CuIn_{1-x}Ga_xSe_2$ solar cell absorbers by all printed multiple species nanoparticulate Se + Cu–In + Cu–Ga precursors
Thin Solid Films ***582****, pp. 60-68, 2015*

Rankl, D., Jokubavicius, V., Syväjärvi, M., Wellmann, P.
Quantitative study on the role of supersaturation during sublimation growth on the yield of 50 mm diameter 3C-SiC
Materials Science Forum ***821-823****, pp. 77-80, 2015*

Riedel, D., Dlugosch, J., Wehlus, T., Brabec, C.
Extracting and shaping the light of OLED devices
Proceedings of SPIE - The International Society for Optical Engineering ***9566****, art. no. 95661H, pp. 1-9, 2015*

Matthias Schuster, Monica Distaso, Stefan A. Möckel, Ulrike Künecke, Wolfgang Peukert, Peter J. Wellmann
Synthesis of In_2Se_3 and $Cu_{2-x}Se$ Micro- and Nanoparticles with Microwave-Assisted Solvothermal and Aqueous Redox Reactions for the Preparation and Stabilization of Printable Precursors for a $CuInSe_2$ Solar Cell Absorber Layer
Energy Procedia ***84****, pp. 62-70, 2015*

Anastasiia Solodovnyk, Benjamin Lipovšek, Karen Forberich, Edda Stern, Janez Krč, Miroslaw Batentschuk, Marko Topič, and Christoph J. Brabec
Improved properties of phosphor-filled luminescent down-shifting layers: reduced scattering, optical model and optimization for PV application
Proceedings of SPIE, SPIE Micro+Nano Materials, Devices, and Systems ***9668****, art. no. 966843, pp. 1-9, 2015*

Andreas Vetter, Bernhard Hofbeck, Peter Kubis, Christoph J. Brabec
Assessing the accuracy of imaging techniques for defect characterization on thin film solar cells
Photovoltaic Specialist Conference (PVSC), 2015 IEEE 42nd ***INSPEC Acc. Nr: 15664772****, pages 3, 2015*

Andreas Vetter, Klaus Burlafinger, Michael Woiton, Christoph J. Brabec
Highly accelerated lifetime testing via extreme illumination at controlled temperature for thin film solar cells
31st European Photovoltaic Solar Energy Conference and Exhibition pp. 1080-1082, 2015

Martin Wilhelm, Felix Beck, Peter J. Wellmann
Towards the growth of SiGeC epitaxial layers for the application in Si solar cells
Energy Procedia ***84****, pp. 236-241, 2015*

André Zweschke, Peter J.Wellmann
Numerical reactive diffusion modeling of stacked elemental layer rapid thermal annealed chalcopyrite absorber layer formation
Thin Solid Films ***582****, pp. 397-400, 2015*

André Zweschke, Peter J.Wellmann
Progress on numerical reactive diffusion modeling of $CuInSe_2$ phase formation for solar cell applications
Energy Procedia ***84****, pp. 86-92, 2015*

Thin Solid Films 582 (2015) 387–391

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Characterization of kesterite thin films fabricated by rapid thermal processing of stacked elemental layers using spatially resolved cathodoluminescence

Ulrike Künecke [a], Christina Hetzner [a], Stefan Möckel [a], Hyesun Yoo [b], Rainer Hock [b], Peter Wellmann [a,*]

[a] Materials Department 6, University of Erlangen-Nürnberg (FAU), Martensstr. 7, D-91058 Erlangen, Germany
[b] Crystallography and Structure Physics, University of Erlangen-Nürnberg (FAU), Staudtstr. 3, 91058 Erlangen, Germany

A R T I C L E   I N F O

Available online 13 October 2014

Keywords:
$Cu_2ZnSnSe_4$
Cathodoluminescence
Secondary phases
Microstructure

A B S T R A C T

We report on the microstructure analysis of kesterite ($Cu_2ZnSnSe_4$) layers from rapid thermal processing of sequential elemental layers by spatially resolved cathodoluminescence in a scanning electron microscope. Energy dispersive X-ray fluorescence, X-ray diffraction and Raman spectroscopy were carried out for the validation of the findings. Special emphasis is put on the discussion of the occurrence of the secondary phases Cu_2SnSe_3, Cu_2Se, ZnSe and SnSe.

1. Introduction

In the kesterite ($Cu_2ZnSn[S_{1-x}Se_x]_4$ or in brief CZTS(e)) thin film solar cell material, the origin of major efficiency limiting factors is widely investigated since recent years. As a successor material of the well-established chalcopyrite (record cells yielding above 20% [1] and modules above 15% [2] efficiency) the physical origin of the detrimental performance in the case of kesterites (best cell efficiencies lie in the 12% to 13% range [3]) is still under intense study. Like in all microcrystalline solar cells, the microstructure and morphology of the absorber material, in particular grain boundaries and in the case of compound semiconductors, secondary phases are of great importance. In addition, point defects strongly determine the overall device performance. In this work the "bulk" electronic properties of the solar cell absorber are addressed using cathodoluminescence (CL). In general, luminescence studies allow the non-destructive investigation of electron hole pair transitions via direct band gap, as well as below band gap defect or material disorder related phenomena. Hence, the presence of the desired CZTSe phase or the detection of secondary phases, as well as point defects should be possible by luminescence. Performing CL studies in a scanning electron microscope (SEM) has the advantage, that simultaneous studies of the layer microstructure are possible so that correlations can be conducted. In CZTS and CZTSe, so far, the correlation of CL and photoluminescence (PL) and defects seems to be rather difficult or even impossible. As pointed out in two review articles by Siebentritt et al. [4,5], disorder on an atomic scale, as well as high concentration of native point defects make it rather difficult to determine their exact energetic level or to identify secondary phases within the broad luminescence spectra. Therefore, there is only a limited knowledge on the luminescence fingerprint of various CZTS(e) properties available in literature, compared to other traditional or even novel semiconductor materials. (Temperature dependent) Optical absorption [5] with low spatial resolution in the mm range was often applied to study the optical bandgap of CZTS and semiconducting secondary phases. Altogether, there is only limited literature available that focus on optical spectroscopy of CZTS(e); often luminescence data on certain defects are published in the frame of extended electro-optical studies where optical spectroscopy played a side role. Nevertheless, even with limited reference data, the study of CZTSe using CL with a spatial resolution on the μm-scale is believed to be valuable for better understanding of the physical layer properties.

In this work we report on the microstructure analysis of kesterite layers from rapid thermal processing of sequential elemental layers (RTP-SEL) by spatially resolved CL in a SEM carried out at room temperature. In addition, energy dispersive X-ray fluorescence (EDX), X-ray diffraction (XRD) and Raman spectroscopy were carried out for the validation of the findings. In the discussion we will put special emphasis on CZTSe and the secondary phases Cu_2SnSe_3, Cu_2Se, ZnSe and SnSe. Intrinsic point defects are not discussed in this work.

2. Experiments

2.1. Sample preparation

Kesterite thin film samples were prepared on float glass by DC magnetron sputtering of the Mo back side electrode (thickness = 400 nm)

---

[*] Corresponding author.
E-mail address: peter.wellmann@fau.de (P. Wellmann).

http://dx.doi.org/10.1016/j.tsf.2014.10.021

Available online at www.sciencedirect.com
ScienceDirect
Energy Procedia
Energy Procedia 84 (2015) 3 – 7

E-MRS Spring Meeting 2015 Symposium C - Advanced inorganic materials and structures for photovoltaics

Optical model for simulation and optimization of luminescent down-shifting layers in photovoltaics

Benjamin Lipovšek[a,*], Anastasiia Solodovnyk[b,c,d], Karen Forberich[c], Edda Stern[b], Christoph J. Brabec[b,c,d], Janez Krč[a], and Marko Topič[a]

[a]*University of Ljubljana, Faculty of Electrical Engineering, Tržaška 25, 1000 Ljubljana, Slovenia*
[b]*Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstr. 2a, 91058 Erlangen, Germany*
[c]*Friedrich-Alexander University Erlangen-Nürnberg (FAU), Martensstr. 7, 91058 Erlangen, Germany*
[d]*Erlangen Graduate School in Advanced Optical Technologies (SAOT), FAU, Paul-Gordan-Str. 6, 91052 Erlangen, Germany*

Abstract

We present an optical model that was developed for the purpose of simulation and optimization of luminescent down-shifting layers based on phosphor particles. The model combines three-dimensional ray tracing with a novel effective scattering approach based on the Mie scattering theory. Verification of the model with experimental results shows that the model accurately takes various layer parameters into account, such as the layer thickness, the phosphor volume concentration, and the phosphor particle size distribution. Finally, using the verified model, we investigate the concept of luminescent down-shifting in organic solar cells and discuss the optimal layer parameters. Preliminary simulation results show that in the case of the studied solar cell, an improvement in the short-circuit current density of more than 6 % can be obtained.

Peer-review under responsibility of The European Materials Research Society (E-MRS)
Keywords: Wavelength conversion devices; Fluorescent and luminescent materials; Optical modelling and simulation; Solar energy

---

1. Main text

Losses attributed to the high-energy photons in the UV and near-UV spectral region present an important source of energy losses that limit the power conversion efficiency of conventional single-junction solar cells. These losses can sum up to almost half of the total energy available in the AM1.5 solar spectrum [1,2]. Among the different techniques proposed to improve solar spectrum harvesting in the UV region, luminescent down-shifting (LDS) has been recognized as one of the promising approaches [3,4]. It is based on the application of photoluminescent (PL) materials (such as organic dyes, semiconductor quantum dots, or phosphor particles) that absorb the high-energy photons and re-emit them at longer wavelengths, typically in the visible spectrum region where the spectral response

Peer-review under responsibility of The European Materials Research Society (E-MRS)
doi:10.1016/j.egypro.2015.12.288

Thin Solid Films 582 (2015) 93–98

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Low temperature formation of CuIn$_{1-x}$Ga$_x$Se$_2$ solar cell absorbers by all printed multiple species nanoparticulate Se + Cu–In + Cu–Ga precursors

Stefan A. Möckel [a,*], Tobias Wernicke [a], Matthias Arzig [a], Philipp Köder [a], Marco Brandl [b], Rameez Ahmad [c], Monica Distaso [c], Wolfgang Peukert [c], Rainer Hock [b], Peter J. Wellmann [a]

[a] Department of Materials Science, Chair of Materials for Electronics and Energy Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Martensstr. 7, 91058 Erlangen, Germany
[b] Chair for Crystallography and Structural Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Staudtstr. 3, 91058 Erlangen, Germany
[c] Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Cauerstr. 4, 91058 Erlangen, Germany

ARTICLE INFO

Keywords:
Low temperature
Copper indium gallium diselenide
Chalcopyrite
Nanoparticulate precursor
In-situ X-ray diffraction
Bimetallic nanoparticles

ABSTRACT

In this work an all nanoparticulate precursor for application in CuIn$_{1-x}$Ga$_x$Se$_2$ solar cell absorbers is presented. Binary Cu–In nanoparticles, Cu–Ga powder and elemental Se nanoparticles were mixed in dispersion and deposited on Mo-coated substrates. Research was focused on CuIn$_{1-x}$Ga$_x$Se$_2$ layer formation kinetics, phase composition characterized by differential scanning calorimetry and in-situ X-ray diffraction (XRD). Furthermore phase composition and morphology were studied by ex-situ XRD, Raman spectroscopy and scanning electron microscopy. The results revealed a fast consumption of the precursor and the formation of CuInSe$_2$ below 300 °C. Binary secondary phases were not observed at any temperature.

1. Introduction

Chalcopyrite thin film solar cells show record power conversion efficiencies of 20.5% [1] and are regarded as a promising alternative to state-of-the-art silicon based photovoltaic. However, while laboratory scale solar cell's efficiency is roughly 4 to 5 percentage points below the 25.6% efficiency of crystalline silicon cells [2], the difference between the module performances of both technologies is higher. The chalcopyrite record module shows an efficiency of 15.8% [3] which is less than 6 percentage points below the silicon record module with its 22% [4,5]. One reason for this relatively low performance of modules is the scalability of the co-evaporation process. Increasing the area of co-evaporation leads to lateral inhomogeneities in the material deposition and to an overall decrease of efficiency.

To increase homogeneity and cost efficiency, research is conducted on different non-vacuum deposition techniques which are suitable for roll-to-roll processes. The most prominent techniques are based on deposition of material from solution [6–8] or deposition of nanoparticles, while there is a difference in the type of used nanoparticles. One has to distinguish between chalcopyrite nanoparticles which consist of a well-formed Cu(In$_{1-x}$Ga$_x$)(Se$_{1-y}$S$_y$)$_2$ phase [9–13] and precursor nanoparticles which can be a mixture of either Cu–Se and In–Se nanoparticles [14] or metallic Cu–In nanoparticles which are selenised after deposition by annealing under highly toxic H$_2$Se or selenium atmosphere [15–17].

In this work a nanoparticulate precursor consisting of different species of nanoparticles is used. Metallic Cu–In nanoparticles (see e.g. [18]) and elemental selenium nanoparticles, comparable to the one used by Dhage et al. [19] containing Cu–In–Ga and Se nanoparticles. Furthermore Cu–Ga powder was prepared and dispersed in an ink. The nanoparticles were dispersed in 2-propanol (IPA), mixed and deposited by doctor blading. The layers were characterised focusing on the formation kinetics, phase composition and morphology by in-situ methods like differential scanning calorimetry (DSC) and in-situ X-ray diffraction (XRD). In addition, samples containing Cu–In and Se nanoparticles were prepared on Mo coated Si substrates and characterised regarding phase composition and morphology by ex-situ XRD, Raman spectroscopy and scanning electron microscope (SEM) combined with energy dispersive X-ray spectroscopy (EDX).

2. Experimental details

2.1. Nanoparticle synthesis

Copper (II) chloride (Sigma Aldrich 97%), indium (III) chloride (Alfa Aesar 99.99% anhydrous), sodium borohydride (Sigma Aldrich 99%), tetraethylene glycol (TEG) (Sigma Aldrich 99%), gallium (Sigma Aldrich 99.9995%), selenium (Alfa Aesar 99.5 + % powder), sodium sulfite (Sigma Aldrich ≥ 98.0% anhydrous) polyvinylpyrrolidone 10 g/mol (PVP) (Sigma Aldrich), and tri-sodium citrate (Merck Millipore) were

---

[*] Corresponding author.
E-mail address: Stefan.A.Moeckel@fau.de (S.A. Möckel).

http://dx.doi.org/10.1016/j.tsf.2014.11.068
0040-6090/

Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 84 (2015) 62 – 70

Energy Procedia

E-MRS Spring Meeting 2015 Symposium C - Advanced inorganic materials and structures for photovoltaics

Synthesis of In_2Se_3 and $Cu_{2-x}Se$ Micro- and Nanoparticles with Microwave-Assisted Solvothermal and Aqueous Redox Reactions for the Preparation and Stabilization of Printable Precursors for a $CuInSe_2$ Solar Cell Absorber Layer

Matthias Schuster[a]*, Monica Distaso[b], Stefan A. Möckel[a], Ulrike Künecke[a], Wolfgang Peukert[b], Peter J. Wellmann[a]

[a]Materials Department 6 (i-MEET), Martensstr. 7, 91058 Erlangen, Germany; Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)
[b]Particle Technology, Cauerstr. 4, 91058 Erlangen, Germany; Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)

Abstract

Micro- and nanoparticles were synthesized and stabilized in order to process a copper indium diselenide (CISe) solar cell absorber layer. A microwave assisted solvothermal reaction for In_2Se_3 particles was performed, finding that smaller particles could be obtained in shorter times and at lower temperatures than with a conventional autoclave based solvothermal synthesis. In a second route In_2Se_3 and $Cu_{2-x}Se$ nanoparticles have been synthesized via aqueous redox reactions and been Zeta potential-stabilized to acquire a nanoparticulate ink. This ink was drop cast in ambient atmosphere and annealed in N_2-atmosphere leading to the formation of CISe at lower temperatures than with state-of-the-art processing routes.

Peer-review under responsibility of The European Materials Research Society (E-MRS)

Keywords: In_2Se_3, $Cu_{2-x}Se$, nanoparticles, microwave, Zeta potential, low temperature, $CuInSe_2$, solar cell

---

* Corresponding author. Tel.: +49 (0)9131 85 27719;
E-mail address: mse.matthias.schuster@fau.de

Peer-review under responsibility of The European Materials Research Society (E-MRS)
doi:10.1016/j.egypro.2015.12.298

Photovoltaic Specialist Conference (PVSC), 2015 IEEE 42nd, 14-19 June 2015

Assessing the accuracy of imaging techniques for defect characterization on thin film solar cells

Andreas Vetter[1,2], Bernhard Hofbeck[1], Peter Kubis[2] and Christoph J. Brabec[1,2]

[1]ZAE Bayern (Bavarian Center of Applied Energy Research), 91058 Erlangen, Germany
[2]i-MEET, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

***Abstract* — Imaging methods are an essential tool for improving processing of solar cells. Unfortunately, it is difficult to validate the imaging methods in detail. One focus of our work was to establish an approach by which one can assess the accuracy of the determination of the influence of defects via imaging on CIGS solar cells. The method is, however, not restricted to CIGS and should be easily transferable to other solar cell types, in particular other thin film technologies. The benefit of such a method is the possibility to validate and optimize imaging techniques and, in turn, improving tools to optimize solar cell material and processing of solar cells.**

***Index Terms* — ILIT, defects, imaging, accuracy, performance loss, CIGS, quality control**

I. INTRODUCTION

Thin film solar cells have a large potential for cheap and sustainably processed solar cells. Thin film solar cell technology has steadily improved in recent years and the progress yields steadily increasing efficiencies. CIGS, one of the thin film technologies, reached a reported record efficiency of 21.7% [1], for example. However, material inhomogeneity and local defects (shunts) may occur due to the deposition method reducing the efficiency. Imaging is one essential tool to address these problems.

The prevailing imaging techniques applied successfully to all solar cell types are infrared (IR) imaging and luminescence imaging, e.g. [2,3]. Main aims are to localize material inhomogeneity and defects on the solar cells or modules. The major advantage of imaging is the high speed of the measurement compared to scanning methods. This allows for an investigation of samples in an acceptable timeframe, an important feature when aiming for a transfer of the methods to quality control, for example. Regarding CIGS, imaging has been carried out to investigate the material properties [4] and also to characterize the influence of defects on the open circuit voltage (V_{oc}) of cells [5]. Also, a proof of principle has been carried out showing IR imaging as a potential tool for inline quality control of CIGS modules [6].

Imaging has been proven to be very successful to yield qualitative results that means, answering questions such as how many and where are defects on a solar cell or module. Quantifying the influence of certain defects via imaging is difficult due to several reasons. One reason is, for example, that there are often several hot spots on a module detected by ILIT (illuminated lock-in thermography) or DLIT (dark lock-in thermography) as by applying lock-in technique, even tiny temperature gradients (equal to several µW heat dissipation [7]) might be detected. Accordingly, quantitative evaluation of IR-maps regarding the influence of defects on the electrical performance have been proposed, but up so far no comprehensive validation of these methods have been carried out.

In this contribution, we present an experimental approach, which allows for assessing the accuracy of IR and luminescence imaging used for determining the influence of defects on the electrical performance of solar cells. We applied CIGS cells for our experiments and induced well defined defects by a femto-second laser. We carried out accompanying characterization methods and computer simulations to investigate the induced defects.

II. MATERIALS AND METHODS

The investigated solar cell type was co-evaporated CIGS, a detailed description of the production process can be found in [8]. The substrate is soda lime silicate glass (3 mm thick) with a sputtered molybdenum layer as back contact. CdS is deposited as buffer layer followed by ZnO and ZnO:Al as front contact. The total thickness of the layers comprising the solar cell is about 3 µm. Specially prepared single cells with a length of 3 cm and 4 mm width were examined in this study.

For the creation of small defects, experimental laser patterning setup LS-Tool was used. The system accommodates femtoREGEN™ UC-1040-8000 5 W (ultra-compact) ultra-fast laser based on an Yb:KYW chirped pulse regenerative amplifier. A variable beam expander expands the beam 7 times. A scanner moves the beam over the sample surface with the speed up to 4000 mm/s. The scanner's objective has a focal length of 330 mm and a focal spot diameter of 12.5 µm (at 1/e² intensity). The alignment of the laser beam is realized with a camera and a software positioning system.

Characterization of the defects has been carried out in various ways. First of all, the topology of the area around the induced defects was investigated with atomic force microscopy and confocal laser scanning microscopy. IV curves were measured by using an LED flasher ([illegible] GmbH, Berlin, Germany) resembling the solar spectrum using 22 different types of LEDs (with different wavelengths) and an

978-1-4799-7944-8/15/$31.00 ©2015 IEEE

HIGHLY ACCELERATED LIFETIME TESTING VIA EXTREME ILLUMINATION AT CONTROLLED TEMPERATURE FOR THIN FILM SOLAR CELLS

Andreas Vetter[1,2,*], Klaus Burlafinger[1,2], Michael Woiton[1,2], Christoph J. Brabec[1,3]
[1]Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, 91058 Erlangen, Martensstraße 7
[2]Energie Campus Nürnberg, Fürther Str. 250, 90429 Nürnberg
[3]Bavarian Center for Applied Energy Research (ZAE Bayern e.V.), 91058 Erlangen, Haberstraße 2a
*author for correspondence: andreas.vetter@fau.de

ABSTRACT: All available solar cells suffer from degradation during their use outdoors. Several accelerated lifetime tests have been established in order to investigate degradation and to optimize solar cells regarding lifetime. Most tests focus on degradation due to the environment, e. g. ingress of water or oxygen. Such degradation mechanisms may be reduced by an improved encapsulation of the cells and / or an optimized cell architecture. With improving encapsulation and cell architecture, lifetime of the solar cells will become more and more restricted by degradation due to illumination by the sun. Lifetime tests under one sun are available to test photo-stability but require very long lasting experiments.

We have designed and built an innovative setup, which allows for testing the photo-stability of solar cells at several hundreds of suns at controlled temperature. Illumination is realized by a high power Xenon short arc lamp (close to sun spectrum) and temperature control of the solar cells by an innovative cooling system. We have verified the testing method with P3HT:PCBM solar cells. Degradation due to photon flux and temperature may be decoupled. It needs to be pointed out that the presented method is not restricted to a certain solar cell type.

Keywords: Thin Film Solar Cell, Lifetime, Experimental Methods, PV Material, Organic Solar Cell

1 INTRODUCTION

Regarding the economic viability of photovoltaics (PV), there are three main aspects: processing, efficiency and lifetime of PV modules. When thinking of new, innovative thin film technologies, for instance organic photovoltaics (OPV) or perovskites, lifetime becomes currently the crucial issue.

When considering OPV, for instance, power conversion efficiency (PCE) has steadily increased over the last years. Material performance has recently strongly improved and values over 10% PCE have been reported on cell level [1]. Next to high performance, a material needs to be processed easily, for example using large area printing techniques. Finally, the material needs to feature a lifetime of several years. Roll-to-roll fabrication of OPV has been optimized [2,3] but there is few progress in regarding material stability. Only considering all three aspects together will pave the way for the economic viability of innovative thin film PV. In particular, investigation and understanding degradation mechanisms helps increasing lifetime and, thus, reducing costs.

The main influences on degradation of solar cells may be classified into internal (inherent) influences and external influences [4,5]. Inherent influences comprise the temperature of the solar cell, illumination power and illumination spectrum. Main contributors to degradation due to external influences are oxygen and water (besides mechanical damage). These external influences can be tackled by an improved cell architecture or by using high grade encapsulation material. From this point of view, there are solutions available to eliminate the impact of external influences on lifetime. However, we want to mention that high grade encapsulation material is still rather expensive today.

The internal or inherent influences, temperature and illumination, cannot be addressed by PV encapsulation. With increasing stability of solar cells, this inherent degradation becomes more and more decisive on the overall solar cell lifetime. Despite this fact, rather few experimental studies have been conducted so far studying inherent lifetime, that means studying degradation due to illumination and temperature without the influence of external influences such as oxygen.

The importance of tools for accelerated lifetime testing (ALT) can be deduced from the number of available commercial setups. ALT is already of essential help in optimizing materials regarding stability and lifetime within an acceptable timeframe. Current setups check in particular the encapsulation of PV cells and modules, for example by damp-heat tests. Our vision is to establish a method for ALT of inherent degradation.

Lifetime of innovative PV should reach about 10-20 year in order to be competitive with conventional electricity sources [6,7]. Roughly speaking, sun shines about 2000 hours a year on an average base world wide. This translates to about 3 months of sunshine in a row when thinking of degradation tests at one sun illumination. Obviously, accelerated life time testing with strong illumination is required to reduce experimental time sufficiently. A test setup with 300 suns would ideally reduce this three months lasting experiment by a factor of 300, which is less than half a day.

In summary, the overall aim of our work is to establish a fast method, which allows for assessing the inherent lifetime of thin film PV. As first crucial step, this requires decoupling of the two influences on inherent degradation: temperature and illumination. Three important aspects need to be covered by an experimental setup tackling this aim: a strong illumination source, powerful cooling and an approach to measure the sample temperature.

2 THERMAL SIMULATIONS

One difficulty when applying extreme illumination to test the photo-stability is to provide sufficient and controlled cooling of the solar cell under test in order to be able to distinguish between photon-induced degradation and thermal degradation. This is one reason why few high-C (highly concentrated) experimental

Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 84 (2015) 236 – 241

Energy Procedia

E-MRS Spring Meeting 2015 Symposium C - Advanced inorganic materials and structures for photovoltaics

Towards the growth of SiGeC epitaxial layers for the application in Si solar cells

Martin Wilhelm[a]*, Felix Beck[a], Peter J. Wellmann[a]

[a]Materials Department 6 (i-MEET), University of Erlangen-Nuremberg (FAU), Martensstr. 7, 91058 Erlangen, Germany

Abstract

For the improvement of today's well established silicon solar cells a further significant increase in light conversion efficiency needs the consideration of multi junction aspects. In this context 3C-SiC with a bandgap of 2.3eV has already been discussed in the past. However, an ideal bandgap match within a silicon tandem cell (Eg(Si) = 1.1eV) requires a lower bandgap of 1.8 eV which may be reached by the incorporation of Ge in the 3C-SiC lattice.
In this work we report on the growth of Si-Ge-C hetero-epitaxial layers on silicon in a MOCVD reactor. A major obstacle in realizing a high Ge-content in the cubic 3C-SiC lattice is the strong trend towards segregation and phase separation in the ternary system. In terms of the atomic diameter, Ge should be more likely to substitute Si in the SiC lattice. However, concerning the excess energy the bond between Ge and C is not supposed to be stable.
We will present several growth runs at different precursor flow-rates and different temperatures in the range of 1090°C - 1330°C and discuss the appearance of a SiGe phase. In order to detect the different bonds in the layers, especially Ge-C bonds, the samples were investigated by means of Raman-spectroscopy and x-ray diffraction. The Ge concentration was investigated by EDX measurements. No proof for the formation of Ge-C was found so far.

Peer-review under responsibility of The European Materials Research Society (E-MRS)

Keywords: 3C-SiC; SiGeC; Epitaxy; Raman; X-Ray diffraction.

---

* Corresponding author. Tel.: +49-9131-85-27719; fax: +49-9131-85-28495.
E-mail address: martin.wilhelm@fau.de

Peer-review under responsibility of The European Materials Research Society (E-MRS)
doi:10.1016/j.egypro.2015.12.319

Thin Solid Films 582 (2015) 397–400

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Numerical reactive diffusion modeling of stacked elemental layer rapid thermal annealed chalcopyrite absorber layer formation

André Zweschke *, Peter J. Wellmann

Department of Materials Science and Engineering, Chair of Materials for Electronics and Energy Technology, Friedrich-Alexander-University Erlangen-Nürnberg, Martensstr. 7, 91058 Erlangen, Germany

ARTICLE INFO

Available online 7 November 2014

Keywords:
Chalcopyrite
Reactive diffusion
Diffusion modeling

ABSTRACT

The diffusion processes during chalcopyrite ($CuInSe_2$) layer formation by rapid thermal annealing (RTA) of stacked elemental layers are still not completely understood. We present a one-dimensional kinetic model, which describes the diffusive reaction kinetics for layers of partial miscible systems to describe the RTA process. The model was applied to a layer stack of elemental Se between the metallic layers Cu and In. First, some binary phases occur. After the Se layer is consumed, $CuInSe_2$ is observed between the binary compounds Cu_2Se and In_2Se_3.

1. Introduction

Thin film solar cells with chalcopyrite absorber have low production costs and are less material consuming compared with the classical Si-based solar cells. Usually, the elements Cu, In, Ga, Se and S are incorporated, which leads to the highest module efficiencies. One route of production is the stacked elemental layer and subsequent rapid thermal annealing (SEL-RTA), which up to now allows the highest efficiency chalcopyrite-based solar cells for large area production up to 16.6% by AVANCIS [1]: First, the Mo backside contact and metallic layers (Cu, In, Ga) are usually sputtered on a glass substrate followed by vapor deposition of Se and S. This so-called precursor is annealed, where reactive diffusion takes place, and several intermediate phases form, which finally react to form the chalcopyrite absorber [2]. However, the mechanisms during the reactive diffusion are still not completely understood. Another not completely solved problem is the occurrence of inhomogeneities in the chalcopyrite absorber, which decrease the efficiency of the solar cells. There have been earlier studies on the growth kinetics of the chalcopyrite absorber formation of the SEL-RTA by fitting dynamic calorimetric measurement curves [3] and recent approaches to model parts of absorber formation process by first principle method [4].

In this paper, we present a numerical tool with the aim to completely model the RTA-step. It will allow a prediction of the phases occurring during the annealing in the future. The initial state is described by a sequence of layers, which can be either elements such as Cu, In, and Se or also intermetallic compounds. It is capable of describing the occurrence of new phases by seed formation and diffusion of species in the layers by implementing a multi-phase and multi-component diffusion model. Although the model has been developed for 3D simulation, we will focus on the 1D case to demonstrate the simulation capabilities in this work.

While the computer code presented in this work is already fully developed in terms of thermal budget, diffusion of elements and reaction kinetics to form $CuInSe_2$ via intermediate binary compounds, the chemical and physical boundary conditions applied to the modeling exhibit a number of assumptions. Most of them are related to the lack of material parameters.

2. Calculation

The absorbers vertical cross section of the layer is represented by a bar, which is divided into cubic cells. A cellular automata is defined on it with the following rules:

1. Each cell has a phase as a state.
2. Cells with different phases must not be located next to each other. A special grain boundary cell must be located between the two cells.
3. A grain boundary is characterized that it belongs to two grains and therefore has two phases as states.

A similar approach has earlier been used by Jacot et al. to simulate the microstructure evolution in Fe-C-alloys [5].

For each cell, the concentrations c_i of the $i = 1 \dots n-1$ atomic species i are stored, where n is the number of the atomic species in the system. The dependent species n can be calculated from the other concentrations because $\Sigma c_i = 1$. $c_{gb,i}$ and $c_{gb,j}$ are the concentration boundary conditions at the grain boundary, in which values are close to the ideal concentrations c_{id} of the phases (e.g., for In_2Se_3 $c_{id}(Cu) = 0$, $c_{id}(In) = 0.4$ and $c_{id}(Se) = 0.6$). To calculate $c_{gb,i}$, the ideal

---

* Corresponding author.
E-mail address: andre.zweschke@fau.de (A. Zweschke).

http://dx.doi.org/10.1016/j.tsf.2014.11.002

Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 84 (2015) 88 – 92

Energy Procedia

E-MRS Spring Meeting 2015 Symposium C - Advanced inorganic materials and structures for photovoltaics

Progress on numerical reactive diffusion modeling of $CuInSe_2$ phase formation for solar cell applications

André Zweschke[a]*, Peter J. Wellmann[a]

[a]Department of Materials Science and Engineering, Chair of Materials for Electronics and Energy Technology, Friedrich-Alexander-University Erlangen-Nürnberg, Martensstr. 7, 91058 Erlangen, Germany

Abstract

Numerical modeling of chalcopyrite ($CuInSe_2$) absorber layer formation by rapid thermal annealed stacked elemental layers provides a valuable tool to address the microscopic phase formation process, which significantly determines the absorber layer properties in solar cell applications. We present a one dimensional kinetic modeling tool describing the diffusive reaction kinetics for layers of partial miscible systems. The diffusion is described temperature dependent and by calculating the latent heat the results were compared with differential scanning calorimetry measurement curves. Applying the numerical simulation to elemental layers of Cu, In and Se, first binary compounds are observed. With the presented progress in the model the absorber can completely react to $CuInSe_2$, after sufficient intermixing of the elements. The results show a good agreement with experimental data with regard to the temperature range of the reactions taking place.

Peer-review under responsibility of The European Materials Research Society (E-MRS)
Keywords: Chalcopyrite, Reactive Diffusion, Diffusion modeling

1. Introduction

Chalcopyrite thin film solar cells are promising materials for solar cell applications. While the fabrication of silicon solar cells is quite energy consuming and therefore expensive, chalcopyrite thin film solar cells are cost efficient and show an efficiency of more than 20% [1]. While the record cells are fabricated with co-evaporation, the industrial production of large area solar cells is done with the stacked elemental layer rapid thermal annealed process

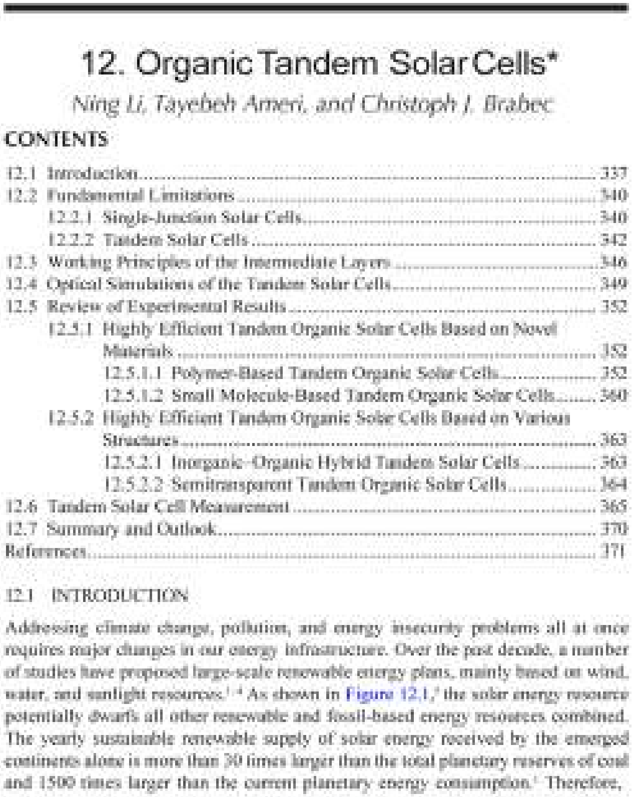
---

* Corresponding author. Tel.: +49-9131-85-27719; fax: +49-9131-85-28495.
E-mail address: andre.zweschke@fau.de

Peer-review under responsibility of The European Materials Research Society (E-MRS)
doi:10.1016/j.egypro.2015.12.299

8. Books & Book Chapters

Ning Li, Tayebeh Ameri, Christoph J. Brabec
Organic tandem solar cells
Organic Solar Cells: Materials, Devices, Interfaces and Modeling
(Editor: Q. Qiao), CRC Press, pp. 337-377, 2015, ISBN: 9781482229837



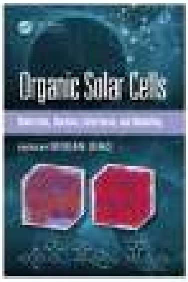
12. Organic Tandem Solar Cells*

Ning Li, Tayebeh Ameri, and Christoph J. Brabec

CONTENTS

12.1 INTRODUCTION

Addressing climate change, pollution, and energy insecurity problems all at once requires major changes in our energy infrastructure. Over the past decade, a number of studies have proposed large-scale renewable energy plans, mainly based on wind, water, and sunlight resources.[1–4] As shown in Figure 12.1,[1] the solar energy resource potentially dwarfs all other renewable and fossil-based energy resources combined. The yearly sustainable renewable supply of solar energy received by the emerged continents alone is more than 30 times larger than the total planetary reserves of coal and 1500 times larger than the current planetary energy consumption.[1] Therefore,



9. Presentations at Conferences, Workshops, Events

Ameri, Tayebeh

23.-24.01.2015
Final meeting of DFG-Schwerpunktprogramm 1355 (SPP 1355) Elementarprozesse der Organischen Photovoltaik, Badhonnef, Germany
Talk: *Near IR sensitization of the polymer / fullerene solar cells*

15.-17.06. 2015
11th International Conference on Organic Electronics 2015 (ICOE 2015), Erlangen, Germany

08.-09.06.2015
Mid-term review meeting of Organic Semiconductors for NIR Optoelectronics (OSNIRO), Brussels, Belgium

08.-23.09.2015
Organic Semiconductors for NIR Optoelectronics (OSNIRO) workshop on "Healthier Life by Green Chemistry", Athens, Greece

08.-24.09.2015
2nd progress meeting of Organic Semiconductors for NIR Optoelectronics (OSNIRO), Athens, Greece

04.-07.10.2015
3rd Symposium on Synthetic Carbon Allotropes, Erlangen, Germany,

Batentschuk, Miroslaw

15.-18.09.2015
European Materials Research Society (E-MRS) Fall Meeting, Warsaw, Poland
Talk: *Colloidal nanoparticles LaPO4:Dy3+ as a printable material for the luminescent thermometry*

Brabec, Christoph J.

09.01.2015
TU Wien, Solids for Fun, Graduate School, Vienna, Austria
Invited talk: *Alternative Mateirals and Concepts for Innovative Solar Technologies*

13.02.2015
Besuch von MdB Stefan Müller , Erlangen, Germany
Talk: *Das ZAE auf dem Weg in das neue Energiezeitalter*

03.03.2015
LFE Workshop, Fürth, Germany
Invited talk: *Laser Processes for Printed Photovoltaics Applications*

15.-20.03.2015
79. Jahrestagung der DPG und DPG-Frühjahrstagung (Deutsche Physikalische Gesellschaft e.V.), Berlin, Germany
Invited talk: *Neue Optoelektronische Materialien, Verfahren und Anwendungen in der Photovoltaik*

15.-17.06. 2015
11th International Conference on Organic Electronics 2015 (ICOE 2015), Erlangen, Germany
Talk: *Welcome speach at the International Conference for Organic Electronics in 2015*

21.-25.06.2015
2015 Conference on Lasers & Electro-Optics / Europe and European Quantum Electronics Conference (CLEO® / Europe-EQEC)
Invited talk: *Light manipulation concepts for thin film photovoltaics*

14.07.2015
Chinese Academy of Sciences (CAS), Beijing, China
Invited talk: *Novel concepts and architectures for sustainable solar technologies*

16.07.2015
Soochow University, Soochow, China
Invited talk: *Innovative material concepts for printed photovoltaics*

17.07.2015
South China Univeristy of Technology (SCUT), Guangzhou, China
Invited talk: *Exploring the potential of printed mulitjunction technologies*

21.-22.07.2015
Cluster Forum: Modellprojekt Smart Grid Solar - Wegweiser für nachhaltig dezentrale Energiekonzepte, Hof, Germany
Invited talk: *Das Modellprojekt "Smart Grid Solar"*
Invited talk: *Potentiale dezentraler Stromerzeugung*

21.09.2015
2nd International Fall School on Organic Electronics (IFSOE 2015), Moscow, Russia
Invited talk: *Photostability and photodegradation mechanisms in pi-conjugated semiconducting BHK composites*

22.-23.09.2015
The 15th International Symposium on Advanced Organic Photonics (ISAOP-15), Moscow, Russia
Invited talk: *Metal Organic Perovskites for Advanced Opto-electronic Applications*

05.10.2015
3rd Erlangen Symposium on Synthetic Carbon Allotropes 953, Erlangen, Germany
Invited talk: *Photoinduced microstructure degradation processes in pi-conjugated BHJ composites*

06.10.2015
13. Österreichische Photovoltaik-Tagung, Schwaz, Austria
Invited talk: *Perspektiven und Zeithorizonte der Dünnschicht Photovoltaik*

08.-10.12.2015
Asia-Pacific Solar Research Conference, Brisbane, Australia
Invited talk: *Metal Organic Perovskites for Advanced Photovoltaic Applications*

11.12.2015
University of New South Wales, Sydney, Australia
Invited talk: *Novel Materials for Advanced Photovoltaic Devices*

Bronnbauer, Carina

09.-13.08.2015
SPIE Optics + Photonics, San Diego, California
Talk: *Efficiency enhancement of semitransparent organic solar cells by using printed dielectric mirrors*

Burlafinger, Klaus

14.-18.09.2015
31st European PV Solar Energy Conference and Exhibition EU PVSEC 2015, Hamburg, Germany
Talk: *Highly Accelerated Life Time Testing via Extreme Illumination at Controlled Temperature for Thin Film Solar Cells*

Falbusch, Lars

04.-09.10.2015
16th International Conference on Silicon Carbide and Related Materials ICSCRM 2015, Giardini Naxos, Italy
Talk: *High temperature solution growth of SiC by the Vertical Bridgman method using a metal free Si-C-melt at 2300 °C*

Gasparini, Nicola

10.-13.2015
Hybrid and Organic Photovoltaics Conference (HOPV15), Rome, Italy
Poster: *In-depth study of the binary and ternary organic solar cells based on a novel indacenodithieno[3,2-b]thiophene based conjugated polymer*

15.-17.06. 2015
11th International Conference on Organic Electronics 2015 (ICOE 2015), Erlangen, Germany
Talk: *In-Depth study of the binary and ternary organic solar cells based on a novel indacenodithienothiophene based conjugated copolymer*

Guo, Fei

06.-10.04.2015
2015 MRS Spring Meeting & Exhibit, San Francisco, CA, United States.
Talk: *Silver Nanowires for Solution-Processed Multi-Junction Polymer Solar Cells*
Poster: *Printed Semitransparent OPV Modules: Materials, Processing and System Integration*

Kahmann, Simon

20.-21.01.2015
Physics @FOM Velhoven, Veldhoven, The Netherlands
Poster: *Hybrid organic-inorganic blends comprising lead sulphide quantum dots for solar cell applications*

22.-27.02.2015
Gordon Research Conference on Nanomaterials for Applications in Energy Technology, Ventura, USA
Poster: *Hybrid organic-inorganic blends comprising lead sulphide quantum dots for solar cell applications*

28.06.-01.07.2015
Next-Generation Organic Photovoltaics II Conference, Groningen, The Netherlands
Poster: *Lead sulphide quantum dot solar cells by blade coating from hybrid organic-inorganic solutions*

Langner, Stefan

27.02.2015
Zwischenbilanz-Veranstaltung von UMWELTnanoTECH, Straubing, Germany
Poster: *Umweltverträgliche Hocheffiziente Organische Solarzellen (UOS)*

15.-18.09.2015
European Materials Research Society (E-MRS) Fall Meeting, Warsaw, Poland
Talk: *Organic solar cells processed from environmentally friendly solvet blends*

Li, Ning

20.-21.04.2015
Organic Semiconductors for NIR Optoelectronics (OSNIRO) Workshop, Erlangen, Germany

15.-17.06.2015
11th International Conference on Organic Electronics 2015 (ICOE 2015), Erlangen, Germany
Talk: *Processing perspectives on high-performance fully-printed organic tandem solar cells*

17.07.2015
South China University of Technology (SCUT), Guangzhou, China
Talk: Recent activities and results on FBT-Th4 and PCE11

06.-09.10.2015
1st CENEM Summer School for X-ray Scattering 2015, Erlangen, Germany

12.11.2015
Armor/i-MEET/ZAE Workshop, Erlangen, Germany
Talk: *Strategies for Developing High-Performance OPV Materials towards Commercialization*

29.11.-04.12.2015
2015 MRS Fall Meeting & Exhibit, Boston, Massachusetts, USA.
Talk: *Processing perspectives on fully-printed organic tandem solar cells and modules*
Talk: *Overcoming electrode induced losses in organic solar cells by tailoring a quasi-ohmic contact to fullerenes via solution-processed alkali hydroxide layers*

Levchuk, Ievgen

02.-04.03.2015
4th International Symposium on Ceramics Nanotune Technology (ISCeNT4), Nagoya , Japan
Invited talk: *Smart nanophosphor material for effective Near-UV-light conversion: synthesis, upscaling and photovoltaic application*

15.-18.09.2015
European Materials Research Society (E-MRS) Fall Meeting, Warsaw, Poland

23.-25.11.2015
7th EAM Symposium, Kloster Banz, Bad Staffelstein, Germany
Poster: *Organometallic perovskites for optoelectronic applications*

Osvet, Andres

24.-27.08.2015
2th International Conference on Hole Burning, Single Molecule and Related Spectroscopies: Science and Applications, Tartu, Estonia
Talk:

Parea Ospina, Jose Dario

27.02.2015
Zwischenbilanz-Veranstaltung von UMWELTnanoTECH, Straubing, Germany
Poster: *Umweltverträgliche Hocheffiziente Organische Solarzellen (UOS)*

Richter, Moses

09.04.2015
Open Talks Series at the InnovationLab, Heidelberg, Germany
Talk: *Charge Carrier Mobility in Organic-Hybrid Layers*

29.09.2015
Summerschool of DFG Graduate School 1896, Zandt, Germany
Poster: *Charge Transport in ZnO nanoparticle layers*

11.09.2015
SPIE Optics & Photonics 2015, San Diego (CA), USA
Talk: *X-ray generated Charge Extraction by Linear Increased Voltage - Electrical Characterization of novel hybrid X-ray Detectors*

23.-25.11.2015
7th EAM Symposium, Bad Staffelstein, Germany
Poster: *Solution Processed X-ray Detectors*

Salvador, Michael

11.-15.05.2015
European Materials Research Society (E-MRS), Lille, France
Talk: *Degradation processes in organic solar cells: The critical role of environmental contaminants on active layers and interfaces*

04.-11.06.2015
European Summer School on Organic Photovoltaic Stability (ESOS), Cargese, France
Talk: *Lifetimes of OPV Cells and Modules*
Talk: *Tracking water diffusion as the primary cause for device failure in organic solar cells*

19.-24.07.2015
12th International Symposium on Functional π-Electron Systems (Fπ-12), Seattle, USA
Talk: *Tracking water diffusion as the primary cause for device failure in organic solar cells*

Schimmel, Saskia

04.-06.2015
Deutsche Kristallzüchtungstagung 2015, Frankfurt am Main, Germany
Talk: *In Situ X-Ray Imaging of GaN under Ammonothermal Conditions – Application for GaN Solubility Measurements*

Schuh Philipp

04.-09.10.2015
16th International Conference on Silicon Carbide and Related Materials ICSCRM 2015, Giardini Naxos, Italy
Poster: *Physical vapor growth of double position boundary free, quasi-bulk 3C-SiC on high quality 3C-SiC on Si CVD templates*

Schuster, Matthias

11.-15.05.2015
European Materials Research Society (E-MRS), Lille, France
Poster: *Synthesis of* In_2Se_3 *and* $Cu_{2-x}Se$ *Micro- and Nanoparticles with Microwave-Assisted Solvothermal and Aqueous Redox Reactions for the Preparation and Stabilization of Printable Precursors to a* $CuInSe_2$ *Solar Cell Absorber Layer*

15.-18.09.2015
European Materials Research Society (E-MRS) Fall Meeting, Warsaw, Poland
Poster: *Synthesis and ink formulation of selenium nanoparticle dispersions*

Shen, Yilei

09.-11.09.2015
European Coating Symposium (ECS) 2015, Eindhoven, The Netherlands
Talk: *Phosphor-filled luminescent down-shifting layers for organic PV: Reduced scattering, optical model and optimization*

Shrestha, Shreetu

13.-18.09.2015
26th International Conference on Amorphous and Nanocrystalline Semiconductors (ICANS 26) 2015, Aachen, Germany
Talk: *Organo-lead Halide Perovskite based Direct X-ray Detectors*

23.-25.11.2015
7th EAM Symposium, Kloster Banz, Bad Staffelstein, Germany
Poster: *Solution Processed X-ray Detectors*

Solodovnyk, Anastasiia

08.-09.10.2015
4th Congress on Organic & Printed Photovoltaics, Würzburg, Germany
Poster: *Phosphor-filled luminescent down-shifting layers for organic PV: Reduced scattering, optical model and optimization*

14.11.2015
Annual Meeting of Scholarship Recipients of Bavarian Center for Central, Eastern and Southeastern Europe (BAYHOST), Nürnberg, Germany
Talk: *Energiewende in Deutschland*

08.12.2015
SPIE Micro+Nano Materials, Applications and Systems, Sydney, Australia
Talk: *Improved properties of phosphor-filled luminescent down-shifting layers: reduced scattering, optical model, and optimization for PV application*

Vetter, Andreas

14.-19.06.2015
42nd IEEE Photovoltaic Specialists Conference, New Orleans, USA
Talk: *Assessing the accuracy of imaging techniques for defect characterization on thin film solar cells*

14.-18.09.2015
31st European PV Solar Energy Conference and Exhibition EU PVSEC 2015, Hamburg, Germany

Wellmann, Peter

02.02.2105
Denmark Technical University (DTU), Kopenhagen, Denmark
Visit talk: *Analysis of light efficiency limiting defects in f-SiC*

23.-25.03.2015
1st Annual Word Congress of Smart Materials WCSM-2015, Busan, South-Korea
Invited talk: *Crystal growth of bulk SiC for application in power electronic devices – Process design, 2D and 3D X-ray in situ growth monitoring and advanced doping*

26.03.2015
Dong-Eui University, Pusan, South-Korea
Invited talk: *SiC PVT crystal growth & characterization*

27.03.2015
Kite, Jinju, South-Korea
Invited talk: *SiC PVT Crystal Growth Technology*

10.5.2015
EU-Korea Workshop on Advanced Materials, Lille, France
Invited “short” talk: *Knowledge transfer & Common R&D – Processing of SiC Crystals as Key-Enabling Material for Energy Saving*

11.-15.05.2015
European Materials Research Society (E-MRS), Lille, France
Poster: *Towards the growth of SiGeC epitaxial layers for the application in Si solar cells*
Poster: *Progress on Numerical Reactive Diffusion Modeling of* $CuInSe_2$ *Phase Formation for Solar Cell Applications*

20.05.2015
Industrial Technology Research Institute ITRI, Taiwan
Invited talk: *SiC bulk crystal growth and characterization*

28.-29.05.2015
New applications of cubic SiC (NACSIC), Oslo, Norway
Invited talk: Growth and Characterization bulk of 3C-SiC – from early Attempts to current Status

15.-18.09.2015
European Materials Research Society (E-MRS) Fall Meeting, Warsaw, Poland
Poster: *Epitaxial growth and spectroscopic characterization of Si-Ge-C layers on silicon*

Wilhelm, Martin

11.-15.05.2015
European Materials Research Society (E-MRS), Lille, France
Poster: *Towards the growth of SiGeC epitaxial layers for the application in Si solar cells*

15.-18.09.2015
European Materials Research Society (E-MRS) Fall Meeting, Warsaw, Poland
Poster: *Epitaxial growth and spectroscopic characterization of Si-Ge-C layers on silicon*

Zhang, Chaohong

28.-29.08.2015
27th Annual Conference of Chinese-German Chemical Association (CGCA): Chemistry Makes a Better Life, Jena, Germany.
Poster: *Synthesis and Characterization of A Polymeric Fullerene Derivatives Based on Non-conjugated Polymer Backbone*

04.-07.10.2015
3rd Erlangen Symposium on Synthetic Carbon Allotropes 953, Erlangen, Germany
Poster: *Synthesis and Characterization of Polymeric Fullerene Derivatives Based on Non-conjugated Polymer Backbone*

16.-18.10.2015
27th Gesellschaft Chinesischer Chemiker und Chemieingenieure in Deutschland e.V.(GCCCD) Annual Conference, Karlsruhe, Germany

Zwescke André

11.-15.05.2015
European Materials Research Society (E-MRS), Lille, France
Poster: *Progress on Numerical Reactive Diffusion Modeling of* $CuInSe_2$ *Phase Formation for Solar Cell Applications*

10. Seminar Presentations

Chair Seminar

27.01.2015
Chaohong Zhang (Doctoral thesis report)
Studies on fullerene derivatives in photovoltaics

10.02.2015
Paul Dicke (Bachelor thesis)
Investigations of structural intermediate layers of multi-junction organics solar cells

24.02.2015
Michaela Göbel (Master thesis)
Homogenisierung des Gefüges der UFC-Keramik

06.03.2015
Sebastian Besold (Master thesis)
Organic solar cells - Investigation of charge transport dynamics

Lisa Sommerer (Bachelor thesis)
Strukturelle Untersuchung an flüßigprozessierten Siliziumnanopartikelschichten auf Hochtemperatursubstraten

10.03.2015
Johannes Hepp (Master thesis)
Contactless detection of unwanted substances in organic solar cells via illuminated lock-in IR-imaging

24.03.2015
Kerstin Schaumberger (Master thesis)
Hybrid ternary solar cells based on CdSeTe nanoparticles

Philipp Schwamb (Doctoral thesis report)
Lighting OLEDs on Foil Substrates

31.03.2015
Dr. Boris Kosog (Candidate for postdoctoral position)
Ligand Influences on Properties of Uranium Coordination Complexes - Structure, Reactivity, and Spectroscopy

Dr. Sebastian Jäger (Candidate for postdoctoral position)
Symmetry matching excitation of rotational symmetric plasmonic anostructures

07.04.2015
Simon Kahmann (Doctoral thesis report)
Hybrid organic-inorganic blends comprising lead sulphide quantum dots for solar cell applications

Ashray Udaya Shankar (Master thesis)
Investigation Of Ternary Organic Solar Cells Using Steady State Pump Probe Spectroscopy

Damhee Kim (Master thesis)
Evaluation of solution-processed transparent electrodes for full-printed flexible Semitransparent polymer solar cells Non-halogenated and non-toxic fabrication of OPV Non-halogenated and non-toxic fabrication of OPV

21.04.2015
Christopher Kick (Master thesis)
Light Conversion in Luminescent Down-Shifting Layers for Photovoltaics

Stefan Langner (Literature review)
Non-halogenated and non-toxic fabrication of OPV

05.05.2015
Michael Herzog (Bachelor thesis, Conti Temic microelectronic GmbH, Nürnberg)
Untersuchung des Driftverhaltens von gedruckten Widerständen auf einem HTCC-Schaltungsträger

Nicola Gasparini (Literature review)
Novel high-efficient ternary and multiple donor organic BHJ solar cells

12.05.2015
Jose Dario Perea (Literature review)
Solubility of conjugated molecules and polymers: A numerical approach by COSMO-RS

Kerstin Krebs (Literature review)
Touch Panel Technologies

12.06.2015
Jakob Kornhas (Bachelor thesis)
In search of effective flux materials for the optimisation of the synthesis and luminescent properties of $Sr_2Y_8(SiO_4)6O_2$*:Eu as a UV to VIS light converter*

23.06.2015
Stefan Langner (Doctoral thesis report)
Environmental friendly fabrication of OPV

30.06.2015
George Spyropoulos (Doctoral thesis report)
Smart materials and processing for Optoelectronic Devices: Laminated Organic Solar Modules

Dr. Stefanie Fladischer (Work progress report)
Nanoanalytical TEM investigations of ternary solar cells

14.07.2015
Marius Adler (Bachelor thesis)
Spray coating and characterization of homogeneous transparent electrodes of silver nanowires

28.07.2015
Anna Rössler (Bachelor thesis)
Realisierung eines Aufbaus zur Messung der Reflexions- und Emissionsspektren von Oberflächen bei hohen Temperaturen

11.08.2015
Leon Beickert (Bachelor thesis)
Synthesis and Characterization of Y-Ca-Al- and Ca-Al silicates with garnet and Anorthite structure for light conversion in solar cells

22.09.2015
Carsten Fehn (Master thesis)
Fabrication and characterization of solvent processed and scaled-up OLECs

Johannes Steiner (Bachelor thesis)
Leuchtstoffe mit Granat – und Merwinit Struktur als Lichtkonverter für die Beschichtung von Solarzellen

29.09.2015
Nicola Gasparini (Doctoral thesis report)
NIR-sensitized organic ternary solar cells

Lili Ke (Doctoral thesis report)
Synthesis of Silicon Phthalocyanine and Naphthalocyanine and their application in ternary solar cell

06.10.2015
Alexander Bode (Bachelor thesis)
Determination of Electric Parameters of Thin-Film Solar Cells with Imaging Measurements

20.10.2015
Lena Eisenhofer (Master thesis)
Process development for inkjet printing of PEDOT:PSS hole injection layers

Philipp Maisch (Doctoral thesis report)
Inkjet printing as manufacturing method for organic solar cells and modules

27.10.2015
Iftikhar Ahmed Channa (Doctoral thesis report)
Review On Barrier Materials For Packaging Thin Film Electronics

03.11.2015
André Karl (Master thesis report extern, potential doctoral candidate)
Inorganic-Organic hybrids for artificial water splitting

10.11.2015
Nusret Sena Güldal (Doctoral thesis report)
In-situ investigation methods on organic bulk-heterojunctions

17.11.2015
Yi Hou (Doctoral thesis report)
Tailoring planar heterojunction interfaces in fully low-temperature solution processed perovskite based solar cells

Shuai Gao (Master thesis report extern, new doctoral candidate)
Laser Collimation Measurement: Errors crosstalk analysis and compensation in the simultaneous measuring system for five-degree-of-freedom geometric error

24.11.2015
Moses Richter (Doctoral thesis report)
Charge Transport in hybrid X-ray detectors & UV-soaking in ZnO nanoparticles - the story continues

Fabian Carigiet (EUPVSEC Beitrag, potential doctoral candidate)
Case study of a low-voltage distribution grid with high PV penetration in Germany and simulation analyses of cost-effective measures

01.12.2015
Cesar Omar Quiroz (Doctoral thesis report)
Overcoming Efficiency Limitations of Semitransparent Perovskite Solar Cells

Jose Dario Perea (Doctoral thesis report)
Thermodynamical, electrical and transport properties of conjugated semiconductors by QC methods

08.12.2015
Atif Makhdoom (Doctoral thesis report)
Functionalized Si-np for printable solar cells

15.12.2015
Florian Högl (Master thesis report)
Generalized full solution-process fabrication of organic-inorganic metal halide perovskites for photovoltaic, X-ray and optoelectronic applications

Johannes Voll (Bachelor thesis report)
A detailed study of UV-soaking conditions and the effect on organic solar cell performance

Willi Kogler (Master thesis report)
Growth and characterization of micron-sized inorganic semiconductors for solar cell applications

Visitors & Guest Talks

27.01.2015
Dr. Eric Glowacki (Johannes Kepler Universität Linz)
Learning from nature - sustainable bioelectronics based on hydrogen-bonded pigments

10.02.2015
Dr. Jan Vogelsang (University of Regensburg)
Connecting single molecule and bulk spectroscopy of conjugated polymers by solvent vapor annealing

24.02.2015
Prof. Masaki Tanamura (NITech, Multi-Energy Innovation Center, Nagoya Institute of Technology)
Graphene Research at Multi-Energy Innovation Center in NITech

10.03.2015
Prof. Fahmi (Hochschule Rhein-Waal)

16.04.2015
Dr. Souren Grigorian (Soft Matter Physics Group, Institute of Physics, University of Siegen, Germany)
Surface-Sensitive X-ray Studies of Low Dimensional Systems

28.04.2015
Olga Zhovtiuk (City University of Hong Kong, Department of Physics and Materials Science)
Synthesis,optical studies and application of colloidal nanocrystals

05.05.2015
Dr. David Kaftan (University of South Bohemia, Department of Experimental Plant Biology)
Light utilization by plants: benefits and dangers

19.05.2015
William Tumas (Associate Laboratory Director, Materials and Chemical Sciences Directorate, National Renewable Energy Laboratory)
Functional Materials by Design for Solar Energy Conversion

06.07.2015
Dr. Larry Lüer (IMDEA Nanoscience, Madrid, Spanien)
Tracing performance loss channels in organic photovoltaic cells

08.09.2015
Taylor Uekert (Summer internship student, ZAE)
Nanostructured Organosilicon Luminophores as a Novel Luminescent Down-Shifting Material for Photovoltaics

28.10.2015
Dr. Christoph Waldauf (CrystalSol, Austria)
Concept and Technology of Monograin Solar Cells

29.10.2015
Dr. Mauro Morana (Morphwize, Italy)
"Hands-on" intro seminar on mPER-INM thin film solar cell simulator

16.11.2015
Prof. Kurt Hingerl (Universität Linz, Österreich)
A classical model for depolarization through decoherent superposition

17.12.2015
Ms Izuna Tsuboi MSc, (Department of Environmental and Materials Engineering Nagoya Institute of Technology, Japan)
Thermoelectric properties of magnetic semiconductor $CrFeO_3$

11. Conferences organized by Members of the Institute

Ameri, Tayebeh

20.-21.04.2015
The international school of “Application / Integration of Organic Electronics”, Erlangen, Germany

Brabec, Christoph J.

June 2015
Imperial College Workshop

15.-17.06. 2015
11th International Conference on Organic Electronics 2015 (ICOE 2015), Heinrich-Lades-Halle, Erlangen, Germany

08.-09.10.2015
4th Congress on Organic & Printed Photovoltaics, Würzburg, Germany

12. Cooperation in Committees

Ameri, Tayebeh

Guest Editor of *“Journal of Photonics for Energy”* (SPIE), Special Section on “Solution-Processable Organic Solar Cells”

Brabec, Christoph J.

Editor of *“Journal of Photonics for Energy”* (SPIE)

Chairman of the Editorial Board *“Advanced Energy Materials”*, Wiley VCH

Member of the Editorial Board of *“Progress in Photovoltaics”*, Wiley VCH

Member of the Editorial Board of *“Emerging Materials Research”*, ice publishing

Serving as referee for several funding organizations, among them the Austrian Science Fund (FWF), for the German Research Foundation (DFG), the Baden-Württemberg Stiftung, and for more than 15 top ranked journals

Serving as reviewer for multiple journals in the field of materials, semiconductors and energy (Nature Family, EES, Advanced Family,....)

Serving as expert referee for European Community

Chairman of the Executive Board of the Bavarian Center for Applied Energy Research, ZAE Bayern, Würzburg

Scientific Director Department Renewable Energies, ZAE Bayern, Erlangen

EnCN – Deputy Spokesman, Member of the Academic Heads, Member of the Steering Committee, Nürnberg

EnCN e.V. – Member of the Board of Directors, Nürnberg

Spokesman of the Department of Material Science, Friedrich-Alexander University Erlangen-Nürnberg

Representative for the Material Science Department in the Board of the Technical Faculty of the FAU Erlangen-Nürnberg

Member of Scientific Board of the PE graduate school, Imperial College, London

Member of the Scientific Advising Board, CRANN AMBER, Trinity College Dublin, Ireland

Member of the Board of the "Kompetenznetzwerk Wasser und Energie Oberfranken-Ost e.V. ", Hof

Member of the Board of the International Conference on Organic Electronics (ICOE) & Organizer of the 11th ICOE conference, Erlangen

Co-Organizer of the Congress series on Organic and Printed Photovoltaics, Erlangen and Würzburg

Principal Investigator of the Erlangen Cluster of Excellence *"Engineering of Advanced Materials" (EAM)*

Principal Investigator of the *"Solar Energy goes Hybrid"* Initative (SolTech) of the Bavarian State

Member of Graduate School in Advanced Optical Technologies (SOAT) Friedrich-Alexander-Universität Erlangen-Nürnberg

Collaborating PI of the CSC "111" Initative of the Heeger Center, Beijing, China
Principal Investigator of the CRC 953 "Carbon Allortopes", Friedrich-Alexander University Erlangen-Nürnberg

Principal Investigator of the GRK 1896 "in Situ Microscopy with Electroncs, X-Rays and Scanning Probes", Friedrich-Alexander University Erlangen-Nürnberg

Solodovnyk, Anastasiia

Member of Graduate School in Advanced Optical Technologies (SOAT) Friedrich-Alexander-Universität Erlangen-Nürnberg

1st doctoral canditate representative in Graduate School in Advanced Optical Technologies (SOAT) Friedrich-Alexander-Universität Erlangen-Nürnberg (elected for 1 year)

Wellmann, Peter

Member of the Exectuve Committee of the European Materials Research Society (EMRS).

Treasurer of the German Crystal Growth Association (DGKK e.V.)

Program Committee "German Crystal Growth Association DK-2015"

Program Committee "International Conference on Silicon Carbide and Related Materials ICSCRM-2015"

Chair of the European Research Society Fall Meeting EMRS Fall 2015

Externer Gutachter von Forschungsprojekten, ITRI, Taiwan, Mai 2015

13. Research Projects

Advanced Optical Technologies (SAOT) (Germany)
January 2013 – December 2015

Advanced Optical Technologies (SAOT) (Germany)
July 2014 – June 2015
Light Propagation in Phosphor-Filled Layers for Photovoltaic Application

Bayerische Forschungsstiftung, AZ-1006-11 (Germany)
July 2012 – May 2016
Intelligenz im Solarglas

Bayerische Forschungsstiftung, DOK-170-14 (Germany)
01.04.2014 – 31.03.2017
Entwicklung neuer Leuchtstoffe für die Hochtemperatur-Thermometrie

COLCIENCIAS (Columbia)
1 November 2014 – 30 September 2018
(Perea Ospina, Jose Dario)

CONACYT (The Mexican National Council for Science and Technology) (Mexico)
August 2013 – August 2018
(Ramirez Quiroz, César Omar)

China Scholarship Council (China)

CSC grant No. 201206820002
Inorganic/Organic light conversion composite for organic photovoltaic application (Chen, Wei)

CSC grant No. 2011613029
Semitransparent organic solar cells (Guo, Fei)

CSC grant No. 201206130055
Design and Fabrication of organic solar cells based on solution-processed small molecules (Ke, Lili)

CSC grant No. 2011643004
Solution-processed small molecule bulk heterojunction organic solar cells (Min, Jie)

CSC grant No. 201204910209
The Interfacial Layer of Organic Solar Cells (Zhang, Hong)

CSC grant:
Tang, Xiaofeng
Chen, Haiwei
Chen, Shi
Chen, Xie
Zhang, Chaohong

DFG SPP 1355 BR 4031/2-1 and 2-2 (Germany)
01 September 2010 – 31 December 2016
Elementarprozesse der organischen Photovoltaik:
Controlling the electronic interface properties in polymer-fullerene bulk-heterojunction solar cells.

DFG WE 2107/6-2 (Germany)
01 January – 31 December 2017
In situ Visualisierung des ammonothermalen Kristallisationsprozesses mittels Röntgenmesstechnik

EnCN (7502184) (Germany)
September 2011 – 31 December 2016
Solarfabrik

Exzellenzcluster: B1 (Germany)
01 November 2012 – 31 October 2017
Printable solar cells

GRK1896 (Germany)
01.01.2014 – 31.12.2015
In-Situ Microscopy with Electrons, X-ray and Scanning Probes

Helmholtz (Germany)
01.01.2014 – 31.12.2016
Rekombination in bleifreien Perovskite-Solarzellen

MATSOL Energie Campus Nürnberg (Germany)
01 January 2013 – 31 December 2016
Ultraharte Gläser
Beschleunigte Testverfahren
Optik – Optoelektronik
Testlabor / Prüflabor Materialkontakte und Interfaces
Thermophysikalische Auslegung

OSNIRO FP7-PEOPLE-2013-ITN (Germany)
01 October 2013 – 31 December 2017
Organic Semiconductors for NIR Optoelectronics

PHONSI (Germany)
2015-2018
Marie Skłodowska-Curie-Maßnahme Innovative Training Networks - ITN (Variante: European Training Network - ETN) im EU-Rahmenprogramm für Forschung und Innovation Horizont 2020

Real Nano (Germany)
2015-2016
FFG Programm Produktion der Zukunft

SFB 953 B01 (Germany)
01 January 2012 – 31 December 2015
Synthetic Carbon Allotropes

Solprocel (Germany)
01 November 2013 – 31 October 2016
Solution processed high performance transparent organic photovoltaic cells

SolTech StMWFK (Germany)
25 July 2012 – 31 July 2017
Solar technologies go hybrid

Staedtler Stiftung WW/eh 13/15 (Germany)
01 June 2015 – 31 October 2016
Wachstum von Silizium-Germanium-Karbid Halbleiterschichten mittels Chemischer Gasphasenabscheidung für Photovoltaikanwendungen

UOS (Germany)
01 September 2013 – 31 August 2016
Umweltverträglicher Beitrag der Nanotechnologie zur Energiewende

Virtuelle Hochschule Bayern 14-l-03-14Wel1 (Germany)
01 January 2015 – 29 February 2016
Werkstoffkunde für Elektrotechnik/Materialien der Elektronik und Energietechnik

14. Teaching

Winter Term 2014/2015

Lectures (VORL)

Grundlagen der Halbleiterphysik, *W. Heiß*

Grundlagen des Kristallwachstums und der Halbleitertechnologie, *P. Wellmann*

Kolloidale Nanokristalle, *W. Heiß*

Materialien der Elektronik und der Energietechnologie, *P. Wellmann*

Materialien und Bauelemente für die Optoelektronik und Energietechnologie: Grundlagen [MaBaOpEnGr], *Ch. J. Brabec*

Photophysics and Electronic Transport [PhPhys], *H.-J. Egelhaaf, Ch. J. Brabec, M. Halik*

Technische Grundlagen medizinischer Diagnostikverfahren [TGMDV], *M. Thoms*

Werkstoffe und Verfahren der medizinischen Diagnostik I, *M. Thoms*

Werkstoffkunde für Studierende der Elektrotechnik (EEI) [Werkstoffk.(ET)], *P. Wellmann*

Exercises and laboratory courses (PR, PJS, UE)

Lab Work Organic Electronics, *T. Ameri*

Lab Work Organic Electronics NT, *M. Batentschuk*

Praktikum Materialien der Elektronik und Energietechnik [PR2-ET], *P. Wellmann*

Praktikum Materialien der Elektronik und der Energietechnologie (5.Sem.) [PR2-ET], *P. Wellmann*

Praktikum Funktionswerkstoffe in der Energietechnologie [PFE], *P. Wellmann*

Praktikum Transporteigenschaften in HL [PrTrpeHL], *A. Osvet*

Praktikum Wahlfach Crystal Growth, *P. Wellmann*

Praktikum Werkstoffe 2 [PW2], *M. Batentschuk*

Projektarbeit - Arbeitsgemeinschaft Kristallisation von SiC und CIS [AG SiC CIS], *P. Wellmann*

Projektarbeit – Arbeitsgemeinschaft Photovoltaik und Solarenergie [AG OPV], *Ch. J. Brabec*

Seminars (AWA, SEM)

Anleitung zur wissenschaftlichen Arbeit, *T. Ameri*

Kern-/ Nebenfachseminar i-MEET (für Studierende im 3. MA-Semester) [SEM], *Ch. J. Brabec, E. Meißner*

Neuere Fragen zu Werkstoffen der Elektronik und Energietechnologie, *Ch. J. Brabec, P. Wellmann, M. Batentschuk*

Seminar "Organic Electronics" [SOE], *T. Ameri*

Seminar on Solar Energy [SemSolE], *Z. Rahimi, CH. Pflaum, Ch. J. Brabec*

Seminar über Bachelor- und Masterarbeiten, *Ch. J. Brabec, P. Wellmann*

Seminar über Bachelor-, Master und Doktorarbeiten – Crystal Growth, *P. Wellmann*

Seminar über spezielle Probleme der MEET (Lehrstuhl-Seminar), *Ch. J. Brabec, M. Batentschuk*

Summer Term 2015

Lectures (VORL)

Devices, *Ch. J. Brabec, G. Matt, T. Ameri, H. Azimi*

Elektrische, magnetische, optische Eigenschaften, *W. Heiß*

Elektronische Bauelemente und Materialfragen (Technologie II), *P. Wellmann*

Halbleiter großer Bandlücke, *P. Wellmann*

Halbleitercharakterisierung, *M. Batentschuk, G. Matt, E. Meißner, K. Forberich, A. Osvet*

Leuchtstoffe, *M. Batentschuk, A. Winnacker*

Materialien und Bauelemente für die Optoelektronik und Energietechnologie: Anwendung [WET II], *Ch. J. Brabec*

Technologie der Züchtung von Halbleiterkristallen und Photovoltaik, *J. Friedrich*

Thin films: processing, characterization and functionalities, *Ch. J. Brabec, M. Halik, H.-J. Egelhaaf, H. Azimi*

Werkstoffe der Elektronik in der Medizin, *M. Batentschuk, A. Winnacker*

Werkstoffe und Verfahren der medizinischen Diagnostik II, *M. Thoms*

Exercises and laboratory courses (EX, PJS, PR, UE)

Kernfachpraktikum I, Werkstoffe der Elektronik und Energietechnik, *M. Batentschuk*

Kernfachpraktikum II, Wahlfach Organic Electronics, *M. Batentschuk*

Lab Work Organic Electronics, *M. Batentschuk*

Numerische Modellierung des Kristallwachstums mithilfe des Programmpakets COMSOL Multi-Physics [CGL-Comsol], *P. Wellmann*

Praktikum Eigenschaften von Leuchtstoffen [PREgsLs], *P. Wellmann*

Praktikum Wahlfach Crystal Growth, *P. Wellmann*

Projektarbeit - Arbeitsgemeinschaft Kristallisation von SiC, CIS und CZTS [AG Kristallisation], *P. Wellmann*

Projektarbeit - Arbeitsgemeinschaft Lösungsprozessierte Halbleiter [AG HL], *Ch. J. Brabec*

Seminars (SEM, HS)

Druckbare Elektronik, *M. Batentschuk*

How to start a company, *Ch. J. Brabec*

Kernfachseminar, *Ch. J. Brabec*, *M. Batentschuk*

Literaturseminar, *M. Batentschuk*

Neuere Fragen zu Werkstoffen der Elektronik und Energietechnologie (Lehrstuhl-Seminar), *Ch. J. Brabec*, *P. Wellmann, M. Batentschuk*

Seminar on Solar Energy [SolarSem], *Ch. Pflaum, Ch. J. Brabec, J. Hornich*

Seminar über Bachelor- und Masterarbeiten, *Ch. J. Brabec*

Seminar über Bachelor- und Masterarbeiten (Wellmann), *P. Wellmann*

Winter Term 2015/16

Lectures (VORL)

Grundlagen der Halbleiterphysik, *W. Heiß*

Grundlagen des Kristallwachstums und der Halbleitertechnologie, *P. Wellmann*

Materialien der Elektronik und der Energietechnik, *P. Wellmann*

Materialien und Bauelemente für die Optoelektronik und Energietechnologie: Grundlagen [MaBaOpEnGr], *Ch. J. Brabec*

Nano-Bauelemente-Sensoren, MEMS, Micromachining [(NanoDev)], *A. Vetter*

Nanospektroskopie [NanoSpek], *W. Heiß, M. Batentschuk*

Photophysics and Electronic Transport [PhPhys], *H.-J. Egelhaaf, Ch. J. Brabec, M. Halik*

Photovoltaik-Technologie, *Th. Kunz*

Technische Grundlagen medizinischer Diagnostikverfahren [TGMDV], *M. Thoms*

Werkstoffe und Verfahren der medizinischen Diagnostik I, *M. Thoms*

Werkstoffkunde für Studierende der Elektrotechnik (EEI) [Werkstoffk.(ET)], *P. Wellmann*

Exercises and laboratory courses (PR, PJS, UE)

Lab Work Organic Electronics, *T. Ameri*

Lab Work Organic Electronics NT, *M. Batentschuk*

Praktikum Materialien der Elektronik und der Energietechnologie (5.Sem.) [PR2-ET], *P. Wellmann, M. Batentschuk*

Praktikum Funktionswerkstoffe in der Energietechnologie [PFE], *P. Wellmann*

Praktikum Nanotechnologie 2 (Master), *W. Heiß, E. Spiecker*

Praktikum Transporteigenschaften in HL [PrTrpeHL], *M. Batentschuk*

Praktikum Wahlfach Crystal Growth, *P. Wellmann*

Praktikum Werkstoffe 2 WS 2015 2016 [PW2], *M. Batentschuk*

Projektarbeit - Arbeitsgemeinschaft Kristallisation von SiC und CIS [AG SiC CIS], *P. Wellmann*

Projektarbeit – Arbeitsgemeinschaft Organische Photovoltaik [AG OPV], *Ch. J. Brabec*

Übung Nano Devices [(ÜbNanoDev)], *A. Vetter*

Seminars (AWA, SEM)

Anleitung zur wissenschaftlichen Arbeit, *T. Ameri*

Kern-/ Nebenfachseminar i-MEET (für Studierende im 3. MA-Semester) [SEM], *Ch. J. Brabec, E. Meißner*

Neuere Fragen zu Werkstoffen der Elektronik und Energietechnologie, *Ch. J. Brabec, P. Wellmann, M. Batentschuk*

Seminar "Organic Electronics" [SOE], *T. Ameri*

Seminar on Solar Energy [SemSolE], *CH. Pflaum, Ch. J. Brabec, J. Hornich*

Seminar über Bachelor- und Masterarbeiten, *Ch. J. Brabec*

Seminar über Bachelor-, Master und Doktorarbeiten – Crystal Growth, *P. Wellmann*

Solution Processed Semiconductors [SoPSem], *W. Heiß*

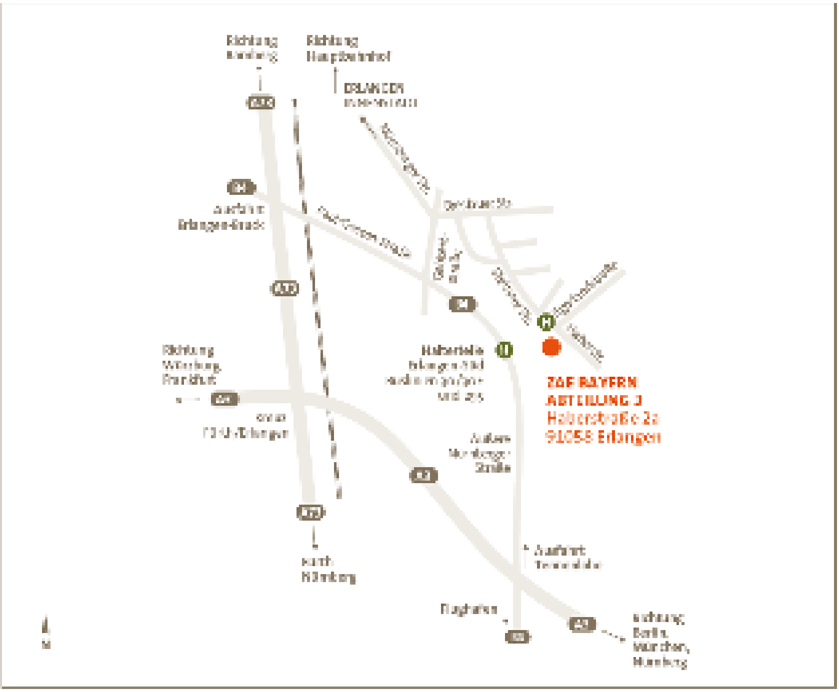
15. Addresses and Maps

Department of Materials Science & Engineering
Materials for Electronics and Energy Technology
Friedrich-Alexander University of Erlangen-Nürnberg
Martensstr. 7
D-91058 Erlangen, Germany
Phone: +49 (0) 9131 85-27633 (Secretary)
Fax: +49 (0) 9131 85-28495
E-Mail: i-meet@ww.uni-erlangen.de
Internet: http://www.i-meet.ww.techfak.fau.de

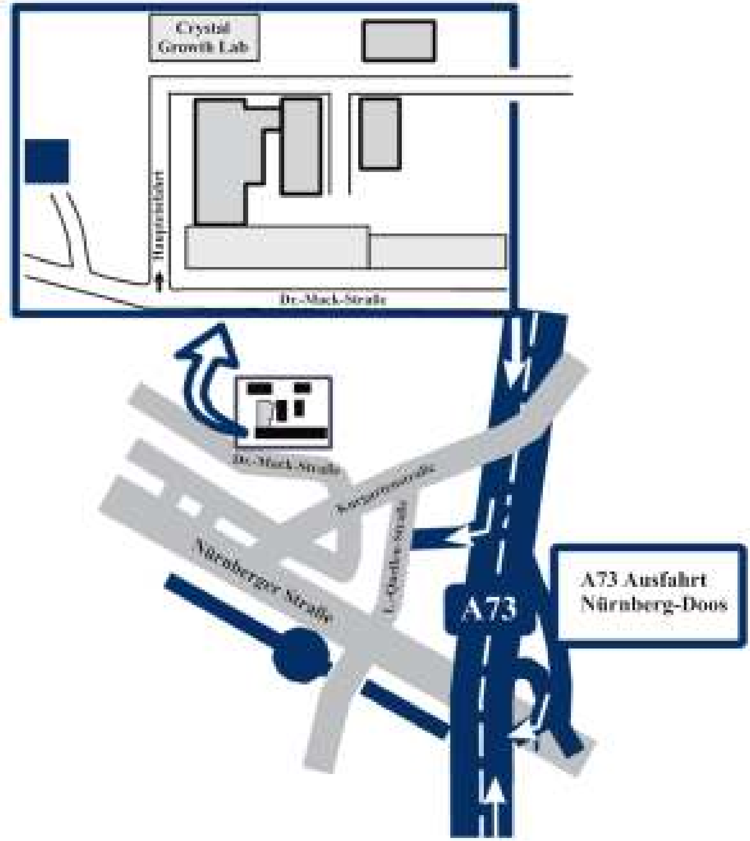
By car:
Highway A3 exit **Tennenlohe**; direction to Erlangen (B4). Follow the signs "**Universität Südgelände**"**.** After junction **"Technische Fakultät"** please follow the map.

By train:
Railway station **Erlangen.**
Bus line No. 287 direction **"Sebaldussiedlung"**. Bus stop **"Technische Fakultät".** 50 meters to a layout plan; search for **"Insitut für Werkstoffwissenschaften"**.

ZAE Bayern Erlangen Abteilung 3
Thermosensorik und Photovoltaik
Haberstr. 2a
D-91058 Erlangen, Germany
Phone: +49 (0) 9131 / 9398 – 100
Fax: +49 (0) 9131 / 9398 – 199
E-Mail: info3@zae.uni-erlangen.de
Internet: http://www.zae-bayern.de/das-zae-bayern/standorte/erlangen.html



Technikum 2
Crystal Growth Lab
Dr.-Mack-Strasse 77
D-90762 Fürth
Phone: +49 (0) 911 / 65078-65081
FAX: +49 (0) 911 / 65078-65083
Email: crystals@fau.de
Internet: http://crystals.tf.fau.de



Geschäftsstelle Energie Campus Nürnberg e.V.
Fürther Str. 250
"Auf AEG", Gebäude 16
D-90429 Nürnberg
Phone: +49 (0) 911 / 56 854 9120
Fax: +49 (0) 911 / 56 854 9121
E-Mail: info@encn.de
Internet: http://www.encn.de