

DS 23: Focus Session: Thin Film Photovoltaic Materials and Solar Cells II

Time: Wednesday 14:45–18:15

Location: H8

DS 23.1 Wed 14:45 H8

Oxygen vacancy doping of TiO₂ — ●SIMON MOSER^{1,2}, LUCA MORESCHINI², JACIM JACIMOVIC¹, OSOR BARISIC³, HELMUTH BERGER¹, ARNAUD MAGREZ¹, YOUNG JUN CHANG^{2,4}, KEUN SU KIM², AARON BOSTWICK², ELI ROTENBERG², LASZLO FORRO¹, and MARCO GRIONI¹ — ¹Ecole Polytechnique Federale de Lausanne — ²Advanced Light Source, Lawrence Berkeley National Laboratory — ³University of Zagreb — ⁴University of Seoul

The titanium oxide TiO₂ has been object of extensive studies because of its suitability in many practical fields, ranging from photovoltaic applications, to catalysis, memristors, and others. As for many other transition metal oxides, great attention has been devoted to the impact on the electronic structure of different doping mechanisms, either extrinsic or due to the creation of oxygen vacancies. Here we report an angle-resolved photoemission (ARPES) work on TiO₂ single crystals and epitaxial films grown with the *in situ* pulsed-laser-deposition (PLD) system available at beamline 7.0.1 of the Advanced Light Source. We show the evolution of the electronic structure as a function of the amount of oxygen vacancies induced by the photon beam.

DS 23.2 Wed 15:00 H8

Work function determination of degenerately Al-doped ZnO by thermionic emission — ●CHRISTIAN WILDE, BERND SCHMIDT, MYKOLA VINNICHENKO, and SYBILLE GEMMING — Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Dresden, Germany

Degenerately Al-doped ZnO (AZO) is a transparent conductive oxide (TCO) widely used, especially as electrode material in solar cells. The work function of these electrodes is of crucial importance, because it determines the electronic barrier between the TCO and the semiconducting absorber. Therefore, this barrier directly affects the charge collection and thus solar cells efficiency. In this contribution we report the results of experiments carried out to determine the work function of AZO by using the thermionic emission theory. AZO, as a degenerately doped semiconductor with the Fermi level in the conduction band shows a metal-like behaviour, and, if it is brought into contact with a semiconductor, it forms a Schottky barrier. From measurements of temperature-dependent current-voltage characteristics the work function of AZO can be determined. We demonstrate that this model of metal/semiconductor contact is applicable to the contact between AZO and a non-degenerately doped substrate (silicon or germanium). The Schottky barrier formation is studied with respect to the substrate conductivity type and surface cleaning. The determined AZO work function variation will be discussed in relation to the film properties and process parameters of reactive and non-reactive DC magnetron sputter deposition.

DS 23.3 Wed 15:15 H8

Laser Based Shunt Removal of Silicon and Chalcopyrite based Thin Film Solar Cells — ●CHRISTOF SCHULTZ¹, MANUEL SCHÜLE¹, SVEN KÜHNAPPEL³, KAMIL STELMASZCZYK¹, MOSHE WEIZMAN¹, HOLGER RHEIN², BJÖRN RAU², RUTGER SCHLATMANN^{1,2}, VOLKER QUASCHNING¹, BERT STEGEMANN¹, and FRANK FINK¹ — ¹HTW Berlin - University of Applied Sciences, Wilhelminenhofstr. 75a, 12459 Berlin, Germany — ²PVcomB/ Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Schwarzschildstr. 3, D* 12489 Berlin, Germany — ³Helmholtz-Zentrum für Materialien und Energie, Institut für Silizium-Photovoltaik, D-12489 Berlin, Germany

In commercial thin film solar cell production defective areas can occur due to material impurities or by "rough" sample handling between the different deposition steps. Such defects can cause disproportionate losses or even shortcuts in the solar cells. The removal of these defects would increase the solar cell performance as well as the overall manufacturing yield. In our study we present a technique for identification of shunted regions by means of lock-in thermography and successful laser based removal of shunts in silicon and chalcopyrite thin film solar cells. These results show that the removal of point-like defects increases the overall device performance significantly.

DS 23.4 Wed 15:30 H8

First-principles electronic structure of β -FeSi₂ and FeS₂ sur-

faces — ●PENGXIANG XU, TIMO SCHENA, STEFAN BLÜGEL, and GUSTAV BIHLMAYER — Peter Grünberg Institut & Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

Applying density functional theory in the framework of the full-potential linearized augmented plane-wave (FLAPW) method FLEUR [1], we investigate the electronic structure of potential future photovoltaic materials, β -FeSi₂ and FeS₂, for selected surface orientations and terminations with and without surface passivation. We also study the electronic structure of bulk β -FeSi₂ including recently observed stacking faults.

By comparing surface energies, the most stable orientations are determined for different terminations among different orientations. Detailed electronic structure calculations show that surface states originating from Fe play an important role and might determine the photovoltaic properties. For selected systems, we present the effects of passivation on the electronic structure and study how the bandgap is affected by stacking faults found in β -FeSi₂. Our results furthermore indicate that anti-ferrimagnetic ordering exists for Fe-terminated surfaces.

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[1] www.flapw.de

DS 23.5 Wed 15:45 H8

Oxide Heterostructures for Efficient Solar Cells — ●ELIAS ASSMANN¹, PETER BLAHA², KARSTEN HELD¹, SATOSHI OKAMOTO³, and GIORGIO SANGIOVANNI⁴ — ¹Institut für Festkörperphysik, Technische Universität Wien — ²Institut für Materialchemie, Technische Universität Wien — ³Materials Science and Technology Division, Oak Ridge National Laboratory, USA — ⁴Institut für Theoretische und Astrophysik, Universität Würzburg

We propose an unexplored class of absorbing materials for high-efficiency solar cells: heterostructures of transition-metal oxides. In particular, LaVO₃ grown on SrTiO₃ has a direct band gap ~ 1.1 eV in the optimal range as well as an internal potential gradient, which can greatly help to separate the photo-generated electron-hole pairs. Furthermore, oxide heterostructures afford the flexibility to combine LaVO₃ with other materials such as LaFeO₃ in order to achieve even higher efficiencies with band-gap graded solar cells. We use density-functional theory to demonstrate these features.

DS 23.6 Wed 16:00 H8

New insights into the mechanisms of photodegradation / stabilization of P3HT:PCBM active layers using poly(3-hexyl-d13-thiophene) — ●AURÉLIEN TOURNEBIZE¹, PIERRE-OLIVIER BUSSIÈRE¹, PASCAL WONG-WAH-CHUNG¹, AGNÈS RIVATON¹, JEAN-LUC GARDETTE¹, KION NORRMAN², FREDERIK C. KREBS², HUSSEIN MEDLEJ³, ROGER C. HIORNS³, and CHRISTINE DAGRON-LARTIGAU³ — ¹Institut de Chimie de Clermont-Ferrand, Equipe Photochimie Clermont-Ferrand, France — ²IPREM, Université de Pau et des Pays de l'Adour, France — ³Technical University of Denmark, Department of Energy, Denmark

The use of deuterated P3HT permitted distinction of carbon originating from the hexyl-d13 chain and carbon originating from PCBM and the non-deuterated thiophene unit. The photooxidation of both components of the blend was monitored using the combination of various analytical techniques (ToF-SIMS, XPS, infrared and UV-visible spectroscopy, gas phase analysis) to probe the bulk and the surface of the deposit.

The results show that the stabilization of P3HT by PCBM is due to morphological changes during photooxidation. In parallel, the wavelength effect has been investigated.

The results obtained in this work advance the understanding of active layer stability and will help improve the design of organic solar cells resulting in longer lifetimes thanks to the use of cut-off filter in the substrate or encapsulation of the devices.

DS 23.7 Wed 16:15 H8

Electrodeposition of aromatic compounds on silicon and subsequent cross linking - first steps towards a novel bottom-up synthesis of graphene — ●JANEK ZEUSCHNER, GERALD V.

TROPPEZ, JÖRG RAPPICH, and NORBERT H. NICKEL — Helmholtz-Zentrum Berlin, Institut für Siliziumphotovoltaik, Kekuléstr. 5, 12489 Berlin, Germany

The state-of-the-art method for the production of high-quality macroscopic graphene sheets is CVD synthesis on copper. However, during the growth process holes and grain boundaries are introduced in the material, resulting in adverse effects on its electronic properties. Furthermore, future technological applications of graphene require a transfer step from copper to silicon. This is expected to disturb the ordered structure of the graphene sheets even further. Therefore it would be highly desirable to grow single-layer graphene on silicon directly. We present first steps of a novel approach to synthesize graphene from small molecules on single-crystal silicon. During electrodeposition of suitable aromatic organic compounds, the defect density on the silicon-solution interface is monitored by in-situ photoluminescence spectroscopy. The mechanism of deposition is analyzed and results from cross-linking experiments are shown.

Coffee break (15 min)

DS 23.8 Wed 16:45 H8

Diffusion of copper in In_2S_3 layers prepared by ion layer gas reaction method — ●ALBERT JUMA, RODRIGO SÁEZ-ARAOZ, CHRISTIAN-HERBERT FISCHER, and THOMAS DITTRICH — Helmholtz-Centre-Berlin for Materials and Energy, Hahn-Meitner-Platz 1, 14109 Berlin, Germany.

Diffusion of copper in semiconductors remains an important phenomenon in photovoltaics because it affects the electronic properties, formation of interfaces, solar cell characteristics and stability. In_2S_3 layers were prepared by ILGAR (ion layer gas reaction) method with InCl_3 and $\text{In}(\text{OCCH}_2\text{CHOCCH}_2)_3$ as precursor salts to obtain Cl-containing and Cl-free layers, respectively. Diffusion experiments were performed by annealing $\text{Si}/\text{In}_2\text{S}_3/\text{CuSCN}$ layer systems at different temperatures and times and then etching away CuSCN in pyridine solution. The concentration profiles of Cu in In_2S_3 were obtained using Rutherford backscattering spectrometry (RBS) from which the diffusion coefficients were determined as a function of temperature. The diffusion in Cl-containing layers was limited by a lower solubility limit while the Cl-free layers showed one diffusion process with a relatively higher solubility. The activation energies for Cu diffusion were 0.041 eV and 0.24 eV for In_2S_3 layers with and without Cl respectively. The influence of In-Cl bond on the local structure of $\text{In}_2\text{S}_3:\text{Cl}$ and on the diffusion process of Cu^+ are discussed.

DS 23.9 Wed 17:00 H8

Time-Resolved Photoluminescence Studies on $\text{Cu}(\text{In,Ga})\text{Se}_2$ Thin Film Solar Cells — ●VIKTOR GERLIZ, DIMITRIOS ANASTASSIOU, JÖRG OHLAND, DIRK OTTEKEN, INGO RIEDEL, and JÜRGEN PARISI — Carl von Ossietzky Universität Oldenburg

The aim of this study is to evaluate the qualification of time-resolved photoluminescence (TR-PL) measurements as tool for quality management for inline production of $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin film modules. Prior to the interpretation of TR-PL measurements regarding device-characteristic quality parameters, the first stage of the study addresses the technical requirements for reliable data acquisition via time-correlated single photon counting. We observed that decay curves taken at low-injection (LI) levels generally exhibit mono-exponential decay characteristics, while high injection (HI) causes superposition with a slower relaxation process. Short measurement times are required for industry applications of this technique. These can only be achieved at sufficiently high excitation intensity (HI). Under such conditions we observe a correspondence between open circuit voltage and the second order decay constant.

DS 23.10 Wed 17:15 H8

Device analysis of CIGSe superstrate solar cells — ●MARC D. HEINEMANN, CHRISTIAN A. KAUFMANN, BRITTA HÖPFNER, THOMAS UNOLD, and HANS-WERNER SCHOCK — Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany

$\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells in the superstrate configuration offers a number of advantages regarding industrial device fabrication as well as the option of direct application in tandem device structures. The drawback is the lower efficiency due to the difficulty to design the heterointerface, which traditionally relies on buffer layers like CdS that are unstable at the high process temperatures. In this work superstrate $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells are prepared by coevaporation at different temperatures di-

rectly on a variety of ZnO coated glass substrates. Depending on the process conditions, the formation of a thin GaO compound or InO compound layer has been observed at the interface. It was found that the InO layer enables the Zn diffusion into the absorber and induces a low shunt resistance, whereas the GaO layer acts as a diffusion barrier for Zn. Currently a max conversion efficiency of around 7% has been achieved. The device performance of these superstrate devices is modeled by numerical simulation, taking into account results from admittance and photoelectron spectroscopy of the interface. To overcome the efficiency limiting effects derived from this device model, different interface conditionings in combination with the application of a variety of buffer layers are carried out and will be presented.

DS 23.11 Wed 17:30 H8

Laser Patterning of CIGS absorber layers with short nanosecond laser pulses — ●MANUEL SCHÜLE¹, CHRISTOF SCHULTZ¹, KAMIL STELMASZCZYK¹, MOSHE WEIZMAN¹, HOLGER RHEIN², BJÖRN RAU², RUTGER SCHLATMANN^{1,2}, VOLKER QUASCHNING¹, BERT STEGEMANN¹, and FRANK FINK¹ — ¹HTW Berlin - University of Applied Sciences, Wilhelminenhofstr. 75a, 12459 Berlin, Germany — ²PVcomB / Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Schwarzschildstr. 3, D-12489 Berlin, Germany

Laser based patterning of chalcopyrite thin film solar cells is an essential step towards high efficiencies since the dead area of the solar module is reduced. When manufacturing solar modules, the second laser patterning step typically comprises the removal of very fine lines in the absorber material by ultra-short laser pulses in order to create a direct contact between the back contact of one cell and the front contact of the adjacent cell. Such ultra-short ps or fs laser pulses are necessary to avoid melting of the absorber which might create a binary conductive phase and thereby shunts in the solar cell. In our study we demonstrate successful laser patterning by using a low-cost nanosecond laser source (532 nm) for local phase transformation of the absorber material instead of removing the material. This patterning step is performed after complete deposition of all layers through the front contact allowing for a simplified and accelerated manufacturing process.

DS 23.12 Wed 17:45 H8

Stöchiometrieabhängigkeit des Ladungsträgertransports in CZTS-Solarzellen — ●JUSTUS JUST^{1,2}, MELANIE NICHTERWITZ¹, STEFFEN KRETZSCHMAR¹, DIRK LÜTZENKIRCHEN-HECHT², RONALD FRAHM² und THOMAS UNOLD¹ — ¹Helmholtz-Zentrum-Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, D-14109 Berlin — ²Fachbereich C - Physik, Bergische Universität Wuppertal, Gaußstraße 20, D-42097 Wuppertal, Germany

Mit $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) in Chalkopyrit-verwandter Kesteritstruktur als Absorbermaterial in Dünnschichtsolarellen werden bereits Wirkungsgrade von über 8,4 % erreicht, während der Zusammenhang zwischen Abweichungen von der Stöchiometrie des Materials und den resultierenden elektronischen Eigenschaften bislang kaum verstanden ist. Hier werden CZTS-Solarzellen unterschiedlicher Zusammensetzung mittels EBIC-Aufnahmen (ortsaufgelöste Elektronenstrahl-Angeregte Ladungsträgergeneration) am Querschnitt der Solarzelle untersucht. Daraus können die Diffusionslänge sowie die Ladungsträgerdichte abgeschätzt werden. Zusammen mit Messung der Kapazität bei Raumtemperatur, der externen Quanteneffizienz und der I-V-Kennlinie entsteht so ein konsistentes Modell der Ladungsträgertransporteigenschaften. Um diese in Zusammenhang mit der tatsächlichen Zusammensetzung der CZTS-Phase zu bringen, die sich aufgrund von Fremdphasen signifikant von der Probenzusammensetzung unterscheiden kann, wird eine vollständige Phasenanalyse mittels Röntgenabsorptionsspektroskopie durchgeführt.

DS 23.13 Wed 18:00 H8

Photoluminescence and Raman scattering in wurtzite $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ nanocrystals — ●SERGEJ LEVCENKO¹, THOMAS UNOLD¹, AJAY SINGH^{2,3}, SHALINI SINGH^{2,3}, and KEVIN M RYAN^{2,3} — ¹Helmholtz Zentrum Berlin für Materialien und Energie, Berlin, Germany — ²SFI-Strategic Research Cluster in Solar Energy Conversion, University of Limerick, Ireland — ³Materials and Surface Science Institute, University of Limerick, Ireland

$\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ (CZTSSe) semiconductors gain much attention due to their potential photovoltaic application. Recently, by nanocrystal chemistry approach the formation of the new wurtzite crystal phase of CZTS and CZTSe which is thermodynamically unstable in a bulk phase (kesterite/stannite) were reported. Here we present the vibra-

tional and optical properties of wurtzite- CZTSSE nanocrystals as a function of x characterized by Raman and photoluminescence. The pseudo-spherical CZTSSE nanocrystals with the diameter of about 20 nm were prepared by colloidal chemistry method. The Raman spectra of the CZTSSE nanostructures show a two mode behavior. The intensive CZTSSE-like mode strongly shifts from 191 cm^{-1} for $x=1$ to

225 cm^{-1} for $x=0.15$, while the intensive CZTS-like mode barely shifts from 333 cm^{-1} for $x=0$ to 329 cm^{-1} for $x=0.8$. The low temperature CZTSSE PL spectra show one broad PL band which is gradually tuned from 1.4 eV for $x=0$ to 0.9 eV for $x=0.15$. The observed PL band most likely originates from near band edge emission of wurtzite CZTSSE nanocrystals.