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E-MRS Spring Meeting 2003
June 10 - 13, 2003

SYMPOSIUM D

Thin film and nano-structured materials for
photovoltaics

Symposium Organizers:

Christoph J. Brabec, Siemens AG, Erlangen, Germany

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E-MRS 2003 SPRING MEETING

SYMPOSIUM D

Tuesday, June 10, 2003
Mardi 10 juin 2003

Morning
Matin

Session I: Compound TF

Session chair: A. Jäger-Waldau

- D-I1** 9:00 -Invited- MATERIAL REQUIREMENTS FOR CIS SOLAR CELLS
I. Konovalov, Wilhelm Ostwald Institute, Universität Leipzig, Linnéstr. 2, 04317 Leipzig, Germany
A checklist with requirements for materials to be used in CIS solar cells for assessment of new materials and new technologies will be presented. A short explanation, list of suitable analytical methods and an example application to mature Cu(In,Ga)Se₂ cells on glass as well as to novel Cu-In-S cells on Cu tape (CISCuT) are included. The following requirements are discussed: For the absorber material: high optical absorption coefficient; optimal band gap width; small density of intrinsic recombination states; abundant constituents; optimal dopability and no Fermi level pinning limitations in the band gap; compensation of excess intrinsic doping and natural mechanisms of composition control; good ohmic contacts. For the buffer layer: high barrier height; wide band gap; interdiffusion properties; optical transparency; optimal electrical conductivity; low interface density of states. For the window layer: wide band gap; high carrier mobility; convenient way of intrinsic doping. For all the materials: Cheap reproducible process-compatible deposition technique for homogeneous large area film deposition; environmental acceptability; stability, also in combination.
- D-I2** 9:30 MICROSTRUCTURE AND OTHER PROPERTIES OF CVD-GROWN CuGaSe₂ THIN FILMS AND THIN FILM SOLAR CELLS
D. Fuertes Marrón, A. Meeder, Th. Glatzel, U. Bloeck, P. Schubert-Bischoff, R. Würz, S.M. Babu, **Th. Schedel-Niedrig**, M.Ch. Lux-Steiner, Hahn-Meitner-Institut, Germany, L. Weinhardt, C. Heske, E. Umbach, Experimentelle Physik II, University of Würzburg, Germany
The microstructure and electronic structure of interfaces involved in CVD-grown CuGaSe₂ (CGSe) based thin film solar cells as well as the surface and bulk related properties of CGSe thin absorber films have been investigated. The absorber films were grown in two stages by means of an open-tube chemical vapor deposition (CVD) process [1]. High-resolution transmission electron microscopy (HRTEM) combined with scanning energy dispersive X-ray (EDX) analysis have shown microstructural aspects related to the CVD-deposition technique of the absorber films, like the presence of an interfacial MoSe₂ layer between back contact and absorber, and directly linked to the poor PV performance of devices based on Cu-rich compositions [2]. Complementary information on the electronic structure has been imaged of the complete solar cell cross section by using Kelvin probe force microscopy (KPFM) [3]. Device grade CVD-CGSe thin films reveal a nearly stoichiometric chemical bulk composition while, on the other hand, the surface/near-surface chemical composition is Cu-poor, pointing towards a highly non-stoichiometric surface layer. Furthermore, an increase of the band energy gap has been found for the surface/near-surface region by means of UV- and inverse photoelectron spectroscopy (UPS and IPES, resp.), suggesting the presence of a defect-rich surface/near-surface phase and a defect-poor bulk phase [4]. In this paper, examples of novel lift-off CVD-thin film absorber solar cells [5] will also be presented.
[1] German Patent DE 198 55 021 C1.
[2] D. Fuertes Marrón *et al.*, Thin Solid Films (in press)
[3] Th. Glatzel *et al.*, Appl. Phys. Lett., **81** (2002) 2017.
[4] A. Meeder *et al.*, Proc. 13th ICTMC 2002
[5] German Patent pending.
- D-I3** 9:45 INTERFACE FORMATION BETWEEN POLYCRYSTALLINE Cu(In,Ga)Se₂ AND II-VI COMPOUNDS
T. Schulmeyer, A. Klein, R. Hunger, W. Jaegermann, Darmstadt University of Technology, 64287 Darmstadt, Germany, R. Kniese, M. Powalla, Zentrum für Sonnenenergie und Wasserstoff-Forschung, 70565 Stuttgart, Germany
The interface between Cu(In,Ga)Se₂ (absorber) and CdS (buffer) is crucial for the performance of CIGS thin film solar cells. Although the presence of ordered defect compounds (ODC) and interdiffusion is known at these interfaces, their impact on interface band alignment and interface defect states is not clear. The outstanding cell performance with CdS buffer layers, in comparison to other buffer materials, is also not resolved. We have performed systematic studies of interface formation between Cu(In,Ga)Se₂ and II-VI semiconductors CdX and ZnX (X= S, Se, Te) using in-situ photoelectron spectroscopy. Contamination-free Cu(In,Ga)Se₂ surfaces were prepared by heating-off of Se layers, which were deposited onto the absorber layers in the deposition chamber directly after absorber deposition. In addition also oxidized and chemically treated CIGS surfaces have been used. Interfaces with II-VI compounds were prepared by stepwise evaporation. The determined band alignments are compared to theoretical calculations.

10:00

BREAK

Session II: Compound TF

Session chair: I. Konovalov and K. Ito

- D-II.1** 10:30 -Invited- OPTIMISING THE OPEN CIRCUIT VOLTAGE OF Cu(In,Ga)S₂ SOLAR CELLS - DESIGN AND ANALYSIS
R. Klenk, S. Bakehe, R. Kaigawa*, A. Neisser, J. Reiss and M. Ch. Lux-Steiner, Hahn-Meitner-Institut, Glienickestr. 100, 14109 Berlin, Germany, *Ryokoku University, Seta, Otsu, 520-2194, Japan
Exploiting the potential of wide-gap chalcopyrites requires a heterojunction design where the open circuit voltage is determined by the band gap of the absorber, i.e., a design that avoids barrier reduction by tunneling and/or interface recombination. Furthermore, any variation of the band gap within the absorber should be such that it assists in minority carrier generation and collection while maintaining a high barrier for majority carrier recombination. In Cu(In,Ga)S₂ wide-gap absorber films the band gap is mainly determined by the Ga/(In+Ga) ratio. Based on the analysis of films prepared by different methods and of solar cells based on them, we show to which extent these requirements are already fulfilled. The Ga/(Ga+In) depth profile depends on the phase formation sequence during preparation. Models of the corresponding growth and diffusion mechanisms are presented. Up to now, barrier reduction could not be totally avoided. Our measurements identify the charge density at internal surfaces as an important parameter governing the recombination mechanism.
- D-II.2** 11:00 MINORITY CARRIER COLLECTION IN CuGaSe₂ SOLAR CELLS
R. Kniese(a), U. Rau(b), M. Powalla(a), (a)Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Wuerttemberg (ZSW), Hessbrühlstrasse 21c, 70565 Stuttgart, Germany, (b)Institut für Physikalische Elektronik, Universität Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart, Germany
The photovoltaic performance of CuGaSe₂ thin-film solar cells is limited by their relatively low open circuit voltage and by poor carrier collection that reduces the short circuit current of these devices. In addition, the photocurrent exhibits a strong voltage dependence that additionally degrades the fill factor of the solar cell. This contribution provides an experimental investigation and quantitative modelling of the spectral quantum efficiency (QE) of CuGaSe₂ solar cells with and without bias voltage. Experimentally, we find two different types of current collection in CuGaSe₂ solar cells. In the first case, application of reverse bias voltage leads to an increase of the QE in the long wavelength regime. This behaviour results from the increase of carrier collection by increasing the space charge region and the bias-independent part of carrier collection results from a minority carrier diffusion of about 0.25 μm. Other cells, though having as well a low response in the long wavelength regime of the QE spectra, do not exhibit a voltage dependence of carrier collection. In these cells, a part of the absorber material appears not to contribute to the photo current at all.
- D-II.3** 11:15 INFLUENCE OF IN-DIFFUSION ON SOLAR CELL PARAMETERS OF CELLS USING CVD OR MOCVD GROWN INSE-BUFFER LAYERS
S. Lindner, S. Siebentritt, J. Albert, M.Ch. Lux-Steiner, Hahn-Meitner-Institut, Glienicke Str. 100, 14109 Berlin, Germany
For solar cells based on chalcopyrite absorber layers ZnSe is used as an alternate buffer layer. It can be grown by CVD or MOCVD process at temperatures at and above 280°C. As shown in an earlier publication, the solar cell key parameters decrease as deposition temperature increases [1]. In order to explain the behaviour a set of samples has been prepared and consequently post-annealed at different temperatures. Thus it was possible to distinguish temperature related from other changes. Quantum efficiency measurements revealed no changes in effective collection length for the samples. Therefore changes in layer doping can be excluded as the origin of the alterations. Current voltage measurements on the other hand showed clear changes. The two diode model reveals a clear shift in the recombination path of the carriers. A path corresponding to recombination processes in the space charge region shows an exponential increase with annealing temperature. Taking this into account the changes in solar cell parameters are explained. In combination with results published before [2] the alterations in solar cell parameters can be attributed to the diffusion of indium from the absorber to the buffer layer.
[1] S. Siebentritt, T. Kampschulte, A. Bauknecht, U. Blieske, W. Harkeit, U. Fiedeler, M.Ch. Lux-Steiner, Solar Energy Materials & Solar Cells 70 (2002) 447
[2] S. Lindner, W. Bohne, A. Jäger-Waldau, M.Ch. Lux-Steiner, J. Röhrich, G. Vogl, Thin Solid Films 403-404 (2002) 432

- D-II.4** 11:30 **CHARACTERISATION OF DEEP DEFECTS IN CdS/CdTe THIN FILM SOLAR CELLS USING DEEP LEVEL TRANSIENT SPECTROSCOPY**
J. Versluys, P. Clauws, Ghent University, Department of Solid State Sciences, Krijgslaan 281 – S1, 9000 Gent, Belgium, P. Nollet, S. Degrave, M. Burgelman, Ghent University, Electronics and Information Systems (ELIS), Pietersnieuwstraat 41, 9000 Gent, Belgium
 The presence of deep defect levels in thin film solar cells can highly affect the characteristics of the photovoltaic energy conversion. Therefore, knowledge of the origin and nature of these defects is desirable.
 Deep level transient spectroscopy (DLTS) was performed on a series of CdS/CdTe thin film solar cells. Temperature scans between 5 and 320K revealed semi-shallow and mid-gap majority traps. These mid-gap traps were also investigated using isothermal DLTS (region 250 to 330K) where the temperature is kept constant and the rate window is varied. This way the mid-gap traps can be characterised completely. Using optical DLTS minority traps could be revealed. The optical excitation was performed using laserdiodes with wavelengths of 850 and 635 nm. These wavelengths were particularly chosen for their specific excitation region in the CdTe: 850nm excites the complete layer (sub bandgap wavelength), where 635nm only excites the CdS/CdTe interface because of the high absorption. A complete characterisation of the defect levels was performed. The effect of these defects on the solar cell characteristics is discussed, and an assignment for their origin and nature is proposed. The results are compared with literature data.
- D-II.5** 11:45 **DEPENDENCE OF CARRIER CONCENTRATIONS ON OXYGEN PRESSURE FOR Ga-DOPED ZnO GROWN BY ION PLATING METHOD**
Tetsuya Yamamoto, Kochi University of Technology; Toshiyuki Sakemi; Sumitomo Heavy Industries; Kiyoshi Awai, Sumiju Technical; Syo Shirakata, Ehime University, Japan
 We develop a technology for the fabrication of transparent conductive zinc oxide (ZnO) thin films in a large area. We grow the films by using ion plating systems with the plasma beam controller on glass substrates. On the basis of the analysis of both calculated data on the electronic states around the Fermi level in the conduction band obtained by a first-principle-electronic-band-structure calculations and thermodynamic properties, such as dissociation pressure of oxides, we selected a gallium (Ga) species as donor dopants. Low-resistivity ZnO:Ga with a film thickness of 200nm were grown at a discharge current of 100 A. The resistivity of the thin film was about $2 \times 10^{-4} \Omega \cdot \text{cm}$ in which the Ga content was about 3at%. Based on the analysis of the data on the dependence of the carrier concentrations on the oxygen pressure, we find that the carrier concentrations decrease slowly as the oxygen pressure increases at the low pressure. Based on the thermal-equilibrium theory, we conclude that the carriers are mostly generated by ionization of the Ga donors at the zinc sites (GaZn). On the other hand, beyond the oxygen pressure described above, we find that there decrease very rapidly the carrier concentrations with an increase in the oxygen pressure. Considering that the Ga can only diffuse when it is near a vacancy, the associate giving the proper oxygen dependence should be (GaZnVZn), where VZN means zinc-vacancy, which will exhibit as a donor killer since VZn can bind two electrons. This gives rise to a drastic decrease in the carrier concentrations. We will also present data on a fabrication of ZnO:Ga deposited by using the ion-plating systems in the range of width 550×650 mm.
- D-II.6** 12:00 **HIGH QUALITY TRANSPARENT ZINC OXIDE FILMS DEPOSITED AT RT**
Elvira Fortunato, Alexandra Gonçalves, Vitor Assunção, António Marques, Hugo Águas, Luís Pereira, Isabel Ferreira, Rodrigo Martins, Department of Materials Science/CENIMAT, FCT-UNL and CEMOP-UNINOVA, Campus da Caparica, 2829-516 Caparica, Portugal
 Transparent conducting oxide (TCO) with optical transmission more than 80 % in the visible region and resistivity less than $10^{-3} \Omega \cdot \text{cm}$ have been widely used as electrodes for optoelectronic devices. Most of the previous research on TCOs has been focused on ITO and FTO. However, TCO films based on zinc oxide are taking a great impact because of the advantages of low cost, resource availability (about a factor of 1000 more abundant than In), non-toxicity and high thermal/chemical stability. Al, In and Ga have been reported as an effective dopant for zinc oxide based films. Most of the works related to zinc oxide use Al as dopant. Nevertheless, Al presents a very high reactivity leading to oxidation during the growth of the film, which may become a problem. Ga is less reactive and more resistant to oxidation compared to Al. On the other hand, the covalent bond lengths of Ga-O and Zn-O are estimated to be 1.92 and 1.97 Å, respectively. The slightly smaller bond length of Ga-O than that of Zn-O is an advantage since it allows to minimize the deformation of the ZnO lattice even in the case of high Ga concentrations. In this work Ga-doped polycrystalline zinc oxide (GZO) thin films have been deposited at high growth rates by rf magnetron sputtering. The dependence of electrical, optical and morphological properties on the rf power density were investigated. The lowest resistivity ($1.9 \cdot 10^{-4} \Omega \cdot \text{cm}$) was obtained at RT. The films are polycrystalline with a hexagonal structure and a strong crystallographic c-axis orientation (002). The films present an overall transmittance in the visible spectra of about 90%. The low resistivity, accomplished with a high growth rate deposited at RT, enables the deposition of these films onto polymeric substrates for flexible applications.
- D-II.7** 12:15 -Invited- **R&D ROADMAP**
A. Jäger-Waldau, European Commission, DG JRC, Ispra, Italy
- 12:45 **LUNCH**

Tuesday, June 10, 2003
Mardi 10 juin 2003

Afternoon
Après-midi

14:00-15:30

POSTER SESSION I

Organic based SC

Chair: D. Vanderzande and J.H. Sloff

- D/PI.01** DONOR-ACCEPTOR DOUBLE-CABLE POLYTHIOPHENE COPOLYMERS WITH TUNABLE SPECTROSCOPICAL PROPERTIES
M. Catellani, S. Luzzati, N. Lupsac, R. Mendichi, R. Consonni, Istituto per lo Studio delle Macromolecole, Consiglio Nazionale delle Ricerche, Milano, Italy, F. Giacalone, J.L. Segura and N. Martin, Departamento de Química Orgánica I, Universidad Complutense, Madrid, Spain
The "bulk heterojunction" approach for organic photovoltaic applications suggests the preparation of intrinsically bipolar materials as a way to control both electronic and morphological properties at once. On these bases, the covalent grafting of the acceptor molecules to conjugated backbones can be a promising approach.
We have designed a thiophene substituted with a side chain containing, as acceptor, an anthraquinone moiety, that has been copolymerized with 3-alkylthiophene. The random copolymerisation of two monomers is a powerful and easy strategy to tune both the chemical composition and the electronic properties of the material. We have prepared a series of new polyalkylthiophene copolymers containing in the backbone thiophene rings substituted with electron acceptor. The macromolecular characterisation by GPC and NMR indicates that this synthetic approach leads to the formation of macromolecules with tunable acceptor/donor content. Emission measurements of this novel double-cable series show a photoinduced electron transfer from the donor backbone to the acceptor substituents, and this process can be tuned as a function of the anthraquinone content in the materials.
- D/PI.02** SOLAR CELLS BASED ON ORGANIC DISCOTIC MATERIALS
P. Destruel(a), M. Oukachmih(a), S. Fouet(b), S.Archambeau(a), I. Seguy(a), P.Jolinat(a), H. Bock(b) and G. Ablart(a), (a)Laboratoire de Génie Electrique de Toulouse, 118 route de Narbonne, UPS, Toulouse 31062, France, (b)Centre de Recherche Paul Pascal, 115 avenue Schweitzer, Pessac 33600, France
In organic solar cells, the generation of photocurrent is based on diffusion and dissociation of excitons and the transport of the resulting separated charges to the electrodes. To reach high efficiencies, each of these steps has to be optimized. Long exciton diffusion lengths and high charge-carrier mobilities have been reported in the self-assembled liquid crystalline phases of discotic molecules.
Our study concerned the use of such materials in organic photovoltaic cells. Triphenylene ether was used as hole transporting material, combined with perylene ester and benzo[ghi]perylene imides as electron transporting materials. Quantum efficiencies (~5%) were obtained with heterojunction cells made by vacuum deposition of amorphous layers. The carrier mobilities and energy levels were investigated using Time of Flight measurements and Cyclic Voltammetry respectively. Methods to improve this mobility by allowing the discotic molecules to self-assemble into homogeneously oriented layers will be reported. The performances could strongly be influenced by modifications of the different interfaces. The ITO was modified using argon plasma and UV-Ozone treatments which lead to different current-voltage characteristics. Coevaporation of the hole and electron transporting organics led to enhanced photocurrents. This indicates that the mixed layer consists of microsegregated domains separated by a large interface. Hence, an effective charge separation was achieved.
- D/PI.03** NEW COPOLYMERS FOR PHOTOVOLTAIC APPLICATIONS
L. Lutsen, K. Colladet, S. Fourier, M. Nicolas, D. Vanderzande, Limburgs Universitair Centrum, Universitaire Campus, Building D, departement SBG, 3590 Diepenbeek, Belgium
New copolymers having a low band gap between 1.5 eV and 1.8 eV have been synthesised and used as thin film in organic solar cells.
The monomers were chemically- and electro-polymerised. The band gap of both materials were studied and found to be similar. Organic solar cells were made and showed promising results.
- D/PI.04** ELECTRICAL AND OPTICAL CHARACTERIZATIONS OF MEH-PPV/C60 SOLAR CELLS
A. Ltaief(a,b), J. Davenas(b), A. Bouazizi(a), R. Ben Chaâbane(a), P. Alccouffe(b) and H. Ben Ouada(a), (a)Laboratoire de Physique et Chimie des Interfaces, Faculté des Sciences de Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisia, (b)Laboratoire des Matériaux Polymères et des Biomatériaux, Bâtiment ISTIL, 43 Boulevard du 11 Novembre 1918, Université Claude Bernard, Lyon 1, France
Due to the photoinduced charge transfer evidenced in conjugated polymer/fullerene (C60) composite; i.e. from non-degenerate ground state conjugated polymer to fullerenes, this novel class of materials became of considerable interest to be used in large-area, flexible and low cost photovoltaic devices [1,2].
In this work, we used the poly(2-methoxy-5,2'-ethylhexyloxy)-1,4-phenylenevinylene (MEH-PPV) as an electron donor and the buckminsterfullerene (C60) as an electron acceptor, mixed together to realize an interpenetrating network bulk-heterojunction. In this contribution, we first analyze the effect of solvent (THF and 1,2 dichlorobenzene) on the performance of MEH-PPV/C60 bulk heterojunction solar cell, using AFM images of the blend morphology and Photoluminescence spectroscopy; we have noticed that the quenching of PL intensity depends strongly on the solvent used; indicating the effect of the dispersion on the charge transfer efficiency between the MEH-PPV and the C60. In a second step, our interest is focused on photovoltaic parameters such as: ISC, VCO and FF versus the concentration of C60 in MEH-PPV polymer, with the aim to show the existence of a threshold concentration in the blend.
[1] S.N.Sariciftci, L.Smilowitz, A.J.Heeger and F.Wudl, Science 258 (1992) 1474.
[2] C.J.Brabec and S.N.Sariciftci, Monatshefte für Chemie, 132 (2001) 421-431.
- D/PI.05** **withdraw**
- D/PI.06** **withdraw**

D/PI.07

Au/CuPc INTERFACE: A PHOTOEMISSION INVESTIGATION

L. Lozzi, S. Santucci, INFN and Department of Physics, University of L'Aquila, L'Aquila, Italy, S. La Rosa, Sincrotrone Trieste SCpa, SS 14 Km 163.5 in Area Science Park, 34012 Basovizza, Trieste, Italy

Copper phthalocyanine (CuPc) properties are strongly investigated for photovoltaic applications as thin film. One of the most important parameters for highly efficient photovoltaic thin film is the quality of the interface between the active film and the metals which will extract the carriers. In this study we will show our results on the investigation of the interface of between CuPc and Au by means of photoemission. We have deposited, by means of thermal evaporation in ultra high vacuum conditions, very thin Au films on a 70 nm thick CuPc film and we have investigated both core levels and valence band features as a function of the Au thickness. We have used different photon energies (from X-ray to UV) to investigate surface and in depth properties. Moreover we have performed high spatial resolution photoemission experiments to investigate the homogeneity of the Au film on the organic film. Our results indicate the formation of Au clusters which diffuse inside the CuPc film. This diffusion decreases the ionisation energy of the organic film from about 5.1 eV to less than 4.5 eV and, when a Au bulk like film is obtained, the film work function is still quite low, about 4.4 eV. Moreover we have calculated a carrier barrier at the Au/CuPc interface of about 0.8 eV. The investigation with the high spatial resolution photoemission has shown a good spatial homogeneity of the gold deposition, even where defects on the surface film are present.

D/PI.08

COPPER PHTHALOCYANINE BASED THICK FILM P-I-N DEVICES FOR SOLAR CELL APPLICATIONS

K. Arshak, J. Harris, S. O'Connor, O. Korostynska, Electronic & Computer Engineering Department, University of Limerick, Plassey Technological Park, Limerick, Ireland

Single-crystal and polycrystalline silicon, along with cadmium-based compounds are the three most studied systems for photovoltaic applications. Since technology for growing silicon crystal is rather expensive, and CdTe has toxicity problems, there is a need to search for viable alternatives. This work explores the development of solar cell using organic materials. In this study the devices were constructed on silicon wafers that were doped n-type by the vendor. The polished front-side of the wafers forms the intrinsic layer. Copper Phthalocyanine (CuPc) was used as a p-type material due to its high temperature and chemical stability. Band gap of 2.1 eV makes CuPc suitable candidate for solar cell material. Carbon powder was added to polymer CuPc based thick film paste in different percentage ranging from 0.1 % to 40 % to fluctuate the conductivity of the material, while PVB was used as a polymer and C8H18O3 as a solvent. These p-type pastes were screen-printed onto the front side of the silicon wafers to complete the junctions. Different compositions of the paste with carbon were explored, resulting in various device configurations. All fabricated devices showed p-i-n behaviour. Their current-voltage characteristics were examined in darkness and under the light illumination. Devices containing 2% and 4 % of Carbon performed as solar cells under bias conditions. Such parameters as Short Circuit Current I_{sc} , Open Circuit Voltage V_{oc} and Fill Factor FF were measured.

D/PI.09

PENTACENE BASED PHOTODIODE WITH SCHOTTKY JUNCTION

Jiyoul Lee, D.K. Hwang, C.H. Park, S.S. Kim and Seongil Im, Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Korea

Pentacene based Schottky photodiode has been fabricated with pentacene films deposited on a thin Cr metal. The energy band gap of pentacene was characterized by ellipsometry and direct absorption spectroscopy determined to be 1.82 eV. Photovoltaic effects were observed from the Cr / pentacene Schottky contact under a monochromatic red light of 1.85 eV (670 nm) and dynamic photo-response were also measured by pulsing the red light. Spectral photo-responses on our new photodiode were measured in the range of 325 ~ 650 nm and more details on the spectral photo-response are to be discussed.

D/PI.10

SELF-ASSEMBLED CHROMOPHORES FOR HYBRID SOLAR CELLS

T.S. Balaban, Forschungszentrum Karlsruhe, Institute for Nanotechnology, Postfach 3640, 76021 Karlsruhe Germany

One of the main problems encountered in the dye-photosensitization of wide band semiconductors which have potential use for low-cost hybrid solar cells is the non-specific aggregation of the dye molecules. This effect leads to strong quenching of the dye fluorescence and thus to low device efficiencies. We have designed and synthesized novel chromophores which self-assemble by specific supramolecular interactions forming nanostructures which are strongly fluorescent. Our fully synthetic molecules are mimics of the natural self-assembling bacteriochlorophylls c, d and e which form the light-harvesting apparatus of green photosynthetic bacteria. Our biomimetic approach has allowed us to prepare, in fairly large amounts, various self-assembling porphyrins and chlorins with tailored properties. We can control both the chirality and the optical properties through ordering the transition dipole moments of the chromophores within the self-assembled nanostructure. Very broad absorption spectra, beneficial for efficient light collection over almost the entire visible spectrum, characterize some of our assemblies. Upon anchoring the self-assembled chromophores onto nanocrystalline titania with different grain sizes the fluorescence is not quenched. This fact encourages us to fabricate hybrid devices and measure their photocurrent generation efficiencies.

D/PI.11

A COMPARISON OF CHARGE CARRIER MOBILITIES BY TIME OF FLIGHT BETWEEN STATE-OF-THE-ART 'GILCH' AND 'SULPHINYL' SYNTHESISED MDMO-PPV

Lionel Sicot, Jocelyne Leroy, Carole Sentein, CEA Saclay, DRT/DECS/SE2M/ Laboratoire Composants Organiques Fonctionnels (LCOF), Bâtiment 451, 91191 Gif-sur-Yvette Cedex, France and Laurence Lutsen, Dirk Vanderzande, IMEC-IMOME division, Organic and Polymer Chemistry Group, Limburg Universitair Centrum, SBG department, building D, 3590 Diepenbeek, Belgium

Production and transport of electrical carriers from generation sites to electrodes are two key-processes in organic solar cells. The conversion efficiency is then highly dependant on charges mobility in organic thin films. Best efficiencies of organic solar cells are obtained today for organic bulk hetero-junctions photovoltaic cells based on an interpenetrating donor-acceptor network in the bulk. Poly(2-methoxy-5-(3,7-dimethyl-octyloxy))-p-phenylene vinylene (MDMO-PPV) as an electron donor and (6,6)-phenyl-C61-butyric-acid (PCBM) as an electron acceptor yielded the highest efficiency until now in this class of devices. Different ways of synthesis are possible for the MDMO-PPV leading to different conformations for polymers with different controlled defect level rates. Hence, several MDMO-PPV obtained by different synthesis routes have been used to investigate the relation between structural defects, mobility of the electric charges and power efficiency.

D/PI.12

PRINTABLE ANODES FOR FLEXIBLE ORGANIC SOLAR CELL MODULES

Tom Aernouts, Peter Vanlaeke, Wim Geens, Jef Poortmans, Paul Heremans, Staf Borghs, Robert Mertens, IMEC vzw, Kapeldreef 75, 3001 Leuven, Belgium, Ronn Andriessen, Luc Leenders AGFA-GEVAERT NV, Septestraat 27, 2640 Mortsel, Belgium

A relatively recent field for applications of organic conjugated materials is that of photovoltaic devices. Our particular interest concerns the concept of the interpenetrating bulk donor-acceptor heterojunction. Spin-coated organic blends of poly(phenylene-vinylene)s (PPVs) and a soluble fullerene derivative (PCBM) have been used as active material sandwiched between a transparent electrode and an Al backside contact.

Up to now, expensive material like ITO (indium-tin oxide) has been commonly used as a transparent electrode. Nevertheless, an interesting alternative in the form of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) is emerging. Combining its low-cost and ease of processing will make large-scale production of fully flexible organic solar cells possible. In this work, a comparison is made between cells with either ITO or PEDOT/PSS as a transparent contact. Different techniques such as spin coating and screen printing are used to deposit this latter material. In this way, large area devices are developed making it possible to realize serially connected solar cells. The performance of these devices will also be reported.

D/PI.13

THE INFLUENCE OF THE DONOR/ACCEPTOR RATIO ON THE PERFORMANCE OF ORGANIC BULK HETEROJUNCTION SOLAR CELLS

Tom Aernouts, Peter Vanlaeke, Wim Geens, Jef Poortmans, Paul Heremans, Staf Borghs, Robert Mertens, IMEC vzw, Kapeldreef 75, 3001 Heverlee, Belgium

Bulk donor/acceptor (D/A) heterojunction solar cells are examined with an active layer that consists of a spin coated blend of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) and a soluble C60-derivative (PCBM). The light absorption in these organic devices appears mainly in the MEH-PPV donor material, whereas a sufficient amount of fullerene acceptor material is necessary to have good percolation for generated negative charges. Therefore, solar cell devices with different D/A ratio have been characterised by dark and illuminated IV-measurements to study their relative device performance. Rectification ratio, short circuit current, open circuit voltage and fill factor reflect a clear dependence on the used donor/acceptor ratio. The blends have also been incorporated in field-effect transistors (FETs) to examine the influence of the different ratios on the charge carrier mobility.

A discussion of these results with respect to the optimal device performance of the organic solar cells will be presented.

D/PI.14

SYNTHESIS AND CHARACTERIZATION OF POLYTHIOPHENE DONOR-ACCEPTOR DOUBLE-CABLE CONTAINING NIKEL PHTHALOCYANINE

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In polymeric solar cells the active layer is a bulk heterojunction in which a conjugated macromolecule and an electron acceptor are blended together. Another route to obtain a nanoscopic phase-segregated network is the "double-cable" approach in which the acceptor molecule is covalently linked to an electron donating conjugated backbone.

Following this strategy we have designed a polyalkylthiophene copolymer containing in the side chains a new electron acceptor moiety, a nickel phthalocyanine. The random copolymer has the 10% in mole of phthalocyanine respect to the thiophene rings and exhibits a good solubility. The macromolecular and optical characterisations of the copolymer by GPC, NMR, absorption and emission are reported. The electronic absorption features of the copolymer show that this material exhibits an improved match to the solar spectrum with respect to other conjugated polymers.

D/PI.15

PROBING THE SUBGAP ABSORPTION OF PHOTOVOLTAIC POLYMER BLENDS BY THE CONSTANT PHOTOCURRENT METHOD

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The Constant Photocurrent Method (CPM) is a well-established technique used to determine subgap absorption in inorganic amorphous or microcrystalline semiconductors. In contrast to conventional photoconductivity measurements, CPM measures the incident photon flux required to keep the observed photocurrent constant while the photon energy is scanned.

In a first series of experiments we investigated pristine films of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV), (6,6)-phenyl C61-butyric acid methyl ester (PCBM) and photovoltaic blended films of both compounds in a MEH-PPV:PCBM weight ratio of (1:4). An exponential dependence of the absorption coefficient on the photon energy, also called the Urbach tail, is observed in all three layers. For MEH-PPV the onset at high energy of the Urbach tail is located at ~2.1 eV, in PCBM it lies at ~1.7 eV. For MEH-PPV:PCBM the tail is shifted to ~1.3 eV, indicating the formation of new bandgap states. The Urbach parameter, determined by the logarithmic slope of the absorption, is 0.043 eV for both MEH-PPV and the MEH-PPV:PCBM composite, which indicates that their structural disorder is comparable. Finally there is a distinct trailing off from the Urbach tail at energies below 1.9eV observed for pristine MEH-PPV. This reflects the presence of a considerable amount of defects states. Similarly, the results of ongoing measurements on poly(3-hexylthiophene) (P3HT) and a series of photovoltaic blends of P3HT and PCBM will be discussed.

D/PI.16**HIGHLY ORDERED, ANISOTROPIC THIN FILM STRUCTURES BASED ON PARA-SEXIPHENYL**

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Para-sexiphenyl (PSP) based structures are interesting for optoelectronic applications due to high blue luminescence of PSP itself, and the possibility of photoinduced charge transfer to the fullerenes in PSP/C60 bilayers. Recently, we demonstrated that highly ordered structures of PSP and C60 can be grown by Hot Wall Epitaxy (HWE) on mica substrate. In this work we performed a detailed study of the PSP growth on other crystalline substrates like MoSe₂, MoS₂, GeS, KCl, NaCl and SrF₂, in order to find the growth process controlling parameters. It is shown that the substrate temperature and substrate type are the most decisive parameter for the morphology of epitaxial films and therewith for their optical and electrical properties.

Using HWE we were also able to grow the PSP layers for light emitting diodes as well as PSP/C60 multilayer donor-acceptor structures for photovoltaic cells. Such optoelectronic devices sandwiched between ITO and Al electrodes are fabricated and their characteristics are presented and discussed.

D/PI.17**EFFECT OF SURFACE CHEMISTRY ON ELECTRON TRANSPORT IN MESOPOROUS TiO₂ FILMS**

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In dye sensitized solar cells (DSSCs) interconnected, nm-sized, wide bandgap semiconductor particles (usually TiO₂), are deposited on a transparent conducting oxide electrode (TCO) and sensitized with a dye, which, upon illumination, injects electrons into the TiO₂ conduction band. For a DSSC it is crucial that most of these photoinjected electrons can be collected at the TCO electrode. For this we need to understand how electrons are transported through the TiO₂ network. We investigate the transport properties by depositing mesoporous TiO₂ films on metal electrodes, separated by a 5-20 micron lateral gap, depending on the individual electrode. The sample was immersed into an electrolyte solution and the conductivity between the metal electrodes was measured as a function of the electrodes' potential vs. a reference electrode using a bipotentiostat. It is commonly assumed that TiO₂ surface states play a major role in DSSC operation, because they can act as electron traps and recombination centers. These strongly influence electron transport and, thus, cell efficiency. Molecular adsorption can quench surface states and was therefore used to modify the mesoporous film surface. We investigated the electron transport as a function of different molecular binding groups and dipole moments and find that the TiO₂ CB level can be systematically shifted with molecular dipole moment. Different molecular binding groups affect the measured conductivity. Measurements on several electrodes with different gap widths suggest that the current density does not scale linearly with (gap width)⁻¹, as would be expected from a simple electron drift or diffusion model. Possible reasons for this will be discussed.

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D/PI.18**CURRENT LIMITING MECHANISMS IN POLY(3 HEXYLTHIOPHENE) THIN FILM DEVICES**

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Current limiting mechanisms in Indium Tin Oxide/ Poly(3hexylthiophene)/Aluminium (ITO/P3HT/Al) thin film devices were studied through the analysis of temperature dependent current-voltage characteristics. The study showed that current flow across these devices, of about 20 nm thickness, may be limited by hole injection at the Al/P3HT interface at temperatures below 240K, when the device is reverse biased, with high potential on Al. Above this temperature, the bulk transport properties control the characteristics. For the forward bias, the ITO/P3HT contact does not limit the current, instead a space charge that accumulates due to the low charge carrier mobility in the polymer, does. An expression that provides a criterion for the determination of the validity of application of either the Richardson-Schottky thermionic emission model or the Fowler-Nordheim field emission (quantum mechanical tunneling) model was deduced. This allows the determination of the field at which the charge injection through thermionic emission equals that through field emission, for a given temperature, and interface potential barrier height, and hence the transition conditions thereof. Our data, as well as that from other scientific publications, fitted very well to the deduced expression. Theoretical limits of the model were also discussed. The calculated barriers using the field emission model gave 0.4 eV for the ITO/P3HT interface and 1.08 eV for the Al/P3HT interface, in conformity with the observed contact limitation and space charge limitation of current respectively.

D/PI.19**HIGHLY EFFICIENT ORGANIC PHOTOVOLTAIC DEVICES**

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We present results on photovoltaic devices based on donor-acceptor organic small molecule blends and doped charge transport layers. The doped transport layers are formed using high vacuum co-evaporation deposition technique (i.e. co-sublimation of matrix and dopant). Solar cell devices have been fabricated based on zinc-phthalocyanine (ZnPc) as donor (D) and fullerene (C60) as electron acceptor (A) with doped charge transport layers. The highest energy conversion efficiencies of these cells under 1/10 sun (10 mW/cm²) and under 1 sun, standard AM1.5 illumination (100 mW/cm²) are over 3% and about 2%, respectively. We have observed that the performance of such 'bulk heterojunction' photovoltaic devices is critically dependent on the transport properties of the interpenetrating network D/A system and doped charge transport layers. In this report, comparative results of I-V characteristics, energy or power conversion efficiencies as well as the dependence of short circuit current on incident white light illumination will be discussed. Further possible enhancement is discussed by analyzing the single parameters that contributing to the power conversion efficiency on such organic solar cells.

D/PI.20

PHOTOINDUCED CHARGE TRANSFER IN A POLYTHIOPHENE COPOLYMER CONTAINING NICKEL PHTHALOCYANINE SUBSTITUENTS

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The use of conjugated polymers as photoactive materials in photovoltaic devices is based on the photoinduced charge transfer between organic materials with different ionisation potential and electron affinity. To obtain a good charge photogeneration and transport it is necessary to attain an intimate mixing of the donor-acceptor components and to control the morphology of the photoactive layer. A proposed approach to get these properties is the covalent linking of the electron acceptor moieties to an electron donating conjugated polymer backbone.

According to this strategy, we have designed an alkylthiophene copolymer containing nickel phthalocyanine acceptor substituents. The content of the acceptor in the copolymer is 10 % in mole respect to the thiophene rings. The electronic absorption features of the copolymer display a better matching to the solar spectrum with respect to other conjugated polymers, due to the contribution to the spectrum of the phthalocyanine Q-band transition, peaked around 700 nm, which exhibits an intense oscillator strength. In this work we report a photophysical characterisation of this material by FTIR photoinduced absorption. The measurements indicate that photoinduced charge transfer is occurring either by the selective excitation of the thiophene backbone or by the selective excitation of the phthalocyanine Q-band. Thus the phthalocyanine moiety has the double function of acceptor and of light absorber to get charge photogeneration. These features open up interesting perspectives for the use of this copolymer in photovoltaic devices.

D/PI.21

RUTHENIUM PHTHALOCYANINE THIN FILM FOR PHOTOVOLTAIC APPLICATIONS

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In the last few years organic and polymeric materials have been deeply investigated for low cost photovoltaic purposes, even considering the poor conversion efficiency. In fact they are potentially cheap and easy to process in thin film also on plastic substrate. In this work we focus first on ruthenium phthalocyanine (RuPc)₂ and fullerene (C₆₀) materials obtained by evaporation process. They show good performance in transport properties that can be easily modified by doping process. Furthermore the absorption in the visible spectrum of phthalocyanine film joined to the (C₆₀) absorption can be useful to extend the device absorption of the solar spectrum. In particular we have grown ITO/(C₆₀)/(RuPc)₂/Au stacked structure on corning glass substrate. Different thickness of both n-type (C₆₀) and p-type (RuPc)₂ have been considered to evaluate compatibility between material properties to obtain photovoltaic performances. Encouraging 0.05mA/cm² has been achieved for the short circuit current evaluated by both quantum efficiency and current voltage under AM1.5G measurements. On the base of preliminary results we are confident to investigate the potentiality of (RuPc)₂-based solar cell introducing Langmuir-Blodgett, useful to obtain higher order molecular film, or other wet method as deposition system. These processes represent a very low cost solution to obtain higher quality material for photovoltaic conversion. Comparison of results obtained by evaporation and other techniques will be presented and discussed.

D/PI.22

MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF PLASMA SPRAYED POROUS TiO₂ COATINGS CONTAINING ANATASE

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The electrical properties of TiO₂ are very sensitive to microstructure and phase composition. In the present study, plasma sprayed porous TiO₂ coatings containing anatase were prepared using the starting powders composed of anatase and Ar-He-H₂ and Ar-He-N₂ as plasma gases. The microstructure and phase composition of the coatings were characterized with scanning electron microscopy and X-ray diffraction, respectively. The electrical properties of the coatings were investigated by impedance spectroscopy in the frequency range from 1 Hz to 106 Hz and at temperature from room temperature to 400 °C. The obtained coatings had porosity values from 32% to 43% and pore size from 1 μm to 80 μm. They were mainly composed of rutile phase with 13.6% to 14.7% anatase phase. The measured electrical data could be clearly correlated with the microstructure and phase composition of the coatings.

D/PI.23

POLYMER SOLAR CELLS WITH NOVEL FULLERENE-BASED ACCEPTOR

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We investigated a novel fullerene acceptor material, DPM-12, for polymer-fullerene bulk-heterojunction solar cells. Surprisingly high open circuit voltage in the range 0.92V-0.94V was measured in these devices. Although the Voc is expected to correlate with the acceptor strength, the measured value is by at least 100mV higher than the expected from the redox potential. Measurements of the optical absorption and the external quantum efficiency demonstrated no significant improvement of the spectral sensitivity upon the replacement of conventional PCBM acceptor by DPM-12. However, the IPCE indicates lower short-circuit currents. From the temperature profiling of the solar cell parameters we found a nearly temperature independent Voc of 0.93V-0.97V in the temperature range 200-300K followed by a decrease at temperatures below 200 K. A nearly linear increase of Voc in the whole temperature range, however, is expected. The light intensity dependence of the short-circuit current density obeys a superlinear growth in the range 0.1-20mW/cm² and changes into sub-linear one with the scaling exponent of 0.8. We conclude that the molecule DPM-12 has a good potential to optimise the efficiency of bulk-heterojunction solar cells in terms of increasing the open circuit voltage.

D/PI.24**PHOTOGENERATION OF CHARGE CARRIERS IN BLENDS OF CONJUGATED POLYMERS AND SEMICONDUCTING NANOPARTICLES**

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We investigated the photoinduced charge transfer reactions in blends of CdSe and InP nanoparticles with conjugated polymer MDMO-PPV. The advantages of using semiconducting nanoparticles is the combination of electron acceptor properties with size dependent optical properties. Further, the particles size is assumed to influence their electron affinity. Two different types of particles were used: with a TOPO-TOP shell and pyridine treated nanoparticles. Particle size was in the range 3.1- 4.9nm. The photoinduced absorption spectroscopy revealed structured features attributed to photoexcited polaronic states in conjugated polymer at energies 0.5eV and 1.3eV. They are similar to fullerene-doped conjugated polymers, however, very different from those in a undoped polymers, where only the triplet absorption is present. A strong ESR signal was observed under photoexcitation of blends, whereas no dark signal prior and after photoexcitation was found. Generally, all the spectroscopic features showed up much stronger in composites with uncapped nanoparticles. All these features together with a strong quenching of the polymer photoluminescence support the scenario of electron transfer from polymer to nanoparticles. Although no spectral signatures of anion radicals related to nanoparticle were identified, the fate of electrons was studied from the recombination kinetics by means of light intensity and modulation frequency dependence at various temperatures. The lifetimes and recombination mechanisms were determined.

D/PI.25**ELECTRICAL-OPTICAL CHARACTERISATION OF POLYTHIOPHENE BASED BULK HETEROJUNCTION SOLAR CELLS WITH DIFFERENT DONOR/ACCEPTOR RATIOS**

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Spin coated blends of regio-regular poly(3-hexyl-thiophene) (P3HT) and a soluble fullerene derivative (PCBM) have been used as the active layer in organic solar cells. Whereas pristine P3HT films show a certain ordering due to the regio-regularity of the material, completely amorphous films are formed upon mixing PCBM acceptor material with the conjugated polymer. However, the ordering of the thiophene matrix can be restored in the blend by thermal treatment of the film. This phenomenon can be clearly observed by comparison of e.g. the absorption spectra of the treated and untreated devices.

Optimization of the thermal treatment with respect to the performance of the solar cells for different donor/acceptor ratios has been examined. Dark and illuminated IV-measurements have been used to study the relative performance of treated or untreated devices. In this way, characteristic temperatures have been determined to obtain optimized values for short circuit current, open circuit voltage and fill factor for each donor/acceptor ratio. Incorporation of the blends in field-effect transistors (FETs) made it possible to examine also the charge carrier mobility in these films.

D/PI.26**STUDY OF THE ROLE OF CHEMICAL DEFECTS IN MDMO-PPV FOR PHOTOVOLTAIC APPLICATIONS USING PHOTOTHERMAL DEFLECTION SPECTROSCOPY**

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The 'bulk heterojunction' is one of the most promising and versatile concepts in the field of organic solar cells. A significant increase in efficiency has been demonstrated for devices based on MDMO-PPV synthesised via the 'precursor' route in comparison with devices based on 'Gilch' synthesised MDMO-PPV. In order to understand the higher efficiency values, the role of chemical defects in the backbone is investigated. These chemical defects could introduce states in the bandgap, acting as trapping centers and limiting the charge carrier mobility. To investigate the density of states (DOS) in the gap of conjugated polymers, we have introduced Photothermal Deflection Spectroscopy (PDS) as a highly sensitive technique to detect defect related optical absorption in thin films of MDMO-PPV. Three variations of 'precursor' MDMO-PPV were synthesised, characterized by a different degree of chemical defects and possible influences on the electronic structure of MDMO-PPV are evaluated. PDS-measurements revealed an increase in defect related absorption with increased amount of chemical defects, implying a detrimental effect on the power conversion efficiency when these polymers act as electron donating material in a 'bulk heterojunction' solar cell. This paper gives clear evidence that PDS is particularly suitable to monitor the defect DOS in conjugated materials comprising a very high sensitivity and measurement speed.

D/PI.27**SYNTHESIS AND PROPERTIES OF CONJUGATED POLYMERS CONTAINING {Ru(terpy)2} UNITS**

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The modification of electrodes using polymeric films has been widely studied in recent years. Particularly, polymers containing ruthenium complexes in the backbone appear to be an interesting class of materials, due to the interesting photophysical and photochemical properties of these complexes [1-2].

In this work, the ligand 2,2':6',2" terpyridine was used as a basic skeleton on which we attached furyl, pyrrolyl, thienyl and bithienyl moieties, at position 4' of the tridentate ligand. Electropolymerisations of the Ru homoleptic complexes with the terpyridine ligands bearing pyrrolyl, thienyl and bithienyl units have been carried out on platinum, glassy carbon and fluorine-doped tin oxide electrodes. The 2 furyl moiety on heteroterpyridyl-complex appears to be an interesting precursor of the carboxylic acid function, which is known to be useful for TiO₂ surface modification.[3] The monomers and/or the corresponding polymers have been characterised by UV-Vis, emission, ¹H NMR spectroscopies, SEM analysis, and by (photo-)electrochemical measurements.

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D/PI.28

INFLUENCE OF SPIN-COATING SOLVENT ON THE EXCITON DIFFUSION LENGTH IN SMOOTH TiO₂/PPV BI-LAYERS

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Conjugated polymers, such as poly-(p-phenylenevinylene)s are promising materials for application in solid state dye sensitized semiconductor solar cells. On light absorption by the polymer electron injection into the conduction band of the semiconductor occurs. In this type of cell the polymer thus acts as both the sensitizing and hole transporting layer. One of the key parameters governing the efficiency of the cell is the exciton diffusion coefficient (D) which determines to what extent photons absorbed not directly in the vicinity of the interface with the TiO₂, contribute to the overall efficiency.

Recent studies have showed that by changing the spin-coating solution the morphology of the polymer layer can be controlled, thereby affecting D. To determine this parameter we have studied the photo-induced charge separation in bilayers of smooth anatase TiO₂ and spin-coated poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene) using the Flash Photolysis Time-Resolved Microwave Conductivity technique (FP-TRMC). This technique allows us to determine the number of injected electrons into the CB without the necessity of applying conductive electrode layers that can introduce additional complications. The different solvents used for spin-coating are chlorobenzene, toluene, p-xylene and o-dichlorobenzene. Preliminary results show that the latter solvent results in a higher efficiency. This may be explained to the more stretched conformation of the polymer chains in solution which is maintained during the spin coating process, resulting in an increased exciton diffusion coefficient.

D/PI.29

THE APPLICATION OF LOW-BANDGAP CONJUGATED POLYMERS FOR SENSITIZATION OF TiO₂, ZnO AND SnO₂

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The application of conjugated polymers in photovoltaic devices has so far been concentrated on different poly-(p-phenylenevinylene)s (PPVs) and polythiophenes. However, to obtain a better spectral overlap between the absorption of the active layer and the solar emission, which peaks at 1,7 eV, polymeric materials such as the low-bandgap compound PTPTB (bandgap 1.8 eV) are essential. We have studied the photoinduced charge separation between bilayer systems of this low-bandgap polymer and different semiconductors (SCs), i.e. TiO₂, ZnO (CB edge -0.67 vs. SCE) and SnO₂ (CB edge 0.03 vs. SCE), using the Time-Resolved Microwave Conductivity technique. This technique allows the intrinsic properties of the sensitizer and the semiconductor to be measured without the necessity of applying conductive electrode layers that can introduce additional complications.

For all bilayer systems the photoconductivity action spectrum closely resembles the optical absorption of the polymer layer, with a maximum at 620 nm. Surprisingly, for the PTPTB/SnO₂ bilayer a 30 times higher efficiency than for the PTPTB/TiO₂ and PTPTB/ZnO combinations is found. Considering the oxidation potential (0.55 vs. SCE) and the optical band-gap of the polymer, interfacial charge separation between PTPTB and SC should be feasible for all PTPTB/SC systems. Although we cannot exclude the electronic coupling between polymer and the SCs to be different, we suggest that the increased energy difference between the PTPTB exciton energy level and the SnO₂ CB edge might be crucial for the dissociation of the coulombic bound electron-hole pair, resulting in the dramatically enhanced efficiency for the PTPTB/SnO₂ bilayer.

D/PI.30

PROSPECTIVES IN POLYMER BULK-HETEROJUNCTION PHOTOVOLTAICS

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Several barriers stand in the way of achieving low-cost polymeric bulk-heterojunction photovoltaics.

The current generation of devices mostly use PPV, and need an oxygen-free atmosphere to prevent destructive photo-oxidation even on a laboratory time-scale: the need for hermetic encapsulation prevents low-cost manufacture. More stable conductive polymers are available and under investigation (notably polythiophenes, which are also cheaper than PPV); however photo-oxidation resistance is degraded if side-groups are attached to make polymers soluble. The side-groups also reduce conductivity, which results in poor charge collection efficiency and/or limits the thickness, which results in poor light absorption. If the problem of encapsulation cost can be overcome, the cost benefit of polymer PV stems from the elimination of vacuum processing. However, devices made by evaporating polymer solutions require very flat TCO layers. These are made by vacuum deposition, as is the back-contact. Therefore a new approach to bulk-heterojunction manufacture is proposed, which eliminates the need to solubilize the conductive polymer(s) using side-groups, and requires no vacuum processing.

D/PI.31

HIGH EFFICIENCY OLEDs AND ORGANIC SOLARCELLS BASED ON SINGLE OR MULTIPLE P-I-N STRUCTURES

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We have recently demonstrated phosphorescent p-i-n-type OLEDs with high power efficiency even at high brightness. Here, we show that also the performance of organic solar cells can be strongly improved using p-i-n-structures with doped wide-gap transport layers and a phthalocyanine-fullerene blend as a photoactive layer. Such cells only absorb light in the photoactive region and thus avoid recombination losses at the contacts and make optimum use of the light reflected at the top contact. They reach about 2% power efficiency at AM 1.5 illumination, nearly 100% internal quantum efficiency and a fill factor of about 50%. We show that it is possible to stack two or more of these optically thin pin-cells into one sandwich structure without significant losses. This principle should soon enable us to prepare organic solar cells with outstandingly high efficiency.

In the solarcells, a new technique of n-doping by cationic dyes is used. Using fullerene or perylene derivatives as a matrix, it yields thermally very stable layers with high conductivity. Spectroscopic details (UV-VIS, FTIR, mass spectroscopy) on the doping mechanism will be presented.

D/PI.32**LUMINESCENCE STUDIES OF HIGHLY-ORDERED NANOSTRUCTURES OF PARA-SEXIPHENYL GROWN BY HOT WALL EPITAXY**

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The para-sexiphenyl (PSP) is a very attractive material for many organic optoelectronic applications due to its good thermal stability, high blue electroluminescence efficiency and ability to be deposited in form of well ordered films. We report photoluminescence (PL) and thermally stimulated luminescence (TSL) studies over a broad temperature range 5-300 K in highly-ordered PSP nanostructures grown by Hot Wall Epitaxy on a mica substrate. A low-energy broad band is observed in PL spectra, which can be attributed to the emission from molecular aggregates. While the intrinsic exciton emission dominates at low temperatures, the emission from aggregates relatively considerably increases with elevating temperature and its pronunciation depends sensitively on film preparation conditions. Time-resolved PL measurements show that the aggregate emission has the life-time of 4 ns, which is about an order of magnitude longer than life-time of singlet excitons. A low-temperature TSL peak at around 30 K, which is principally very similar to that we observed before in weakly disordered conjugated polymers, evidences for a weak energy disorder in PSP films, and have been interpreted in terms the hopping model of TSL in disordered organic materials.

D/PI.33**INVESTIGATION OF EXCITED STATES IN POLYMER/FULLERENE SOLAR CELLS BY MEANS OF PHOTOINDUCED REFLECTION-ABSORPTION SPECTROSCOPY**

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The discovery of a photoinduced charge transfer interaction between conjugated polymers and fullerenes leads to intensive spectroscopic investigations in solid state composites of these materials. Highly efficient photovoltaic devices using bulk heterojunctions [1] could be prepared. Up to now, most spectroscopic investigations were done on thin films, whereas little is known about the behavior of the photoinduced charge carriers under working conditions of the device.

In this work, we used thin film photovoltaic devices composed of a bulk heterojunction of MDMO-PPV and PCBM, ITO as the transparent electrode and aluminum or gold as the second electrode. These devices were investigated by means of photoinduced reflection-absorption spectroscopy at temperatures between 5K and 300K and different applied external electric fields. Significant changes were observed for the density of the positive polarons on the conjugated polymer backbone upon changing the applied voltage. The results are discussed in comparison with current-voltage characteristics of the devices.

[1] 'Plastic Solar Cells'; Christoph J. Brabec, N. Serdar Sariciftci, Jan C. Hummelen, *Advanced Functional Materials*, Vol. 11, No. 1, pp. 15-26 (2001)

D/PI.34**TiO₂ NANOCRYSTALS – CONJUGATED POLYMER THIN FILMS FOR PHOTOVOLTAIC APPLICATION**

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Last years have seen an unprecedented growth of interest in 'soft' solar cells that use the biomimetic approach of the hybrid organic/inorganic nanostructure, due to their suitability to construct large-area devices and the good electrical and optical properties of the organic and inorganic semiconductors. In this work a detailed study of the optoelectronic processes occurring in colloidal TiO₂ nanocrystals and MEH-PPV conjugated polymer composites is presented.

We have employed a novel chemical route to obtain shaped-controlled synthesis of both organic-capped TiO₂ anatase nanorods and spherical nanoparticles. Hydrolysis of titanium alkoxides has been performed in oleic acid as surfactant in presence of tertiary amines or quaternary ammonium hydroxides as catalysts. The obtained titania nanocrystals can be isolated and dispersed in concentrated organic solutions with excellent stability, providing a new source of easy processable oxide material for technological applications. Composite films were prepared by mixing low molecular weight MEH-PPV obtained via organo-metallic methodology with spherical or rod-like TiO₂ nanocrystals in a suitable weight ratio, obtaining a viscous solution to spin coating onto substrates. Optical absorption and emission spectroscopies were used to extensively studying both solutions and composite films at different size and shape of TiO₂ nanocrystals. The hybrid structures, deposited on low resistivity ITO substrates, were investigated as active media in photovoltaic devices, focusing on the photoinduced charge transfer and recombination processes at the interface between the two components, as a function of nanoparticle morphology and size. The charge transport in the polymer and nanocrystal phases was also studied.

D/PI.35**A SYSTEMATIC STUDY OF THE ANISOTROPIC OPTICAL PROPERTIES OF THIN POLY(3-OCTYLTHIOPHENE)-FILMS IN DEPENDENCE ON GROWTH PARAMETERS**

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P3OT is a promising candidate for plastic solar cells. We have determined the anisotropic dielectric function of thin spin-coated and drop-cast poly(3-octylthiophene)-films deposited on Si and glass substrates from both near-normal reflectance and transmittance spectroscopy and from variable angle spectroscopic ellipsometry. The influence of the deposition parameters (such as spin frequency, concentration of the polymer in solvent, type of solvent, type of substrate) on the anisotropic dielectric function of the film was investigated. Further on, X-ray reflection on selected samples was used for providing information on structural film properties. The anisotropy of the dielectric function can be related to the orientation of the polymer chains in the film. The optical anisotropy of spin-coated films increases with increasing spin frequency and decreasing polymer concentration in the solvent, indicating that polymer chains become more aligned parallel to the substrate. The drop-cast films were also found to be anisotropic. In addition, the anisotropy increases considerably if the property of the Si substrate is changed from hydrophilic to hydrophobic (by treatment with HF). Summing up, all results are discussed in dependence of the film thickness as the decisive parameter.

D/PI.36**GROWTH VERSUS NUCLEATION OF CONDUCTING POLYMERS THIN FILMS OBTAINED BY PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION**

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Conducting polymers are an increasingly interesting topic because of its suitable use in microelectronics and lately as photovoltaic coatings.

The main challenge of the conventional techniques is to obtain highly uniform and pin-hole free films in order to have more efficient charge transport properties. With PECVD very uniform and pin-hole free thin films can be obtained. It is important to control the growth to obtain the desired uniformity. With PECVD a great uniformity can be achieved by promoting the growth processes in detriment of the nucleation processes. This can be done by different means: decreasing the power, increasing the flow rate of the gas, using pulsed PECVD or nanostructuring the substrate surface. Pyrrole and thiophene are the monomers that have been used. Samples have been taken over a period of an hour and have been examined by AFM. The images show that the morphology of thin films obtained at 4W is much better than of those obtained at higher power. They grow from fewer and smaller nuclei, giving time to the growth processes to cover the surface before new nuclei start a new layer. Therefore, these films have a very low roughness (0.3nm). With PPy films, the power cannot be lowered as much as with PTh because then some pin-holes appear. Thin films obtained using 4W of power are not only better morphologically but also structurally. As it can be deduced from XPS analysis, these films are more similar to the conventional polymer than those obtained at higher power. Furthermore if this technique is applied on a nanostructured substrate highly ordered films are obtained. As a consequence these films are presented as good candidates to be used as photovoltaic coatings.

D/PI.37**PHOTOVOLTAIC CHARACTERISATION OF VAPOR DEPOSITED SOLAR CELLS BASED ON HETEROJUNCTION OR INTERPENETRATING NETWORKS OF THIOPHENE OLIGOMERS AND C60**

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Organic solar cells based on single active layer present poor efficiencies due to weak electron-hole dissociation and small carrier mobility. Donor-acceptor heterojunction devices can enhance dramatically electron-hole dissociation and thus the device efficiency.

So we have used vacuum deposition of small organic molecules in order to achieve photovoltaic devices. Both heterojunctions (built by successive evaporations) or interpenetrating networks (built by co evaporation) of donor molecules (conjugated thiophene oligomers) and acceptor molecules (C60) are tested as active layers of solar cells sandwiched between metallic contacts. First we will present the I(V) characteristics (in dark and under illumination with high pressure Xe arc discharge lamp) of the heterojunction or interpenetrating network devices achieved with pristine organic compounds (terthiophene, sexithiophene and C60). An optimisation of the donor and acceptor layer thickness (in the case of heterojunctions) or stoichiometry (in the case of interpenetrating networks) will be discussed. In the case of heterojunction devices, and in order to enhance carrier mobility in the both n type (acceptor) layer and p type (donor) layer, implantation of chemically active ions (alkali and halide ions into the n type and p type layers respectively) at very low energy (in the keV range) has been tried. Changes induced by ion implantation on the I(V) characteristics will be exposed.

D/PI.38**ELECTROCHEMICAL COMPARATIVE STUDY OF TITANIA (ANATASE, BROOKITE AND RUTILE) NANOPARTICLES SYNTHESIZED IN AQUEOUS MEDIUM**

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Titanium oxide TiO₂ has found extensive use in a great variety of applications among which electrode materials for dye-sensitized solar cells. The polymorphs of TiO₂, rutile, anatase and brookite exhibit specific physical properties, band gap, surface states... For many applications the size of particles is an important parameter because it determines the surface to volume ratio, which greatly influences many properties [1]. TiO₂ anatase is the most used phase for photovoltaic applications [2] and brookite seems potentially interesting [3,4].

Nanometric particles of the three polymorphs, were synthesized by thermolysis of TiCl₄ in aqueous medium. The control of the precipitation conditions (acidity, nature of anions, ionic strength, titanium concentration...) allows the control of crystalline structure, size and morphology of particles. Spheroidal anatase with nanometric size was synthesized in the range 4 to 10 nm [5]. Recently in our group, pure brookite has been synthesized for the first time by "Chimie douce" in aqueous solution [3]. At last, rutile with various shapes (needle, rod or spherical) was obtained. This presentation is focused on the comparison of the electrochemical and spectroelectrochemical behavior of anatase, rutile and brookite nanoparticles. A priori, brookite could be a good candidate for photovoltaic devices.

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[4] M. Koelsch, S. Cassaignon, J. F. Guillemoles, J. P. Jolivet, *Thin Solid Films* 2002, 403-404, 312.

[5] A. Pottier, S. Cassaignon, C. Chanéac, E. Tronc, J. P. Jolivet, *J. Mater. Chem.* accepted

D/PI.39

NANOCERMETS TiO₂:Au FOR PHOTOANODES

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The systems of photosensitive semiconducting electrodes to photoelectrolyze water using sunlight offer much promise for the inexpensive production of hydrogen, the future fuel. Titanium dioxide, TiO₂ is one of the most suitable candidates for photoanodes in phototoelectrochemical solar cell (PEC) due to its high resistance to corrosion, stability and negative flat band potential. However, its low solar energy conversion efficiency (of about 4%) being a consequence of wide band gap of TiO₂ requires a significant modification of its spectral absorption in order to match the solar spectrum. Noble metal/TiO₂ nanocermets exhibit an additional absorption feature, usually shifted towards longer wavelengths than the fundamental absorption edge of TiO₂, due to the surface plasma resonance (SPR). The position of the SPR depends not only on the intrinsic electronic properties of metallic particles, their concentration, size and distribution but on the local environment as well. This work presents the results of the studies of the microstructure (TEM, GID), optical (spectrophotometry, ellipsometry) and electrochemical properties of nanocermets TiO₂:Au thin films deposited by rf sputtering. Electrochemical measurements have been performed in a three-electrode cell illuminated with the monochromatic electromagnetic radiation from the 450 W Xe lamp through the Yvon-Jobin monochromator. High photocurrent response has been observed over the wavelength range of 400-600 nm

D/PI.40

TiO₂ FOR PHOTOELECTROLYTIC DECOMPOSITION OF WATER

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The photo-electrochemical decomposition of water at the liquid-solid interface in TiO₂-electrolyte system attracts a growing interest for the possible conversion and storage of the solar energy into hydrogen and electricity. Modification of titanium dioxide is necessary in order to increase the efficiency of solar energy conversion. Titanium dioxide thin films were prepared by rf reactive sputtering. The effect of the film thickness on the structural, optical and electrochemical properties was studied. The photoelectrochemical experiments were carried out using a 450 W Xenon lamp as solar simulated source. Solar energy conversion efficiency as a function of applied bias was determined. The maximum conversion efficiency (above 2%) has been observed for voltage bias ca 0.1-0.3 V. The impedance spectra and capacitance of the electrode/electrolyte interface vs. voltage (Mott-Schottky plots) were recorded over a wide frequency range of 1-106 Hz. The flat band potential, effective donor density and depletion layer thickness were obtained from capacitance data as a function of the applied potential at 10 kHz.

D/PI.41

UNIFIED APPROACH TO OPTICS OF CONDUCTING POLYMERS

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We report on the recent progress in the unified theory for electronic and optical properties of conducting polymers. Bringing together languages of the solid state theory for polymers and the quantum chemistry of oligomers allows us to take into account strong electronic correlations upon the semiconductor type approach. Our model combines the long range electron - hole Coulomb attraction with a specific strong on-site e-h repulsion. The theory operates with a few parameters which can be determined experimentally or from ab initio calculations. The model explains, exploits and organizes various experimental and numerical findings. E.g. we connect such different questions as coexistence of shallow singlet and deep triplet excitons in phenylenes, crossing of optically allowed and forbidden transitions in polyenes, common 1/L energy dependencies in oligomers. We can interpret several observed time delay regimes in luminescence, fluorescence and phosphorescence due to conversion between various types of excitons.

D/PI.42

PHOTOVOLTAIC PROPERTIES OF METALLOPHthalOCYANINE-BASED THIN FILMS STUDIED IN HYBRID SOLAR CELLS: INFLUENCE OF THE MOLECULAR STRUCTURE, MORPHOLOGY AND ELECTRICAL PROPERTIES

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Metallophthalocyanine films have high potential for various electronic components such as thin film transistors, LED and solar cells. Depending on the nature of the metal ion and/or substituents on the conjugated ring different physicochemical properties are expected. In this work, vacuum evaporated organic thin films based on p-type metallophthalocyanines MPc (copper phthalocyanine CuPc and zinc phthalocyanine ZnPc) and a n-type metallophthalocyanine (copper hexadecafluorophthalocyanine F16CuPc) were realized on Si, SiO₂ and GaAs. Substrate temperatures were varied between RT up to 180°C in order to study the influence on the structure and the morphology on the one side and on the electrical properties on the other side. The growth behavior of MPc films was studied by Atomic Force Microscopy (AFM) from 10 nm up to 100 nm thickness. The p-type or n-type of metallophthalocyanines as well as the mobility values were characterized by field-effect transistor measurements. Hybrid solar cells based on GaAs/MPc were prepared and allowed to study the photovoltaic properties of MPc thin films in details. Current-voltage and external quantum efficiency measurements (EQE) were put into correlation with the observed film morphology. P-type and n-type MPc performances were compared and combined to realize an organic homojunction p-MPc/n-MPc solar cell.

- D/PI.43** OLIGOTHIOPHENE TO PHTHALOCYANINE THIN FILMS IN HYBRID SOLAR CELLS: MOLECULAR STRUCTURE, MORPHOLOGY AND ELECTRICAL CHARACTERISTICS
C. Videlot(a), J. Ackermann(a,b), H. Oughaddou(a), A. El Kassmi(a), P. Raynal(a), P. Dumas(b), V. Safarov(b), F. Fages(a), (a)LMMB, Université de la Méditerranée, UMR CNRS 6114, Case 901, 163 avenue de Luminy, 13288 Marseille Cedex 09, France, (b)GEPEC, Université de la Méditerranée, UMR CNRS 6631, 163 avenue de Luminy, 13288 Marseille Cedex 09, France
Thin film solar cells based on organic semiconductors are very promising systems for future solar energy application at low costs. However so far only quite small energy conversion efficiency has been demonstrated. Referred to organic single crystals the performance of organic solar cells is partly limited by the morphology of the organic thin films as well as by energy losses at the interfaces. Replacing one organic semiconductor (n-type) by a crystalline inorganic semiconductor substrate opens the possibility to study the photovoltaic properties of the organic film in detail. By producing hybrid solar cells based on n-GaAs and organic thin films we studied the photovoltaic properties of oligothiophene (4T, 6T and 8T) and phthalocyanine (CuPc, ZnPc) thin films with different morphologies. Current-voltage and external quantum efficiency measurements (EQE) in combination with AFM characterization of the film morphology are presented. The influence of the molecular structure, rigid rod or disk, as well as the film morphology on the solar energy conversion of the thin films are discussed.
- D/PI.44** **withdraw**
- D/PI.45** DEGRADATION OF POLYMER SOLAR CELLS: MECHANISMS AND LIFETIME
Stefan Schuller(a), Pavel Schilinsky(a,b), Christoph Waldauf(a,b), Jens Hauch(a), Christoph J. Brabec(a), (a)SIEMENS AG, CT MM1, Innovative Polymers, Paul Gossenstr. 100, 91052 Erlangen, Germany, (b)Department of Energy and Semiconductor Research, University of Oldenburg, 26129 Oldenburg, Germany
Temperature accelerated life time measurements are applied to organic bulk-heterjunction solar cells based on blends from conjugated polymers (MDMO-PPV) with fullerenes (PCBM). The short circuit current under white light illumination is monitored over time for four different temperatures, ranging from 40 °C to 105 °C. An Arrhenius type dependence of the degradation constant with temperature is observed and an activation energy of ~ 15 meV is derived. Lifetimes exceeding 500 hours @ 85 °C under ~ 1 sun are commonly observed for stabilized polymer photovoltaic devices. Degradation of these devices is discussed and analyzed at the hand of two different contributions, one from the interface and one from the semiconductor bulk.
- D/PI.46** MACRO- AND MICROSCOPIC MODELLING OF POLYMER SOLAR CELLS
Pavel Schilinsky(a,b), Christoph Waldauf(a,b), Jens Hauch(a), Christoph J. Brabec(a), Ingo Riedel(b), Vladimir Dyakonov(b), (a)SIEMENS AG, CT MM1, Innovative Polymers, Paul Gossenstr. 100, 91052 Erlangen, Germany, (b)Department of Energy and Semiconductor Research, University of Oldenburg, 26129 Oldenburg, Germany
The presented paper shows two different approaches of modelling polymer solar cells.
By analysing the IV-curves using a 2-Diode model reasonable fits were achieved using the ideality factors 1 and 2 for the first and second diode respectively. Moreover, the model takes care of the observed photoshunt by correlating the change of the parallel resistance to the number of photoinduced charge carriers. Temperature dependent analysis of the short circuit current varying the film thickness reveals that the charge carrier collection efficiency is not limited by transport properties. Further a microscopic model based on the fundamental equations is discussed: A bulk-heterojunction solar cell is described with one ambipolar model semiconductor comprising the essential parameters of the two single p- and n-materials in terms of energy levels, absorption, density of traps, mobility and life time of charge carriers.
- D/PI.47** POLYMER PHOTOVOLTAIC DETECTORS: PROGRESS AND RECENT DEVELOPMENTS
Pavel Schilinsky(a,b), Christoph Waldauf(a,b), Jens Hauch(a), Christoph J. Brabec(a), (a)SIEMENS AG, CT MM1, Innovative Polymers, Paul Gossenstr. 100, 91052 Erlangen, Germany, (b)Department of Energy and Semiconductor Research, University of Oldenburg, 26129 Oldenburg, Germany
Polymer photovoltaic detectors develop rather fast to a mature technological level, significantly faster than the technological closely related solar cells. The lack of near IR absorbing polymers, currently limiting the polymer solar cell efficiency, is not relevant for the performance of UV/Vis detectors. Recent progress improved the polymer photovoltaic detectors to a level sufficient for many applications. External quantum efficiencies exceeding 80% in the visible range, linearity over several decades, low dark currents, a capacitance limited noise and a fast transient behaviour are demonstrated for prototype thin film detectors with an active layer thickness around 100 nm. Uncritical processing via printing methods together with a favourable cost structure suggest these detectors for various applications like chemical/medical sensing and analysis as well as line or matrix arrays for picture recognition and security applications.
- D/PI.48** USE OF MULTIPLE SIZE-QUANTIZED CDSE LAYERS TO SENSITIZE MESOPOROUS, NANOCRYSTALLINE TiO₂ - BASED SOLAR CELLS
Shaibal K. Sarkar(a), Christophe Péjoux(a), Sven Rühle(a), Arie Zaban(b), Gary Hodes(a) and David Cahen(a), (a)Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, 76100 Israel, (b)Department of Chemistry, Bar-Ilan University, Ramat Gan, 52900 Israel
Chemically deposited nanocrystalline CdSe overlayers on screen-printed meso-porous TiO₂ can act as photosensitizer and, thus, serve as a potential replacement of the dye in dye-sensitized solar cells. To improve both optical absorption throughout the entire visible spectrum, as well as electron injection efficiency, we use the quantum size effect of nanocrystalline CdSe. This is possible because we can cover increasingly wide parts of the solar spectrum by decreasing the size-quantization (increasing the particle size) of the CdSe. At the same time the quantum size effect-induced shift in the particles' conduction band edge assures efficient injection without concomitant increase in recombination (because of much smaller quantum size effect-induced valence band shift). To achieve this we use several thin CdSe overlayers with different grain sizes. With proper layer design, an increase in the quantum efficiency of photoconversion, by a few orders of magnitude, compared to that of a single CdSe layer-TiO₂ system, has been achieved experimentally. While still low in absolute terms, our results indicate that this type of co-sensitization presents a promising approach towards efficient nanocrystalline mesoporous solar energy conversion.

D/PI.49

CuInS₂/PEDOT PHOTOVOLTAIC STRUCTURES

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Photovoltaic structures based on combination of electrically conductive polymers with inorganic semiconductors are currently intensively investigated with the aim to prepare photovoltaic devices. Conductive polymers attract interest due to the potential for producing low-cost, large-area and flexible photodiodes and solar cells.

In this study, multilayer structures consisting of CuInS₂ (CIS) and poly(3,4-ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonate (PSS) thin films were prepared and investigated for photovoltaic applications. The polymer layer of p-type is considered as an alternative for the traditional buffer layer and window top layer on the CIS absorber layer in the cell structure. As absorber layers, polycrystalline CIS thin films were synthesized on top of a layered structure on Cu tape substrate using a non-vacuum CISCuT technique. Thin PEDOT films doped with PSS were deposited onto KCN etched and vacuum annealed CIS films from an aqueous dispersion of PEDOT/PSS mixed with N-methylpyrrolidone, isopropanol, glycerin and epoxysilane additives using the spin-casting technique. In order to prepare stable PEDOT films of high quality with a good adherence to the surface of inorganic semiconductor CIS, the optimal parameters of spin-coating were selected experimentally. Average film thickness was determined microscopically and was about of 1500 nm for CIS and 50 nm for PEDOT films. Significant photovoltage and photocurrent of the fabricated CIS/PEDOT structures have been observed under standard white light illumination. Our deposition technique gives us an opportunity to prepare photovoltaic structures based on CIS and PEDOT thin films using relatively simple step-by-step method.

D/PI.50

CHARGE MOBILITY AND PHOTOVOLTAGE IN CARBOCYANINE DYE LAYERS DEPOSITED BY THERMAL EVAPORATION IN VACUUM

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Charge carrier transport, photovoltaic and optical properties of carbocyanine dye layers have been investigated. Molecules of such dyes are known to form a J-aggregate phase of nanosize crystals in the polymer composite enhancing efficient electroluminescence [1]. The dye layers of approximately 1 micron in thickness were deposited by the thermal evaporation in vacuum onto conducting glass support. Treating of the layers in the moist air invoked two new absorption bands in the visible-light range. We believe the short and long wavelength bands belong to dimers and J-aggregates of the carbocyanine molecules correspondingly. The transformation of the absorption spectra is irreversible and time- and temperature- (up to 328K) independent. In an ITO/dye/CuPc/Al structure, photovoltaic current was found to be higher for the modified dye layer than original one. In the dye layer, electron drift mobility studied by a conventional time-of-flight technique appears to increase from 1 to 3x10⁻⁵ cm²/(Vs) as an electric field increases in the range of 20-200 kV/cm. The results are compared with those for charge carrier mobility in the polymer/cyanine dye composite obtained earlier and evidence that the mobility of charge carriers in the systems reaches high values.

The work was supported by the ISTC under Grant 2207 and NWO Project 047.009.019

[1] E.I.Mal'tsev, D.A.Lypenko, V.V.Bobinkin, A.R.Tameev, S.V.Kirillov, B.I.Shapiro, H.F.M.Schoo, and A.V.Vannikov, Appl. Phys. Lett. 81, 3088 (2002).

15:30

BREAK

Session III: Si-based TFSC

Session chair: J. Meier and U. Kroll

D-III.1 16:00 -Invited-

PRESENT STATUS OF MICRO- AND POLYCRYSTALLINE SILICON CELLS BY HOT WIRE CHEMICAL VAPOR DEPOSITION

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Considerable effort is presently put into the development of thin film microcrystalline silicon, because it has a larger long-wavelength response than amorphous silicon while it is at the same time essentially stable. In this review, the latest achievements in this field as obtained by Hot Wire CVD technology will be presented and illustrated by the performance of silicon thin film devices. As microcrystalline silicon has an indirect band gap, the absorption coefficient is low. Using light trapping geometries, the required thickness can be kept below 2 micrometers. Nevertheless, this small thickness still requires long deposition times and therefore the achievement of higher deposition rates is very important. Alternatively, multijunction cells, including amorphous components made at a higher deposition rate, can lead to lower costs while improving the overall efficiency. By doubling the catalytic surface in HWCVD, we have recently achieved a deposition rate of 7 $\mu\text{m/s}$ for polycrystalline silicon. As these layers tend to be more porous, a new optimum in the gas phase reaction chemistry has been investigated in a regime of reduced filament temperature and higher hydrogen dilution. This has led to polycrystalline n-i-p type cells made at more than twice the deposition rate while reproducing the cell efficiency. Allowing an increase of the amorphous volume fraction, microcrystalline silicon (rather than polycrystalline silicon) is obtained. In this mode, the layers more readily possess the compactness that is required. We present the world's first HWCVD multibandgap triple junction cell with an efficiency of 8.5 % on plain stainless steel and show the future potential of this technology.

- D-III.2** 16:30 INFLUENCE OF THE TOTAL GAS FLOW ON THE DEPOSITION OF MICROCRYSTALLINE SILICON SOLAR CELLS
T. Roschek, B. Rech, H. Wagner, Forschungszentrum Jülich, Institute of Photovoltaics, Leo-Brandt-Strasse, 52425 Jülich, Germany
 In the past years, intrinsic microcrystalline silicon $\mu\text{-Si:H}$ emerged as a promising new material for photovoltaics. We succeeded in preparing microcrystalline silicon solar cells with efficiencies up to 9% at high growth rates using 13.56-MHz PECVD in a high pressure regime. These cells were prepared at very high hydrogen dilutions and gas flows (silane concentration $[\text{SiH}_4]/[\text{H}_2] \sim 1\%$ at 360-sccm H_2 flow). In view of a future mass production lower gas flows would be desirable to reduce the gas consumption. Therefore the influence of the total gas flow on the solar cell performance and the deposition rate is systematically studied in this paper. By changing the total gas flow the transition between amorphous and microcrystalline growth can be varied. By adjusting $[\text{SiH}_4]/[\text{H}_2]$ over a wide range of total gas flows ($\sim 100\text{-}1000$ sccm) solar cells with an efficiency of more than 8% could be prepared without an influence on the deposition rate, which remained constant at 3.5-Å/s. The results are interpreted in terms of gas utilization and gas residence time in the plasma space. Furthermore a new technique for the deposition of $\mu\text{-Si:H}$ will be described which produces $\mu\text{-Si:H}$ suitable for high efficiency solar cells with only very low hydrogen supply. The best solar cell prepared by this new method had an efficiency of 7.3% at a growth rate of about 2-Å/s.
- D-III.3** 16:45 THIN FILM SILICON GROWTH FROM SILANE/HYDROGEN/ARGON ECR PLASMAS
 S. Summers(a), G. Ekanayake(a), K. Mahanama(a), T. Quinn(a), C. Jeynes(b) and H.S. Reeha(a), (a)Faculty of Engineering, Science and Technology, South Bank University, 103 Borough Road, London SE1 0AA, U.K., (b)Ion Beam Centre, University of Surrey, Guildford GU2 7XH, U.K.
 Thin films of crystalline Si on foreign substrates are attracting considerable interest for solar cells. Hence the growth of these films is an important area of research. Many growth techniques are being investigated including electron cyclotron resonance (ECR) plasma-assisted chemical vapour deposition (PACVD). This work reports on the preparation of microcrystalline silicon layers on glass-like substrates (SiO_2 -coated Si) at temperatures below 600°C using ECR PACVD. The films have been deposited from silane-hydrogen-argon mixtures. A range of characterisation techniques have been used including Raman spectroscopy and elastic recoil detection analysis (ERDA). The role that argon plays in the growth process has been studied. We find that the addition of argon leads to significant decreases in the deposition rate. Argon is also effective in suppressing the hydrogen content in films deposited at low temperatures. Importantly, argon addition has enabled us to prepare intrinsic microcrystalline silicon films with dark to light ratios of ~ 500 . These layers have been used in simple pin solar cell structures fabricated on silicon wafers and open circuit voltages of up to 560 mV observed. The results will be presented.
- D-III.4** 17:00 -Invited- INTRINSIC AND LIGHT INDUCED GAP STATES IN A-SI:H MATERIALS AND SOLAR CELLS – EFFECTS OF MICROSTRUCTURE
C.R. Wronski, J.M. Pearce, J. Deng, V. Vlahos, R.J. Koval and R.W. Collins, Center for Thin Film Device, The Pennsylvania State University, USA
 There are still difficulties in clearly identifying the nature of both intrinsic and the light induced defects in hydrogenated amorphous silicon (a-Si:H) materials as well as relating them to solar cell characteristics. We report here some new insights into the nature of these defects obtained from studies on thin films and solar cells with a-Si:H materials having different microstructure. Sub band gap absorption results obtained with dual beam photoconductivity measurements on thin film a-Si:H materials are presented here which identify the contributions of distinctly different defects to the light induced changes in the gap states of a-Si:H. Results are also presented on corresponding solar cell structures, which not only clearly establish the absence of the highly non-uniform distributions of defects in the bulk predicted by the defect pool model, but also allow direct correlations to be made with the results on thin films. The effects of the a-Si:H microstructure on the nature of these gap states, their evolution under 1 sun illumination and effects on solar cell characteristics are also presented and discussed.
- D-III.5** 17:30 ALUMINUM INDUCED CRYSTALLIZATION OF AMORPHOUS SILICON: INFLUENCE OF MATERIALS CHARACTERISTICS ON THE REACTION
Carlo Ornaghi, Jef Poortmans, MCP/SSC, IMEC vzw, Kapeldreef 75, 3001 Leuven, Belgium
 Aluminum Induced Crystallization (AIC) of a-Si is a promising path to cheap and simple definition of a seeding-layer for epitaxial growth of a large-grained active layer in thin-film polycrystalline silicon solar cells on foreign substrate.
 The course of the crystallization has been shown to depend on a variety of factors such as temperature of the annealing step and deposition conditions of the aluminum and silicon layers. We suggest and study a dependency on the characteristics of the materials involved in the reaction, focusing particularly on the different reactivity of a-Si deposited with different techniques (namely electron-beam evaporation and PECVD) and in different conditions (pressure, gas dilution). First results of high-temperature layer growth on the seeding layers and cells making are also reported.

D-III.6 17:45

ALUMINUM-INDUCED CRYSTALLIZATION OF AMORPHOUS SILICON

J. Klein, J. Schneider, M. Muske, I. Sieber, S. Gall, W. Fuhs, Hahn-Meitner-Institut Berlin, Kekuléstr. 5, 12498 Berlin, Germany

Thin polycrystalline silicon (poly-Si) layers can be formed by aluminum-induced crystallization (AIC) of amorphous silicon (a-Si). The AIC takes place at annealing temperatures well below the eutectic temperature of the Al/Si system ($T_{eu} = 577^{\circ}\text{C}$). During the annealing step the initial glass/Al/a-Si layer structure is transformed into a glass/poly-Si/Al+Si structure. This process is also called aluminum-induced layer exchange (ALILE). Previous work has shown that a thin oxide layer between the initial Al and a-Si layers is required for the layer exchange. This oxide layer serves as a permeable barrier, which remains at the same position during the annealing process. Usually the Al-layer is oxidized by exposure to air. Here we present results of experiments at controlled oxidation conditions in the deposition chamber (determined oxidation time and defined oxygen pressure). In this manner the thickness of the oxide layers can be controlled in order to influence the growth process of the final poly-Si layer. Very thin oxide layers can be generated which result in a higher number of grains and as a consequence in a smaller grain size compared to the thicker oxide layers generated by exposure to air. However, very thin oxide layers make it possible to form a continuous poly-Si film within a reasonable time even at low annealing temperatures (e. g. 380°C).

D-III.7 18:00

FABRICATION OF UNIFORM POLY-Si THIN FILM ON GLASS SUBSTRATE BY AIC

Atsutoshi Doi, Dept. Electric and Electronic Eng., Kinki Univ., Higashiosaka, Osaka 577-8502, Japan

Preparation of polycrystalline silicon (poly-Si) films on glass substrate has been studied as a way of making large-area electronics devices. Aluminum-induced crystallization (AIC) of amorphous silicon (a-Si) is one way to create a glass/poly-Si structure. Unfortunately the resulting surface proved to be rough, because the process was incomplete and gave rise to voids, and there were Si islands on the poly-Si film. Not enough is known about the AIC mechanism to allow a smoother surface to be prepared. The present work uses differential scanning calorimetry (DSC) to study reactions at the Al/a-Si and Al/poly-Si interfaces. An endothermic peak was observed at 550°C due to the reaction at the Al/a-Si interface, overlapping with an exothermic plateau due to the reaction at the Al/poly-Si interface. This observation implies that, although the interfaces are at the same temperature, the Si concentration in the Al film at the Al/a-Si interface exceeds that at the Al/poly-Si interface, and also that AIC follows a diffusion model similar to the growth model for liquid phase epitaxy (LPE). Since Al/Si systems do not form a stable silicide, Al functions as an effective solvent and transport medium. Analogy with LPE from supercooled solutions suggests that annealing of glass/Al-Si compounds could give a more uniform surface morphology. Flat and uniform poly-Si film having (111) orientation was successfully obtained by annealing an evaporated glass/Al-Si sample at 460°C .

D-III.8 18:15

SOLID PHASE CRYSTALLIZATION OF HIGH-QUALITY SiGe FILMS ON SiO₂ BY LOCAL Ge-INSERTION

I. Tsunoda, K. Nagatomo, T. Sadoh, A. Kenjo and M. Miyao, Depart. of Electronics, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

Oriented crystal growth of SiGe on SiO₂ with grain sizes larger than device dimensions (a few μm) has been expected to realize Si based optoelectronic integrated circuits. To achieve this, effects of local Ge-insertion in a-SiGe films on solid phase crystallization (SPC) were investigated. In the experiment, a-Si_{1-x}Ge_x (x 0.3, 50 nm thick.) and thin a-Ge (10 nm thick.) were deposited on SiO₂ grown on Si wafers. Three types of stacked structures, i.e., (a) a-SiGe/a-Ge/SiO₂, (b) SiO₂/a-Ge/a-SiGe/SiO₂, and (c) a-SiGe/a-Ge/a-SiGe/SiO₂ were fabricated. They were annealed at 600°C . The results obtained by using Auger electron and Raman spectroscopy indicated that Ge atoms were localized in the initial position and Raman peak related to Ge-Ge bonds was very sharp for (a) and (b) structures. In addition, results of spectroscopic ellipsometry showed that SPC of a-SiGe was significantly enhanced by insertion of a-Ge film. On the other hand, the results for (c) structure showed that Ge atoms were diffused into Si layers, and no-enhanced SPC was detected. These results indicated that crystal nucleation was initiated at the thin Ge layers directly contacted to SiO₂, and then propagated into a-SiGe layers. Consequently, interface nucleation driven SPC becomes possible by using (a) and (b) structures. This will be a useful tool to achieve growth of oriented SiGe on SiO₂. Preliminary results indicated the preferential SPC with (111) orientation.

Wednesday, June 11, 2003
Mercredi 11 juin 2003

Afternoon
Après-midi

Session IV: Organic based SC
Session chair: C. Brabec and R. Janssen

- D-IV.1** 14:00 -Invited- **ELECTRICAL ASPECTS OF OPERATION OF POLYMER-FULLERENE SOLAR CELLS**
Vladimir Dyakonov, Department of Energy and Semiconductor Research, University of Oldenburg, 26111 Oldenburg, Germany
Easily processable conjugated polymers for photovoltaic energy conversion is an attractive research field, in which the combined efforts of material science, device engineers, and spectroscopists are welcomed. To improve the efficiency of polymer solar cells, it is vital to understand which mechanisms control the current-voltage characteristics of a given device. Temperature dependence of the main solar cell parameters is very informative for analysing losses. Firstly, temperature studies of Voc clearly show a linear increase towards thermodynamic values given by the HOMO-LUMO gap of the donor and acceptor. The open circuit voltage in the range 0.92V-0.94V was measured with a new DPM-12 acceptor. It is at least 100mV higher than the expected value, whereas the electron affinity is not much different from the widely used PCBM. Moreover, a nearly temperature independent Voc observed in the DMP-cells in contrast to PCBM based cells. The second aspect is the manner in which electrical contact to the polymer or fullerene is created. The current flow across the ITO/P3HT/Al device is limited by hole injection at the Al/P3HT interface at T<240K when the device is reverse biased. Above this temperature, the bulk transport properties control the electrical characteristics. For the forward bias case, the ITO/P3HT contact does not limit the current, instead a space charge accumulates due to the low hole mobility in the polymer. A criterion will be discussed that allows for the determination of the field at which the charge injection through thermionic emission equals that of field emission for a given temperature, and interface potential barrier height. The third aspect to be discussed is the Fermi-level pinning which is currently under debate.
- D-IV.2** 14:30 **MODELLING THE SHORT-CIRCUIT CURRENT OF POLYMER BULK HETEROJUNCTION SOLAR CELLS**
Wim Geens, Tom Aernouts, Peter Vanlaeke, Jef Poortmans, Paul Heremans, Staf Borghs, Robert Mertens IMEC vzw, Kapeldreef 75, 3001 Leuven, Belgium, Tom Martens, Jean Manca, Laurence Lutsen, Dirk Vanderzande, Limburgs Universitair Centrum, 3590 Diepenbeek, Belgium
An analytical model, mainly relying on carrier diffusion and carrier selectivity of the contacts, has been developed to estimate the short-circuit current density of conjugated polymer/fullerene bulk heterojunction solar cells. The model takes into account the solvent dependent molecular morphology of the donor/acceptor blend, which was revealed by transmission electron microscopy. Field-effect transistors based on single and composite organic layers were fabricated to determine values for the charge carrier mobilities in the donor and acceptor networks of such blended films. These values served as input parameters of the model. It is shown that the difference in short-circuit current density that was measured between toluene-cast and chlorobenzene-cast conjugated polymer/fullerene photovoltaic cells [S. E. Shaheen et al., Appl. Phys. Lett. 78, (2001) 841] could be very well simulated with the model. Moreover, the calculations illustrate how increasing the hole and electron mobilities in the photoactive blend can improve the overall short-circuit current density of the solar cell.
- D-IV.3** 14:45 **MATERIAL & DEVICE CONCEPTS FOR ORGANIC PHOTOVOLTAICS: TOWARDS COMPETITIVE EFFICIENCIES**
Pavel Schilinsky(a,b), Christoph Waldauf(a,b), Jens Hauch(a), Christoph J. Brabec(a), (a)SIEMENS AG, CT MM1, Innovative Polymers, Paul Gossenstr. 100, 91052 Erlangen, Germany, (b)Department of Energy and Semiconductor Research, University of Oldenburg, 26129 Oldenburg, Germany
This contribution analyses the performance potential of state of the art organic bulk-heterojunction photovoltaic devices and gives a guideline towards higher device efficiencies. The concept relies on the identification and determination of the relevant material parameters (lifetime, mobility, bandgap, trap density.....) for the pristine components and for the blended photovoltaic composites. This set of material parameters is used as input for a simulation model which has been successfully shown to correctly describe bulk heterojunction solar cells. Results from simulation are compared to experimental device performance. Comparison between experiment and simulation allows to analyse deficiencies of the pristine compounds, of the composite as well as of the device architecture. Based on these findings, material and device parameters for a high efficient bulk heterojunction device are presented.

- D-IV.4** 15:00 -Invited- **CHARGE RECOMBINATION IN POLYMER/FULLERENE PHOTOVOLTAIC DEVICES**
Jenny Nelson, Stelios Choulis, James R. Durrant, Ivan Montanari and Ana Flavia Nogueira, Centre for Electronic Materials and Devices, Departments of Physics and Chemistry, Imperial College London, London SW7 2BW, U.K.
 Solar cells based on polymer-fullerene blends are amongst the most efficient organic photovoltaic devices with power conversion efficiencies now exceeding 3%. The large interfacial area in such dispersed heterojunctions, which is essential for charge separation, also enables charge recombination. Understanding recombination is therefore of key importance in the optimisation of device performance. Recent measurements of charge recombination in blends of poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1-4-phenylene vinylene), (MDMO-PPV) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61 (PCBM) by transient optical spectroscopy reveal that recombination kinetics possess two phases, one fast, intensity dependent phase and a slow, intensity independent phase which dominates at low light intensities. The recombination is thermally activated, and the kinetics are sensitive to background illumination but insensitive to the blend composition. Simple models of bimolecular recombination cannot explain these features. In this paper we present a model for the mechanism of charge recombination which explains the observed recombination kinetics and their dependence on light intensity, temperature and fullerene concentration. We show that under solar illumination conditions, charge recombination is limited by the activation of positive polarons out of deep traps, yet carrier collection competes successfully with recombination in thin films. The model is evaluated by comparison with data on cells and independent measurements of charge transport, and the implications for cell performance are discussed.
- D-IV.5** 15:30 **HIGH EFFICIENCY ORGANIC SOLARCELLS BASED ON SINGLE OR MULTIPLE P-I-N STRUCTURES**
Jens Drechsel, Bert Maennig, Desta Gebeyehu, Ansgar Werner, Karl Leo and Martin Pfeiffer, Institut für Angewandte Photophysik, Technische Universität Dresden, 01062 Dresden, Germany
 We have recently demonstrated phosphorescent p-i-n-type OLEDs with high power efficiency even at high brightness. Here, we show that also the performance of organic solar cells can be strongly improved using p-i-n-structures with doped wide-gap transport layers and a phthalocyanine-fullerene blend as a photoactive layer. Such cells only absorb light in the photoactive region and thus avoid recombination losses at the contacts and make optimum use of the light reflected at the top contact. They reach about 2% power efficiency at AM 1.5 illumination, nearly 100% internal quantum efficiency and a fill factor of about 50%. We show that it is possible to stack two or more of these optically thin pin-cells into one sandwich structure without significant losses. This principle should soon enable us to prepare organic solar cells with outstandingly high efficiency. In the solarcells, a new technique of n-doping by cationic dyes is used. Using fullerene or perylene derivatives as a matrix, it yields thermally very stable layers with high conductivity. Spectroscopic details (UV-VIS, FTIR, mass spectroscopy) on the doping mechanism will be presented.
- D-IV.6** 15:45 **TOWARDS 3% EFFICIENT BULK HETEROJUNCTION PHOTO-VOLTAIC CELLS BASED ON POLYMER:FULLERENE BLENDS**
L.H. Slooff, W.J.H. Verhees, S.C. Veenstra, J.M. Kroon, ECN, PO Box 1, 1755 ZG Petten, The Netherlands, M.M. Wienk, R.A.J. Janssen, Eindhoven University of Technology, The Netherlands, J. Knol, J.C. Hummelen, University of Groningen, The Netherlands
 In an effort to increase the power conversion efficiency () of poly-mer:fullerene bulk heterojunction (BHJ) photovoltaic cells, a new material combination was found with a  of 3%. The material combination was selected based on an improved spectral overlap between the absorption spectra of the individual components and the solar spectrum. It is known that the device performance of BHJ photovoltaic cells is strongly related to the morphology of the photoactive layer. The morphology is mainly determined by the processing conditions, such as solvents, solution temperature, weight ratio and concentrations of the components. We studied the influence of these processing conditions on charge separation by photoluminescence quenching and photoinduced absorption spectroscopy. The morphology of the resulting films was visualised by AFM indicating a strong relation between solvent and the scale of phase separation in the organic film. Compared to standard PPV:PCBM devices, the spectral response of the optimised devices indeed shows an improved spectral overlap with a contribution of both components, leading to an increased photocurrent. Finally, we found a  of 3% under AM1.5 conditions for devices of 0.1 cm².
- 16:00 **BREAK**

Session V: Si-based TFSC

Session chair: R.E.I. Schropp, C.R. Wronski

- D-V.1** 16:30 -Invited- **POTENTIAL OF AMORPHOUS AND MICROCRYSTALLINE SILICON SOLAR CELLS**
J. Meier, J. Spitznagel, U. Kroll, C. Bucher, S. Faÿ, A. Shah, Institut de Microtechnique, A.L. Breguet 2, 2000 Neuchâtel, Switzerland
Thin-film silicon solar cells will play a key role in the next generation of photovoltaic (PV) modules as they allow for a low-cost sustainable production of modules, based on abundant and non-toxic raw materials. Hereby, hydrogenated microcrystalline silicon ($\mu\text{-Si:H}$) deposited at low temperatures (200 °C) by plasma enhanced chemical vapour deposition (PECVD) is a key material thanks to its low bandgap, stability and nanocrystalline microstructure. The microcrystalline / amorphous or "micromorph" tandem solar cell concept has, thus, a potential for combining high efficiencies and low production cost, using thereby the industrial large-area fabrication methods developed for amorphous silicon PV modules and for active-matrix flat panel displays.
In these solar cells light-trapping plays a key role: In cells of p-i-n configuration the front TCO on the glass substrate is essential for the light-trapping properties. IMT has developed its own "in-house" zinc oxide, prepared by low pressure chemical vapour deposition (LP-CVD). This TCO has notable advantages for thin-film solar cells as it is already textured in the as-grown state. Authors report on present progress in amorphous- and microcrystalline-based silicon cells and modules using this LP-CVD ZnO as TCO.
- D-V.2** 17:00 **HIGH EFFICIENCY P-I-N A-SI:H SOLAR CELLS WITH LOW BORON CROSS CONTAMINATION PREPARED IN A LARGE AREA SINGLE CHAMBER PECVD REACTOR**
U. Kroll, C. Bucher, S. Benagli, I. Schönbächler, A. Shah, Institut de Microtechnique, Neuchâtel, Switzerland, J. Ballutaud, A. Howling, Ch. Hollenstein, CRPP/EPF Lausanne, Switzerland, A. Büchel, M. Poppeller, Unaxis Displays, Trübbach, Switzerland
Plasma deposition of amorphous silicon (a-Si:H) p-i-n solar cells in a single-chamber reactor leads to considerable simplifications and reduced costs compared to multi-chamber processes. However, in a single-chamber process, the subsequent deposition of the i-layer on the p-layer can cause boron recycling from the reactor walls. As a result, boron can contaminate the initial i-layer at the critical p-i interface and thereby strongly deteriorate the cell performance. Thus, a process scheme able to suppress or limit the cross-contamination would be desirable.
In this work, a new type of short treatment of the interface between the p- and i-layer will be presented. This special treatment performed under vacuum considerably reduces the i-layer boron contamination. A significant advantage is that the substrate can remain loaded in the reactor during this treatment. The high effectiveness of this treatment in reducing the boron cross-contamination has been directly proven by SIMS, by tracing the boron concentration depth profile across the p-i interface and spectral response measurements of the deposited cells. By applying this treatment, 0.3 μm thick amorphous silicon p-i-n solar cells with high initial conversion efficiencies of over 10% have been deposited in a commercial large-area (35 cm x 45 cm) single-chamber PECVD KAI(tm) reactor. Finally, it will be demonstrated that the treatments performed do not affect the stability of cells.
- D-V.3** 17:15 **OPTIMIZATION OF THE FILAMENT ARRANGEMENT AT CONSTANT RADIANT HEAT IN HW-CVD FOR THE PREPARATION OF COMPACT $\mu\text{-Si:H}$ AT HIGH DEPOSITION RATES**
Jan Lossen, Stefan Klein, Friedhelm Finger Institut für Photovoltaik, Forschungszentrum Jülich, 52425 Jülich, Germany
Solar cells containing microcrystalline silicon prepared with HW-CVD have recently achieved record efficiencies of 9.4 %. These high efficiencies have been obtained at the expense of reduced deposition rates. The substrate temperatures which were required, made it necessary to reduce the filament temperature T_f in order to prevent detrimental substrate heating by radiation from the filaments. A high T_f on the other hand is considered a requirement for efficient process gas decomposition and subsequent high deposition rates.
In the present work we have investigated in how far these restrictions to the deposition process can be overcome by appropriate choice of the filament arrangement. We have varied number, surface area, length and shape of the filaments, T_f and the filament-substrate distance, all under the restriction that T_s is kept at 250°C by radiant heating from the filaments. For all filament arrangements we performed temperature calibration measurements and deposited series of samples with different silane concentrations SC, covering the whole range from highly crystalline to amorphous material. The structural analysis of the material by Raman and infrared spectroscopy shows a dependence of the crystallinity and the compactness on the filament arrangement. Higher T_f shifts the crystalline/amorphous transition to higher SC. For achieving high deposition rates a reduction of the filament substrate distance is preferable to an extension of the filament surface area.

17:30-19:00

POSTER SESSION II CIGS based TFSC

Chair: A. Tiwari and J. Palm

D/PIL.01**TAILORING GROWTH CONDITIONS FOR MODULATED FLUX DEPOSITION OF In₂S₃ THIN FILMS**

T. García(a), C. Guillén(a), M.T. Gutiérrez(a) and F. Briones(b), (a)Departamento de Energías Renovables, C.I.E.M.A.T. Av. Complutense 22, 28040 Madrid, Spain, (b)Instituto de Microelectrónica de Madrid, CNM-CSIC, Isaac Newton 8, Tres Cantos, 28760 Madrid, Spain

Indium sulphide (In₂S₃) thin films present an alternative to conventional chemical bath deposited CdS films as buffer layers for CIS-based thin film solar cells. The objective is to eliminate toxic cadmium; to widen the energy gap; and to grow them in a vacuum reactor in line with other cell layers deposition. In our laboratory, In₂S₃ thin films are grown by Modulated Flux Deposition in a custom-designed chamber in which glass substrates are cyclically transported through different zones for successive metal deposition, heating and chalcogen growth. This technique, inspired in epitaxial growth methods, has shown to provide high quality material films since it allows for an excellent control of the deposition conditions. We have studied the quality of our films in terms of their thickness, crystallinity, phase structure and optical characterization. More importantly, we have gained insight on the dependence of these properties upon several growth conditions such as substrates temperatures during the process, indium flux intensity, deposition rates and film thicknesses. From this work, remarkable conclusions can be drawn on the In₂S₃ thin films growth process. In addition, a deposition procedure can be developed in order to obtain an optimised material for thin film solar cells.

D/PIL.02**PREPARATION OF POROUS CuAlO₂ FILMS BELOW 400°C AND STUDY OF PHOTOELECTRICAL PROPERTIES**

L. Dloczik, Y. Tomm, Th. Dittrich, R. Koenenkamp, M. C. Lux-Steiner, Hahn-Meitner-Institut, Glienicke Str. 100, 14109 Berlin, Germany

Transparent conducting oxides (TCOs) of n- and p-type would be useful for bifacial, semitransparent or folded ultrathin absorber solar cells and for transparent circuits. But most TCOs are n-type. Among the few known transparent p-conductors, CuAlO₂ (Delafossite) promises superior stability. Sputtered CuAlO₂ films are often accompanied by other phases, thus requiring high-temperature annealing. Other preparation methods are laser ablation or CVD.

Here we present a scalable, phase-pure one-step synthesis of CuAlO₂ powder below 400°C with inexpensive starting material and equipment. We prepared films of porous CuAlO₂ on coated glass substrates and studied their photoelectrical properties by transient and spectral photovoltage. First doping experiments and tests for n-TCO/CuInS₂-type thin absorber/p-TCO cells will be reported.

D/PIL.03**DYNAMICS OF BARRIER FORMATION PROCESS IN HETEROSTRUCTURES BASED ON THERMALLY OXIDIZED p-InSe CRYSTALS**

S.I. Drapak, V.B. Orletskii, Z.D. Kovalyuk, P.I. Savitskii, Frantsevich Institute of Materials Science Problems, the National Academy of Sciences of Ukraine, Chernivtsi Department, Ukraine

Dynamical changes of electrical, photoelectric, and noise characteristics for p-type conductivity InSe single crystals are investigated depending on the time of oxidation carried out in the open air at 400°C. It is found that at the first oxidation stage (up to 30 min) on the surface of the semiconductors the crystallites of an oxide phase appear. It leads to the fact that the observed U_{oc} values are comparatively high (above 0.8 V under illumination with a 100 mW/cm² light power). At further oxidation the crystallites achieve the maximum dimension and then merge into an oxide phase film, i.e. the barrier is, in fact, formed. The oxide layer consists of two chemically different sublayer: one with an oxygen available on the surface and another transitional high-resistive - without it. The minimum values of dark saturation current as well as the maximum value of the signal – noise ratio were observed for the structures obtained after oxidation for 1.5 h when the thickness of the intermediate sublayer decreases and its homogeneity becomes higher. A further increase of oxidation time leads to the inversion of the InSe conductivity type and, as a result, to the decrease of contact difference of the potentials. The main photoelectric parameters also become worse. The inversion of the p-InSe conductivity type after its keeping at 400°C for 2 h, which is usually observed at more higher temperatures, is an evidence of the time–temperature character of this process.

D/PIL.04**CIGS THIN FILMS DEPOSITED BY CO-EVAPORATION USING THREE SOURCES**

A. Dricj, J.C. Bernede, S. Marsillac, LPSE, 2 Rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France

It is well known that CIGS is a very promising absorbent in thin film solar cells. The best results have been obtained by co-evaporation of Cu, In, Ga, Se using four Knudsen cells. However for technical and economical reasons it could be interesting to work with only three simple evaporation sources. In the present work Cu and Ga are evaporated simultaneously from the same crucible using a simple tungsten basket. First, we have studied by X-ray photoelectron spectroscopy the distribution of Ga in Cu when the atomic ration Ga/Cu=0.5. It is shown that, when deposited on substrate heated at 770 K, the ratio Ga/Cu is nearly constant all over the thickness of the film. Therefore such Cu, Ga evaporation source has been used simultaneously with Se and In sources to grow CIGS films with good photovoltaic properties i.e. high photoconductivity and ability to achieve good diode contact with a n buffer layer. As shown by XRD these films are crystallized in the expected chalcopyrite structure. The lattice parameters follow the Vegard law when the atomic Ga percentage varies. The films composition varies as shown below:

20<Cu<24, 16<In<20, 4<Ga<10, 47<Se<50, 0<O<0,20

The optical band gap increases with the Ga concentration. All these results testify that the behavior of the CIGS films obtained from three evaporation sources is similar to that deposited by the four evaporation sources.

Thin film solar cells Mo/CIGS/In₂S₃-xO₃x/i-ZnO/ZnO:Al/NiAl have been realized and probed. The CIGS thin films of these cells were deposited in the same apparatus using four and three evaporation sources. The results show that the efficiency of the cells depends more in the film composition than in the source number.

- D/PII.05** HETEROEPITAXIAL CUINS₂ FILMS ON GAAS(100)
Wolfram Calvet, Hans-Joachim Lewerenz, Christian Pettenkofer, Hahn-Meitner-Institut, SE6, Glienicke Strasse 100, 14109 Berlin, Germany
 Thin CuInS₂ layers were grown on wetchemically sulfur treated GaAs(100) single crystals by molecular beam epitaxy. The stoichiometry was varied between 0.5 and 1.5 for the nominal Cu/In ratio and the film thickness was limited to about 150 nm. The composition was analysed by photoelectron spectroscopy (PES) whereas the structural analysis was done by low energy electron diffraction (LEED), x-ray diffraction (XRD), and transmission electron microscopy (TEM). For the first time a (4x1) ordered CuInS₂(100) surface was found in the Cu-rich regime of preparation. From cross section images made by TEM it can be deduced that the GaAs/CuInS₂ interface is strongly intermixed showing ordered crystalline embeddings up to a distance of about 5 nm from the original GaAs surface. Also XPS and LEED experiments investigating the initial growth stages in a step by step deposition approach indicate recrystallisation processes at the interface. Possible interdiffusion phenomena are discussed.
- D/PII.06** INFLUENCE OF THE PHOTOCONDUCTIVE PROPERTIES OF THE THIN FILMS ON THE PROPERTIES OF THE CdS/CdTe SOLAR CELLS
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 Several aspects must be taken into account for the fabrication of high efficiency CdS/CdTe solar cells. One of them is the photoconductivity properties of the high resistivity thin films used as window and absorber materials in the superstrate configuration. In this work we study the changes in the ideal diode factor (n), saturation current (J₀) and the bulk series resistance of the layers, under illumination respect to dark conditions These changes are analysed as due to the photoconductivity effect of each layers. The properties of the heterojunctions are affect for the photoconductivity properties of the CdS and CdTe layers and the therefore is a direct connection between the photoconductivity properties of the layers and the solar cells improvement. Particularly the solar cells efficiency (h), the short circuit density current (J_{sc}), fill factor (FF),the open circuit voltage (VOC),the ideal diode factor (n) and saturation current (J₀) are reported and the influence of the photoconductivity of the layers in the above parameters is discussed.
- D/PII.07** PREPARATION AND CHARACTERIZATION OF CuIn_{1-x}Ga_xSe₂ THIN FILMS OBTAINED BY SEQUENTIAL EVAPORATIONS AND DIFFERENT SELENIZATION PROCESSES
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 CuIn_{1-x}Ga_xSe₂ (CIGS) (x=Ga/(In+Ga)) thin films are one of the promising absorbing materials for polycrystalline thin films solar cells. Several methods have been performed to prepare CuIn_{1-x}Ga_xSe₂ thin films. In our lab, CIGS thin films have been deposited using a two-stage method. In the first stage, the metallic precursors were evaporated sequentially. The sequence of evaporation was In/Ga/Cu/In. The selenization, named the second stage, was carried out with elemental selenium vapour at 500° C in vacuum or flowing Ar environment.
 The effect of the treatment atmosphere (in vacuum or Ar) and chemical treatment after selenization on the main properties of CIGS thin films, such as structural, morphological, compositional, electrical and optical, has been studied. Single-phase chalcopyrite and polycrystalline CIGS films with (112) preferred orientation were obtained. Ar selenization allows achieving an improvement in the crystallite feature and an increase of grain size, as shown by XRD and SEM. The optical properties get better after Ar selenization, too. The high absorption coefficient of thin films was reduced in band tails after KCN chemical etching, which lead to a small increase of the electrical resistivity.
- D/PII.08** STRUCTURAL AND OPTICAL CHARACTERIZATION OF CuInSe₂ FILMS FABRICATED FROM NANO-PARTICLE PRECURSORS
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 The semiconductor CuInSe₂ (CIS) is excellent photovoltaic material due to suitable bandgap and high absorption coefficient. Non-vacuum techniques based on nano-particle deposition in combination with selenization treatment have been successfully used in the preparation of thin film devices. However, no studies on the structural and photoluminescence (PL) properties of this compound are reported.
 This paper focuses on the selenization of nanosized (Cu + In) precursors into CIS films and microstructural and photoluminescence properties of these layers. The composition and morphology of films were analyzed by energy-dispersive X-ray (EDX) analysis. The depth profiling was done by Auger electron spectroscopy (AES). PL spectra were studied from 4.2 to 300 °K at different excitation power using 488 nm radiation from an Ar⁺ laser. It was shown that precursor layers can be transferred into polycrystalline films by selenization treatment. The CIS films had chalcopyrite crystal structure with the grains in the size of 1-2 μm and uniform distribution of elements in the bulk of the layer. The PL experiments showed strong energy shift of the PL bands with temperature and excitation power. Using the knowledge obtained from the composition of the samples, we attempt to identify the nature and origin of the native defects involved in the observed PL spectra.
 The work is sponsored by the Belarus Found of Fundamental Investigations and the Programme SCOPES 2000-2003 (Project No 7IP65688).

- D/PIL.09** ELECTROCHEMICAL DEPOSITION OF COPPER INDIUM ALLOY PRECURSORS FOR CuInSe₂ SOLAR CELLS
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 Our motivation was a low cost production process of copper indium diselenid (CIS) solar cells. Therefore we developed a binary copper indium electrodeposition bath with copper sulphate and indium sulphate. The goal was to deposit a copper indium alloy with a copper indium ratio near by 1:1 and a little excess of indium. By means of a rotating disc electrode we deposited copper as well as indium rich films on metall foils. Afterwards this electrodeposited precursor layers were annealed in an elemental selenium atmosphere to obtain CIS. That was followed by a chemical bath deposited cadmium sulphide layer, an intrinsic zinc oxide layer and aluminum doped zinc oxide layer to produce solar cells. The best solar cells with an area of 0,25 cm² have a conversion efficiency of 1,6 %.
- D/PIL.10** PREPARATION OF STOICHIOMETRIC CuInS₂-SURFACES
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 CuInS₂ films with significant deviation from stoichiometric composition were investigated with photoelectron spectroscopy. For Cu rich films we show that by Ar sputtering and controlled annealing the surface composition varies along a binary cut of the Cu-In-S ternary phase diagram. This procedure leads to a surface composition close to the stability range of the pure CuInS₂ phase. Polycrystalline CuInS₂ samples are an ideal system for photoemission electron microscope (PEEM) studies. We find that the individual grains trend to coagulate, the surface composition becomes more homogeneous, and identify characteristic features of the unoccupied DOS.
 Furthermore, we characterised surfaces of Indium-rich CuInS₂ films, fabricated by coevaporation and a KCN-etching process to remove CuS-segregations at the surface. A combined annealing and evaporation procedure results in surface compositions near the stoichiometric ratio of Cu/In (=1).
- D/PIL.11** LIQUID - PHASE ELECTROEPITAXY OF LOW BAND - GAP InAsPSb/InAs HETEROSTRUCTURES FOR THERMO - PHOTOVOLTAIC DEVICES
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 For thermophotovoltaic (TPV) power convertors semiconductors with appropriate band gap should be chosen. Three material systems are under investigation at present, in various laboratories - In_xGa_{1-x}As, In_xGa_{1-x}Sb and InAs_{1-x}P_x. This report describes our efforts to manufacture epitaxial diode heterostructures on the basis of InAsP and InAsPSb layer grown on InAs substrates for such application.
 For the fabrication of these types of TPV structures the liquid phase electroepitaxy has been employed. First type of structure consists of the n-InAs and compositionally graded p-InAsP layer. Second type of structure consists of Zn-doped quaternary InAsPSb layers directly grown on InAs substrate. The structures have a uniform thickness and mirror-like surface. The interface between two types of epilayers and InAs substrate is very flat. The dislocation density on the surface was no more than 10⁵ cm⁻². The current-voltage characteristics and capacitance-voltage characteristics of n-InAs / p-InAs_{1-x}P_x and n-InAs / p-InAsPSb TPV structures have been investigated. The spectral response of a TPV device fabricated in an epitaxial n-InAs / p-InAsPSb heterostructures has been measured. The results of these studies showed that the second type of TPV structures has better performance in comparison to the first type.
- D/PIL.12** WIDE BANDGAP P-TYPE WINDOWS BY CBD AND SILAR METHODS
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 Transparent n-type windows are well known and are intensively investigated. Transparent p-type conductors on the other hand have only recently come under investigations. The main problem is that the conductivity of p-type conductor is lower than those of n-type materials for the same transparency. Materials such as CuI, CuSCN, and CuAlO₂ are actively studied. In this report, we develop a new process using chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) for the preparation of CuI and CuSCN. Both methods are inexpensive, low temperature (25-90°C) process and can be used for large-scale application. The growth of CuI and CuSCN by CBD and SILAR require the use of Cu(I) cation as a copper ion source. This is achieved by using Na₂S₂O₃ as complexing agent for Cu(II). The anion reactions are achieved by using either KI as iodine or KSCN as thiocyanide sources for CuI and CuSCN, respectively. The deposition was carried out at room temperature (25°C). The preparative parameters were optimized with the aim of using these p-type materials as windows for n-CuInS₂ (n-CIS) based solar cells. Structural, surface morphological and optical studies are investigated.
 This work is supported by the European Commission within the framework of CISLINE project under contract no. ENK6-CT-2001-00519. CISCuT samples are provided by Institut für Solar Technologien, GmbH.

- D/PIL.13** INFLUENCE OF THE GROWTH TEMPERATURE ON THE STRUCTURAL QUALITY OF CU(INGA)SE₂ AND CUINSE₂ THIN FILMS FOR SOLAR CELL APPLICATIONS
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Cu(InGa)Se₂ (CIGS) is a promising material for solar cell applications. Polycrystalline CIGS and CuInSe₂ (CIS) thin films with various elemental composition were synthesised by two-stage selenization process on glass substrates. The surface morphology, phase structure and composition of the films were analysed by Scanning Electron Microscopy, X-ray Diffraction and Energy-Dispersive X-ray Analysis, respectively. Photoluminescence (PL) at temperatures from 4.2 to 300K was used to characterise defects and the structural quality. An increase in the growth temperature from 460 to 5600C was found to improve the structural quality and decrease defect population in the CIS films. The PL spectra indicate a high electronic quality for selenisation at 5200C for 20-30 min. Lower temperatures lead to non-equilibrium effects and the appearance of deep energy levels in the band gap. Temperatures in excess of 5300C lead to a decrease in the PL intensity and the disappearance of excitonic features indicating a degradation of the material. It was shown that by choosing adequate deposition conditions (temperature, annealing time, etc.) homogeneous, high-quality films of CIGS and CIS can be prepared.
- D/PIL.14** XPS AND XPD STUDY OF CU(INGA)SE₂ SURFACE
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CuInSe₂ based solar cells are amongst the most promising thin film photovoltaic (PV) devices. Surface related physical processes play a vital role in the performance of solar cells. The evolution of the elemental composition and chemical bonding of the (112) surface of Cu(InGa)Se₂ single crystals with 5% Ga and 95% In, cleaned by 4keV N⁺ and then annealed at temperatures from 100°C to 750°C in vacuum, was analysed using X-ray photoelectron spectroscopy. Following annealing at 650°C the surface was examined using X-ray photoelectron diffraction. 180° projection maps were constructed from the full hemispherical intensity distributions of In, Cu, Ga photo- and Se Auger-electron emission. These maps, the elemental composition and chemical bonding suggested several options for the surface structure. In order to clarify which structure has been observed experimentally theoretical simulations of the projection maps were performed assuming the suggested surface structures.
- D/PIL.15** LATTICE DYNAMICS AND STABILITY OF CuInSe₂
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CuInSe₂ is a promising material for thin-film solar cells. The origin of its extraordinary radiation stability remains unclear. We performed first-principles simulations of elastic properties, lattice dynamics, and ionic mobility in this material in relation with its electronic structure, as accessible within the density functional theory. Technically, calculations have been done with the SIESTA code [1] making use of norm-conserving pseudopotentials and efficient atom-centered numerical basis functions. Dynamical simulations included structure optimization, frozen phonons and Born-Oppenheimer molecular dynamics, feasible due to the forces available directly with high accuracy. For a perfect crystal, the calculated zone-center phonons and elastic properties were compared with the results obtained by an all-electron method of superior precision (WIEN2k, [2]). The effect of non-stoichiometry and the presence of intrinsic defects on phonon frequencies and on plausible diffusion channels were investigated in the supercell approach. Simultaneously, the changes in the electronic structure due to the presence of defects were analyzed.
[1] J. M. Soler, E. Artacho, J. D. Gale et al., J. Phys.: Cond. Matter 14, 2745 (2002).
[2] P. Blaha, K. Schwarz, G. Madsen et al., WIEN2k, <http://www.wien2k.at>
- D/PIL.16** CHANGES IN SPECTRAL RESPONSE WITH TEMPERATURE AND IRRADIANCE INTENSITY
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The energy yield of a photovoltaic device under outdoor conditions depends on the performance of the device under large variations of three main parameters, the device temperature, the irradiance distribution (spectrum) and the overall irradiance intensity. A performance matrix with the parameters temperature and irradiance intensity can be measured in the laboratory. To correlate this data properly with outdoor data, the changes in the spectrum (during each day and with seasons) has to be accounted for. This requires the knowledge of the spectral response of the device for all conditions. This work presents systematic measurements of the spectral response for various thin film technologies (a-Si, CdTe and CI(G)S). The experiments were performed on a dedicated laboratory test stand at various irradiance intensities and device temperatures. The results serve the following aims:
- Understanding the outdoor device performance: The dependence on temperature and irradiance level is directly measured and the spectral response can be used for modeling the influence of spectral changes.
- Performing the spectral mismatch correction of the performance matrix: These measurements with a solar simulator have to be corrected for spectral mismatch, which depends on temperature and irradiance intensity.
- Optimisation of the spectral response measurement under standard test conditions (25°C and 1000 W/m² with AM1.5G spectral distribution): This measurement is required for a standard device calibration. The results here can serve as an input for a correction procedure to be applied for measurements performed under conditions differing from standard test conditions.

D/PIL.17**MODELING AND NUMERICAL SIMULATION OF HYDRODYNAMIC ELECTRODEPOSITION PROCESSES FOR OBTAINING THIN FILM MATERIALS FOR PHOTOVOLTAICS**

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There are many electrochemical techniques in which the electrode moves with respect to the solution. Those systems, like the rotating electrodes, vibrating electrodes or whose in which there is a forced solution flow passing a stationary electrode, are called hydrodynamic electrochemical processes. The aim of the present work is to model and to numerically simulate the hydrodynamics, electrochemical and chemical phenomenon which are occurring during the electrodeposition process. Electrochemical and chemical processes are then taken into account, obeying a classical EC scheme. Both precipitation and complexation phenomena are taken into account in the numerical example chosen: the zinc oxide electrodeposition. Results show that, because of volumetric precipitation and complexation reactions, the classical Levich diffusion theory, which correlates boundary layer depths for the rotating electrode, are lost and chemical boundary layer thicknesses are greatly modified in the reacting case. In a last point, this study uses the mesoscopic scale results to define local weighted probability for working particles which form the material layer, allowing the local porosity and rugosity estimation by fractal calculation.

D/PIL.18**SPECIAL FEATURES OF ELECTRIC AND PHOTOELECTRIC PROPERTIES OF n-Cd_{1-x}Zn_xS/n-CdS_{1-y}Se_y HETEROJUNCTIONS**

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Wide-band films of Cd_{1-x}Zn_xS and CdS_{1-y}Se_y possess the high photosensitivity and are perspective materials for creation of sources and receivers of a radiation in the visible and infrared (IR) spectral regions. At the same time it is known that the thin film solar cell technology offers the best hope for obtaining photovoltaic devices with low cost and reasonable efficiency. The development of chemical deposition technique opened a possibility to fabricate large-area high-sensitive solar cells on the base of Cd_{1-x}Zn_xS and CdS_{1-y}Se_y films with considerable cost reduction per heterojunction when compared to standard vacuum evaporation technique.

Present work devotes to results of investigations of some electrical and photoelectrical properties of heterojunctions (HJ) in the system Cd_{1-x}Zn_xS-CdS_{1-y}Se_y. The n-Cd_{1-x}Zn_xS/ n-CdS_{1-y}Se_y HJ were prepared by the method of chemical deposition.

For making of HJ, films Cd_{1-x}Zn_xS (0 ≤ x ≤ 0.6) and CdS_{1-y}Se_y (0 ≤ y ≤ 0.4) were used, which were obtained by the method of chemical deposition at temperatures of 350-365 K. Concentration of charge carriers at 300 K was 10¹³ - 10¹⁴ n̄i⁻³ in used films of Cd_{1-x}Zn_xS and 10¹⁵ - 10¹⁶ n̄i⁻³ in films of CdS_{1-y}Se_y.

Ohmic contacts to films Cd_{1-x}Zn_xS and CdS_{1-y}Se_y were manufactured by fusion of the indium. Ohmage of contacts was preliminary controlled of volt-ampere characteristic (VAC) symmetric structures In-Cd_{1-x}Zn_xS-In and In-CdS_{1-y}Se_y-In. VAC of all manufactured HJ possesses by the obvious diode character. Rectification coefficient is 10³ for n-Cd_{0.8}Zn_{0.2}S/n-CdS_{0.6}Se_{0.4} at U = 2 V and smoothly decreases, with increasing of the heat-treatment (HT) temperatures. Observed direct bias of VAC for the system Cd_{1-x}Zn_xS-CdS_{1-y}Se_y at different temperatures shows that forward currents mainly correspond to the recombination-tunnel mechanism. Dependence of I ~ Uⁿ (where n ≥ 2) is observed at relatively high voltages. It may be explained by the injection of charge carriers in CdS_{1-y}Se_y. Reverse bias of VAC correspond to the exponential dependence at relatively high voltages.

Measurements of the junction capacitance as a function of reverse bias were used to determine the built-in voltage (V_d = 0.5; 0.67; 0.95) and the effective doped concentration (N_i = 8.2·10¹⁴; 7.4·10¹⁴; 6.5·10¹⁴cm⁻³) for x = 0; 0.2; 0.4 (CdS_{1-y}Se_y) near the junction.

Spectral distributions of photosensitivity (SPD) of HJ were investigated for different thickness of the CdS_{1-y}Se_y films (d = 0.5; 2 and 8 μm). For structures with d = 0.5 μm, the maximum of SPD lies at 2.4 eV and for 2 μm on SPD appear two maximums - at 1.75 and 2.4 eV. For heterojunctions with 8 μm, the maximum at 2.4 eV is not observed and the second maximum of a photosensitivity in this case lies at 2 eV.

After HT on air at temperature 450⁰N for 11 min, in the spectrum region of 1.3-1.12 eV occurs a considerable photosensitivity of HJ. It is established that the change in the spectral photosensitivity character of heterojunctions under different HT regimes is well explained by means of the mechanism of impurity photovoltaic effect connected with optic transitions from valence band onto r- centers. HT of the HJ on air for 25-30 min results to decrease of long-wave photosensitivity maximum.

The heterojunctions have a current photosensitivity of 0.6 A/W in the spectral region between the band gaps of Cd_{1-x}Zn_xS and CdS_{1-x}Se_x.

D/PIL.19**OPTOELECTRONIC PROPERTIES OF CuGaSe2 FILMS**

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Although thin film solar cells based on CuGaSe2 (CGSe) absorber layers are very promising, their efficiency is still limited by the poor opto-electronic properties of these layers. Using non-contact techniques, transient photoconductivity measurements in the microwave frequency range (TRMC measurements) and photoluminescence spectroscopy (PL) at ambient temperature, we present a systematic study on the optical and electrical properties of single crystal and polycrystalline CGSe thin films. Thin films were deposited in two stages by an open-tube chemical vapor deposition process. The first stage leads to a nearly stoichiometric polycrystalline CGSe film. During the second stage the film is annealed in a Ga- and Se-rich atmosphere leading to a non-stoichiometric (slightly Ga-rich) film.

PL measurements of nearly stoichiometric CGSe, single crystals and thin films from 10K-300K suggest the presence of one main recombination path, dominant over the whole temperature range. After Ga and Se annealing this recombination path vanishes. A large difference in excess charge carrier kinetics between stoichiometric and annealed samples is observed, as stoichiometric films show a very fast decay, where annealed films show an extended photoconductivity decay over several orders of magnitude in time characterized by a power law. These results are attributed to the higher density of deep recombination states in stoichiometric CGSe, also revealed by sub gap absorption spectroscopy. This explains the apparently paradoxical result that the solar energy conversion efficiency is considerably higher in solar cells with annealed CGSe absorbers than in those with stoichiometric absorbers, in spite of the structural superiority of stoichiometric CGSe.

D/PII.20**PHOTOELECTROCHEMICAL DEPOSITION OF BI₂SE₃ CLUSTERS ON COLLOIDAL SE PARTICLES**

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The processes of core(colloidal Se particle)-shell(Bi₂Se₃ clusters) semiconductor structures synthesis were studied. Colloidal Se particles were prepared by the reduction of Se(IV) oxide aqueous solution with Ti(IV)/Ti(III) redox pair. The formation of Bi₂Se₃ clusters on the surface of Se was due to the photoinduced underpotential (upd) deposition of Bi on Se.

In order to generate electrons in Se particles colloidal solution of Se was illuminated. The necessary level of electrochemical polarization of Se particles was achieved by the means of Ti(III)/Ti(IV) redox pair introduced into the solution. The potentials applied were more negative than flat band potential of amorphous Se (E_{fb} = +0,5В). On illumination, electron-hole pairs photogenerated in Se are separated by the field in the space charge region. Photoelectrons move towards the surface of Se particle and reduce Bi(III) ions, resulting in the photoinduced upd. Bismuth adatoms being oxidized with selenium surface atoms form Bi₂Se₃. The formation of Bi₂Se₃ at the surface of Se particles gives a significant rise of absorption in the long-wavelength region of the spectrum, where the colloidal solution of Se absorbs negligibly. The clusters of Bi₂Se₃ were detected by the potential of electrochemical oxidation and by the rise of the absorption in the long-wavelength region of the spectrum.

D/PII.21**ZnO POROUS THIN FILMS GROWN BY CHEMICAL BATH DEPOSITION**

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In order to grow by chemical bath deposition ZnO thin films (CBD-ZnO), the solution used was zinc acetate with ethylenediamine. Its pH was adjusted by addition of NaOH (11.1 < pH < 11.3). During the chemical bath deposition the bath temperature was 65 °C. After deposition the films were annealed in room air half an hour at 500 °C. These films were crystallized in the hexagonal structure, with small grain size. The films were nearly stoichiometric as shown by microanalysis: The films are semiconductors with p-type conductivity. As shown by scanning electron microscopy the films are highly porous: Some ZnO films have been deposited on tin oxide coated glass substrates. These films, which present the same morphology as those deposited on bare glass substrate, have been used to grow n+SnO₂/ZnO/ZnPC structures: The zinc phthalocyanine films have been deposited by spin coating. These structures have been tested using an Al tip as upper electrode. They exhibit a diode like behavior when the SnO₂ is positively biased. When the SnO₂ is submitted to room light, the structures behave as solar cells.

D/PII.22**STRUCTURAL AND OPTICAL CHARACTERIZATION OF AgInS₂ THIN FILMS GROWN BY VACUUM EVAPORATION METHOD**

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Solar cell techniques using I-III-VI₂ chalcopyrite semiconductors have made rapid progress for the solution of environmental and resources problems. Among chalcopyrite semiconductors, AgInS₂ may be also promising material for short wavelength side of tandem solar cell. However, AgInS₂ has two crystal forms such as chalcopyrite and orthorhombic. The orthorhombic form is stable at more than 620°C and the chalcopyrite form is stable at less than 620°C. Therefore, a crystal growth of AgInS₂ crystal is difficult because of high melting point.

Evaporated AgInS₂ thin films on glass substrate were grown at 100 ~ 300 °C. An evaporated source was successfully grown by hot-press (HP) method. The films were examined by the X-ray diffraction (XRD), electron probe microanalysis (EPMA), scanning electron microscopy (SEM) and optical absorption measurements. The XRD spectra indicate that poly AgInS₂ films are grown on glass substrate at 100°C. Composition of AgInS₂ increases with increasing substrate temperatures. The EPMA results show S - poor in the all samples. Surface morphology of the samples is drastically changed. A number of the spots increase with increasing the annealing temperatures. Furthermore, transmittance increases with increasing the temperatures.

D/PII.23**PIEZOELECTRIC PHOTOTHERMAL INVESTIGATION OF URT-IP ZnO THIN FILMS FOR PHOTOVOLTAIC DEVICES**

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Wide bandgap oxide-semiconductors have attracted much attention for liquid crystal displays and photovoltaic devices. Especially, ZnO is a semiconductor with a large bandgap of 3.4 eV at room temperature. The n-type ZnO films for CuInGaSe₂ based photovoltaic devices have been usually grown by the sputtering method. However, the photovoltaic devices have plasma damages by the sputtering method. Therefore, URT - ion plating (IP) method is expected as low damages for photovoltaic devices. In this work, n-type Ga-doped (2~4 wt%) ZnO thin films were grown by URT - IP method on glass substrates at 200 °C under oxygen flow rate of 0 ~ 30 sccm. Piezoelectric photothermal spectroscopy (PPTS) was carried out for characterization of nonradiative recombination processes. One of the great advantages of the PPT measurements is that the nonradiative recombination processes can be measured directly. Therefore, the PPT technique may complement the photoluminescence (PL) technique. All samples indicate (0002) orientations. Transmittance of all samples is obtained more than 90 %. It is not depended on the carrier concentration and oxygen flow rate. A PPT signal which can not obtained in the undoped ZnO sample can be successfully obtained in the Ga-doped ZnO sample. This peak energy is not obtained in the PL and absorption spectrum. Therefore, this signal is due to nonradiative recombination process by Ga-related defects.

D/PII.24

PROPERTIES OF ZnO/Cu₂O AND ITO/Cu₂O HETEROJUNCTIONS PREPARED BY ION-BEAM SPUTTERING
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Cuprous oxide was once extensively studied for photovoltaic purposes in 1970's and later abandoned because then only possible rectifying junction with Cu showed very low conversion efficiency. The results were not promising because of the low internal barrier height of the Cu/cuprous oxide junction and the high resistivity of the cuprous oxide materials. We succeeded in preparing low-resistivity thin cuprous oxide foils with thickness about 50 microns and 1 square centimeter in area by heating Cu foils at 1460 K in oxygen atmosphere of around 20 Pa. The diode prepared by evaporating copper on the cuprous oxide foil showed forward resistance about 2 - 4 ohms, markedly smaller than results reported earlier by more than an order of magnitude. Heterojunctions with ZnO (2 wt% Al) and with ITO were also prepared by bombarding sintered targets with 800 eV argon beam in high vacuum. ZnO/cuprous oxide and ITO/cuprous oxide were found to be rectifying, and characterized by higher barrier height and larger dark resistance than Cu/cuprous oxide. Interfacial properties were studied by observing the depth profile of the junction by X-ray photoelectron spectroscopy. The marked depletion of oxygen at the interface region, as was reported earlier by Herion et al., was not observed in the present experiment. This discrepancy can be traced back to the difference of deposition methods, i.e. R.F. sputtering (Herion et al.) vs. ion-beam sputtering. Present experimental results seem to shed new lights on the possibility of using those metal oxides as photovoltaic materials.

D/PII.25

STRUCTURAL AND OPTICAL PROPERTIES OF Cu(In,Ga)Se₂ SINGLE CRYSTALS AND THIN FILMS

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Chalcopyrite semiconductors (CIS and CIGS) are promising photovoltaic materials due to the optimal band gap and high absorption coefficient. Their properties depend strongly on technological methods and conditions during the growth process of bulk crystals and thin films. The best way to get the data to optimize the growth technology is to compare the physical properties of single crystals and thin films. The results of XRD and SFM analysis, optical spectroscopy of Cu(In,Ga)Se₂ single crystals and thin films are presented in this paper. Single crystals of sufficient perfection with different compositions were grown by horizontal gradient cooling method. To obtain thin films we used thermal evaporation and magnetron sputtering. In the both cases we used glass as a substrate. The results obtained for absorption spectra of CIGS films are interpreted using complicated band structure of chalcopyrite materials, namely the valence band splitting due to the non-cubic crystal field and spin-orbital interaction. Analysis of the experimental data proves that the fluctuations of the molar composition of the thin films could take place in comparison with the composition of bulk crystals, from which the films were obtained.

D/PII.26

THEORETICAL STUDY OF THE EFFECT OF AN INSULATOR TUNNEL BARRIER IN CIS-BASED ETA-SOLAR CELLS

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Insertion of very thin insulator oxide coatings (MgO, Al₂O₃) at the active interface of nano-structured solar cells, has led to significant improvement of solar cell characteristics. This holds both for dye-sensitized cells and all solid state eta-solar cells, where an Extremely Thin inorganic Absorber layer (such as CuInS₂) is applied at the interface of a transparent nano- or microstructured p-n heterojunction (such as n-TiO₂/p-CuSCN). In these kind of cells, materials interfaces are never further away than ~25 nm, and are suspected to play a significant role in cell behavior: the dark current and hence Voc is likely to be determined by interface recombination.

In this article the theoretical base is studied for possible improvements in cell current and voltage for TiO₂/IL/CuInS₂ based solar cells, where the intermediate layer (IL) can be Al₂O₃, MgO or CdS. Depending on the energy barriers imposed by the band alignment, the thickness of the IL should not exceed a few nm, to allow collection of the light current by tunneling. We see three mechanisms to improve Voc without compromising Jsc: (i) the band alignment can be such that the dark current necessitates a tunnel step, whereas the light current does not; (ii) the interface state density at either side of the IL is reduced compared to the structure without IL, for materials reasons; and (iii) the interface state density is unchanged and high, but their effect can be greatly reduced due to a more favourable position of the Fermi levels at the interface, with respect to the band edges.

D/PII.27

HIGHLY RESISTIVE Cu(In,Ga)Se₂ ABSORBERS FOR IMPROVED LOW IRRADIANCE PERFORMANCE OF THIN FILM SOLAR CELLS

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Operation of a solar cell under low irradiance requires a high value of the shunt (parallel) resistance R_p of the cell. In Cu(In,Ga)Se₂ solar cells, R_p ³ 15 kWcm² degrades the cell performance at irradiances below 1/100 sun. However, cells realised with a Cu(In,Ga)Se₂ absorber material with a Cu content of only 18 at.% show a value of R_p that is increased by more than one order of magnitude making those solar cells suitable for application at around 1/1000 sun. We observe that the bulk resistivity of the absorber material is directly proportional to the shunt resistance of the corresponding solar cell. Based on these observations, the physical nature of the parallel resistance R_p in Cu(In,Ga)Se₂ solar cells is discussed.

D/PII.28

ELECTROCHEMICAL ANALYSIS OF CATHODIC DEPOSITION OF ZINC OXIDE THIN FILMS USING A ROTATING DISK ELECTRODE

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We have studied in detail mechanism of cathodic electrodeposition of zinc oxide (ZnO) thin films from aqueous solution of zinc salts using a rotating disk electrode. We show a difference between two precursors of hydroxide ions, namely, nitrate ion and dissolved oxygen. While diffusion limit can be reached for oxygen reduction in a zinc free electrolyte, a significant decrease of cathodic current occurs upon addition of zinc chloride. The current was well described by Koutecky-Levich equation. The growth of ZnO film in this system is therefore under control of both mass transport and charge transfer kinetics. Such a slowdown of charge transfer was not observed when a ZnO coated electrode was measured in a zinc free solution. The origin of the slow electron transfer can therefore be attributed to the surface coverage by zinc hydroxide and its slow chemical conversion into crystalline ZnO. By contrast, ZnO growth from zinc nitrate bath is dominated by charge transfer kinetics when both zinc and nitrate ions are present at sufficiently high concentrations. Nitrate is electrochemically inert in a zinc free solution. However, it has been found that the rate of nitrate reduction increases on increasing the concentration of zinc ion.

D/PII.29

PERFORMANCE AND BEHAVIOUR OF POLYCRYSTALLINE THIN FILM p-CuGa_{0.2}In_{0.8}Se₂/n-CdO HETEROJUNCTION SOLAR CELL

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CuGaxIn_{1-x}Se₂ has proved to be one of the best materials as a heterojunction partner for efficient solar energy conversion. Thin films of this material have been grown by a variety of deposition techniques and the best results reported have been obtained only for the layers deposited using sophisticated techniques. In this work an attempt has been made to deposit high quality CuGaxIn_{1-x}Se₂ layers using a simple and cost effective method, spray pyrolysis. In the present study thin film heterojunctions have been produced with the configuration glass/Mo/p-CuGa_{0.2}In_{0.8}Se₂/n-CdO using sprayed CuGa_{0.2}In_{0.8}Se₂ films as the absorber layer and magnetron sputtered CdO as the window layer in an attempt to test the quality of the sprayed CuGa_{0.2}In_{0.8}Se₂ layers for application in photovoltaic cells. The devices were characterised using current-voltage, capacitance-voltage and spectral response measurements in order to evaluate the junction behaviour and cell performance. The diodes had a saturation current density of 10⁻⁶ A/cm², a diode quality factor of 1.95 and with a barrier height of 0.85 eV. The current transport across the junction was modelled as a composite of tunnelling and interface recombination mechanisms. The best cells have shown solar conversion efficiencies of 2.3 % with quantum efficiencies higher than 70%.

D/PII.30

RAMAN SCATTERING AND PHOTOLUMINESCENCE ANALYSIS OF B-DOPED CDS THIN FILMS

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Heterojunction devices utilizing CdS thin films as one of the components continue to be of considerable interest in optoelectronic applications. The two basic requirement of the CdS film in this heterojunction solar cell application are low electrical resistivity and high optical transparency. Among various techniques, chemical bath deposition yields stable, uniform, adherent films with good reproducibility by a relatively simpler process. However, undoped CdS films prepared by the chemical deposition generally show high electrical resistivity due to near stoichiometric composition. Failure to make these films n-type limited their utilization as a window material in most heterojunction devices. In this work, CdS thin films were prepared with intentional boron doping by chemical bath deposition using boric acid as dopant source, and Raman scattering and photoluminescence were investigated to evaluate proper doping level for good quality films.

The resistivity significantly decreased with increasing boron concentration, reached a minimum, and then increased with further increases in boron concentration. A shift in the absorption edge toward shorter wavelengths due to increasing carrier density was observed. The photoluminescence spectra of the B-doped CdS films consist of two main emission regions of peaks located in the high energy (green emission) at 2.27 eV and in a low energy (red emission) at 1.50 eV. The green bands were attributed to the transition of vacancy sulfur vacancy V_S to the valence band and the donor-acceptor pairs recombination. The red emission band resulted from the transition of bound electrons from surface states to the valence band.

D/PII.31

FORMATION AND CHARACTERIZATION OF THERMAL DEPOSITION AND LASER ABLATED CDTE LAYER ON SI PATTERNED SUBSTRATES

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Scanning electron microscopy, infrared spectroscopy, electron diffraction and I-V characteristics measurement were performed to investigate the growth process, structural, optical, electrical and photoelectrical properties of CdTe epilayers and CdTe/Si heterostructures. The CdTe epilayers were prepared by two different methods: (1) the thermal deposition with substrate temperature from 523 oC up to 753 oC and CdTe target temperature of about 1023 oC; (2) the pulse laser deposition at 523 oC substrate temperature, 300 laser shots and using the Hg_{0.8}Cd_{0.2}Te as the target. Si patterned substrates in the regular tetrahedral pyramid form derived as a result of a chemical anisotropic treatment in KOH solution Si{100}. Layer growth behaviour has been analysed in terms of terrace-step-kink model. The thickness of the deposited layers was changed from a few nanometers up to a few micrometers. A comparison of test results has demonstrated that the thermal deposited layers were monocrystalline with total reflection up to 5%, they had spectral selectivity property and showed sensitivity at 0.03 sun source. They may be used for photosensitivity structures. The pulsed laser deposited layers had not photoresponse and may be used as a buffer layer in HgCdTe/Si structure preparation.

D/PII.32**IN-LINE DEPOSITED CU(IN,GA)SE₂ SOLAR CELLS: INFLUENCE OF DEPOSITION TEMPERATURE AND NA CO-EVAPORATION ON CARRIER COLLECTION**

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We investigated the influence of deposition temperature and sodium co-evaporation on the carrier collection properties of Cu(In,Ga)Se₂-solar cells. I-V and bias dependent quantum efficiency measurements were performed on cell deposited at 550 °C and 420 °C with and without sodium co-evaporation. A reduction of deposition temperature leads to a deterioration of solar cell output parameters. This deterioration is caused by a reduced sodium diffusion from the substrate as well as an increased grain boundary density. Bias dependent quantum efficiency measurements reveal that these effects lead to a decrease of minority carrier diffusion length. When sodium co-evaporation is performed solar cell with VOC and FF values in the range of high temperature devices are realised. However, jsc is not enhanced. Bias dependent quantum efficiency measurements show that an applied bias voltage has no influence on the quantum efficiency curve when sodium is co-evaporated during CIGS growth. This behaviour resembles the behaviour of the high temperature cell. We show that the sodium content in the Cu(In,Ga)Se₂-films has a strong influence on carrier collection.

D/PII.33**HALL MEASUREMENTS ON Al DOPED ZnO THIN FILMS DEPOSITED BY IBICVD**

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ZnO thin films doped with Al have been prepared by Ion Beam Induced Chemical Vapour Deposition (IBICVD) with the aim of obtaining transparent and conductive films. In this deposition method, a flow of a suitable and volatile organometallic precursor is decomposed on the surface of a substrate by a beam of reactive ions (i.e. O₂⁺) which have been accelerated to several hundreds of eV. Because of the kinetic energy supplied by the ion bombardment, the growing films could acquire some potential advantages: a higher purity and density or a particular crystallographic structure and texture. Since electrical conductivity of polycrystalline material is mostly limited by structural defects and grain boundary effects, we have used IBICVD to modify the microstructure of the films, with the aim of decreasing their electrical resistivity.

In this communication, we present the structural and electrical characterization of a collection of ZnO films prepared by IBICVD under different experimental conditions of doping, substrate temperature and composition of the ion beam. Electrical properties (resistivity, type or carriers, concentration and mobility of carriers) were determined by the van der Pauw method and measurement of Hall parameter. Microstructure and texture were obtained by electron microscopy (SEM) and X ray diffraction.

D/PII.34**Te-Ni BACK CONTACT FOR HIGHLY EFFICIENT CdTe SOLAR CELLS**

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In order to enhance the efficiency of CdS/CdTe thin films solar cells prepared by close space sublimation (CSS) was deposited a pure tellurium layer by thermal evaporation at the back of the CdTe. The influence of air treatment of the CdTe surface, before to applying the contact material was studied as a function of the treatment parameters. The primary improvement has been in the fill-factor of the cells, which is due to a more ohmic back contact. There has also been a small increase in voltage. Optimum air anneal temperature of 155 °C was found for these cells, at which short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and the fill factor (FF) peak. The influence of the substrate temperature on the photovoltaic parameters of solar cells show that at a lower substrate temperature the voltage was reduced and the series resistance was increased.

Temperature dependent measurements often reveal additional information about solar cell operation. The temperature dependence of J-V cells with the additional Te layer before the metallic back contact and without the additional Te was studied. In both cases, the cell's open-circuit voltage increased at reduced temperatures at the expected rate of approximately $-2 \text{ mV}/^{\circ}\text{C}$. In both cases also, current flow becomes more limited as temperature is reduced. The mechanism for current limitation in the two cases, however, is clearly different. With the Te layer, as noted above, the curves are quite linear, at higher voltages. Without the tellurium, they show the characteristic "rollover" behavior, which becomes more pronounced as temperature is reduced. The conclusion is that the Te is acting favorably to reduce the back-contact barrier.

The quantum efficiency (QE) for all cells is reasonably good for wavelengths between the band gap of the CdS window layer (510 nm) and that of the CdTe (845 nm). The primary loss over this range is the reflection of the cell. The highest-efficiency cell in this group has the most gradual transition between 500 and 600 nm, which is characteristic of intermixing between the CdTe and CdS layers. A second cell, deposited at a lower substrate temperature, has less intermixing. The cells made without the Te layer are more sensitive to post-deposition annealing, and the one annealed at too low a temperature had a distinctly lower QE at all wavelengths. Below 510 nm the current generation of all cells is negligible.

D/PIL.35**INTERPRETATION OF CAPACITANCE MEASUREMENTS IN CuInS₂ – ON - Cu- TAPE SOLAR CELLS**

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Copper indium disulphide cells fabricated on a continuous copper tape fabricated at IST (D) are continuously improving, now reaching efficiencies above 9 %, with Voc exceeding 650 mV, and fill factors well above 65 %. The internal structure of these cells however is complicated, and far away from that of an ideal flat and homogeneous crystalline cell: in the depth, there is a sequence of several different layers, which is inherent to this technology; also, lateral inhomogeneities cannot always be precluded. An admittance study was undertaken to characterise and explain the internal electronic cell structure.

We carried out C(V,f,T) measurements, i.e. capacitance and conductance versus voltage and versus frequency, at temperatures varying between 200 and 400 K. Light and dark I-V and spectral response measurements complemented this. Maxima are observed in the C-V curves at high forward bias voltage and explained by the occurrence of a reverse diode in series with the main cell (this has no influence in the active cell region, around mpp). A minimum is observed in some cells in the C-V curve at high negative bias, which can be indicative of lateral inhomogeneities acting as a reverse diode (the best cells do not show this effect). C-f and G-f measurements are interpreted in terms of deep states. The internal consistency of the interpretation of various measurements is validated with numerical simulation (SCAPS programme).

D/PIL.36**NON-EQUILIBRIUM PROCESSES IN THE CdTe MATERIAL**

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The study of time life of non-equilibrium charge carriers and their recombination mechanisms are particularly important in the designing of photovoltaic devices. In the present work we investigate the photoconductivity properties of CdTe crystals in wide range of temperature (T=300-10K). The bulk Bridgman CdTe samples were studied in the pulsed activation domain. From measurements the values of deep (E1=0,45 i E2=0,65 eV) and shallow (E3=0,10 eV) recombination levels were determined. These levels are caused by structural defects of Cd sublattice. In the low temperature region (T<40K) a large contribution to the photoconductivity process provide the trapping level E4=0,04 eV. Photoresponse points out also on an asymmetry of the rise and relaxation times, which is caused by macrodefects. In the paper we discuss the model of defects formed in CdTe and their role in the charge carriers recombination processes is addressed too.

D/PIL.37**COMPARATIVE STRUCTURAL AND OPTICAL STUDIES OF CUXGAYSE₂-LAYERS BY PHOTOREFLECTANCE AND PHOTOLUMINESCENCE SPECTROSCOPY**

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The structural and optical properties of MOCVD grown CuxGaySe₂ layers were studied at temperatures between 300 and 20 K in dependence of composition by modulated photoreflectance spectroscopy (MPR) and were compared to the results of photoluminescence studies (PL). In the MPR- spectra of Cu-rich and stoichiometric layers the three valence-split bands Ea, Eb and Ec, which are only weakly present in the PL-spectra, were clearly observed. Line shape analysis of MPR spectra gave following results: a) spectral lines appear less intense, red shifted and broadened with the temperature increasing from 20 to 300 K due to carrier scattering on phonons; the binding energy of the free exciton was obtained from the temperature dependence of the Ea band consistently for both spectroscopic methods, b) spectral lines are red-shifted and broadened with the [Cu]/[Ga] ratio increasing above 1.15, which is indicative of an increase in structural disorder, and c) line broadening is only partially removed after KCN-etching of the CuGaSe₂ layer surface and removal of the CuxSe-crystallites formed from the Cu-excess, which indicates that the disorder of Cu-rich layers is only partially due to the microcrystalline phase on CuGaSe₂ surface. The three valence band splitting is weakly observed in the spectra of Ga-rich layers at 20 K.

With reference to bare CuGaSe₂ layer, comparative MPR- and PL-studies of ZnSe/CuGaSe₂/GaAs and CdS/CuGaSe₂/GaAs hetero-structures at 20 K resulted in significant line shape changes of MPR-bands and intensity reduction of the valence-split PL-bands of CuGaSe₂ in the CdS/CuGaSe₂/GaAs structure, which could be indicative of modifications in excitonic emission.

D/PIL.38**RAMAN STUDY OF STRAINS IN THE Zn_{1-x}Be_xSe /GaAs ALLOY SYSTEMS**

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It was shown recently that Be incorporation in ZnSe lattice enhances bond stiffness, due to an enlarged amount of covalent bonding, and noticeable lattice strengthening has been observed. For example, while a 0.15 μm thick ZnSe/GaAs epitaxial layer is fully relaxed in spite of a lattice mismatch Da/a as low as 0.27%, a 1 μm thick Zn_{1-x}Be_xSe/GaAs remains pseudomorphic for Da/a values up to 1.14% (x=0.15) and becomes fully relaxed only for Da/a as high as 2.08%. This peculiar property gives an opportunity for a complete study of strains in ZnBeSe layers. With 1 μm thickness of the layers Raman scattering can be performed with the incident light parallel as well as perpendicular to the interface plane. As a result, we were able to observe the mode splitting into a singlet and a doublet, induced by the anisotropic strain associated with in-plane lattice mismatch in ZnBeSe/GaAs layers. Using the chemically etched bevelled-edges, it is demonstrated that the strain is uniform in the layers. Using values of the compliance tensor elements Sij in ZnBeSe alloys obtained by the linear interpolation from ZnSe and BeSe data, the deformation deduced from the Raman shifts are similar to those obtained from X-ray diffraction. Finally we can use these linear variations of the Sij coefficients to calculate the value of strains in the layers.

D/PIL39**DEFECTS CHARACTERISATION OF CUINS2 THIN FILMS**

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The study of native defects of CuInS₂ (CIS) thin films is very important for the development of high-efficient CIS solar cells. Defects introduce energy levels in the band gap, which determine the conductivity type and the excited state lifetime, being a key parameter. Here we combine different characterization methods to obtain a clear picture about the defect structure of CIS. Thin films of CIS are obtained by sulphurization of a CuIn metallic alloy. The films have been investigated with modern techniques, such as X-ray diffraction with Rietveld refinement, Raman spectroscopy, photoluminescence spectroscopy, and transient absorption. It is found that deposition parameters such as sulphur pressure and temperature determine the concentration and type of defects. In particular, the fraction of copper-gold ordering is strongly related to the process conditions. Also the famous light-soaking effect is studied in detail. Clearly the concentration of sulphur vacancies and the mobile Cu⁺ ions are involved. At the moment the difference between the theoretical conversion efficiency of CuInS₂ based solar cells and the obtained results are substantial. By obtaining fundamental knowledge of the defect structure, this gap can be reduced drastically.

D/PIL40**NANOCOLUMNAR ZnO FILMS FOR PHOTOVOLTAIC APPLICATIONS**

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Zinc Oxide is a wide gap semiconductor widely used in photovoltaic applications as a transparent conducting contact and, more recently, as a way to enlarge the active part of a solar cell. In the last case, enlarged surfaces of textured or porous substrates should be prepared. If the free space is then filled by a thin absorber the device has the main advantage of short electronic transport distance, which relaxes the requirements of large diffusion lengths. In this study we present structural and optical properties of nanocolumnar ZnO monocrystals obtained by electrodeposition on conductive glasses. Electrodeposition was made in a standard three-electrode reactor using an electrolyte composed by des-ionized water, KCl and ZnCl₂ in presence of dissolved oxygen was used. Crystalline ZnO hexagonal columns with different bases and heights were grown by this procedure. The dimension of the ZnO columns depends mainly on the growth parameters such as current density, deposition time and temperature of the electrolyte. Information about the dimension of ZnO columns was extracted from Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The surface-volume ratio of the ZnO columns and their dependence on the growth parameters will be discussed. Optical properties such as absorbance and photoluminescence were also investigated. The as-growth ZnO columns do not exhibit any photoluminescence property. Post-deposition annealing at low temperatures (300°C) results in a photoluminescence emission peak which, in some samples, is observed at room temperature. The evolution of the optical transmission spectra as well as the X-ray diffraction pattern with the annealing temperature will be also presented.

D/PIL41**CIGSSe THIN FILM PV MODULES: FROM FUNDAMENTAL INVESTIGATIONS TO ADVANCED PERFORMANCE AND STABILITY**

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A process for high efficiency large area Cu(In,Ga)(Se,S)₂ thin film (CIGSSe) solar modules is developed applying rapid thermal processing and controlled Sodium doping. Continuous optimization targets at sufficient process maturity to successfully transfer into cost effective mass production. The pilot line yields aperture area efficiencies of 11% (average) for 30x30 cm² modules and a certified champion efficiency of 13.1% for the first 60x90 cm² demonstrator module (unencapsulated). First Cd-free 30x30 cm² circuits yield up to 11.9% efficiency applying CBD-Zn(S,OH)-buffer layers. Investigations on the absorber formation by structural, compositional, and electrical characterizations will be given. Derived models for the Ga and S distribution will be discussed and experimentally verified. A favorable double band gap grading structure is accomplished by controlled Sulfur profiling and by natural Gallium accumulation towards the back electrode. The stability of the frameless low cost packaged pilot line modules against humidity is confirmed externally by passing the damp heat test sequence according to IEC 61646.

D/PIL42**MATERIAL AND DEVICE PROPERTIES OF SINGLE-PHASE Cu(In,Ga)(Se,S)₂ ALLOYS PREPARED BY THE SELENIZATION/SULFURIZATION OF METALLIC ALLOYS**

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The alloying of CuInSe₂ with CuGaSe₂ and CuInS₂ allows for variations in the band gap of multinary semiconductor compounds from about 1eV to 2.4eV. Higher band gap absorbers in turn generates higher voltages and lower photocurrents, which allows more latitude in the tradeoff between the number of cells in the modules and the power losses in the thin conducting oxide. In this study, a novel two-stage processing technique was developed to produce single-phase Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)₂ alloys with band gap values between 1.1 and 1.5eV. The co-sputtered CuInGa metallic alloys were taken through various rapid heating and cooling stages in the presence of H₂Se and H₂S gases to control the reaction pathways from the binary selenides to the ternary and quaternary alloys in order to produce homogeneous Cu(In_{0.75}Ga_{0.25})(Se_{1-y}S_y)₂ pentenary compounds. The Cu/In+Ga, Ga/In+Ga atomic ratios were carefully controlled at 0.9 and 0.25 respectively, while the S/Se+S atomic ratio was varied between 0.1 and 0.6. Control of the selenization parameters at low temperatures around 400°C predominantly determined the degree of sulfur incorporation and hence the shift in lattice parameters and band gap. The total processing time was well below 60 minutes of which only 15 minutes was above 500°C. Grazing-incidence x-ray diffraction (GIXRD) between 0.2° and 10° revealed virtually no shift in the lattice parameters. The reproducibility of the process was clearly demonstrated by the performance of preliminary devices. At least 100 devices were fabricated of which more than 90% had Voc above 600mV with a maximum around 670mV. The conversion efficiencies showed a small variance between 11% and 13% in the band gap range between 1.1 and 1.3eV.

D/PIL43**OPTICAL AND ELECTRICAL PROPERTIES OF URT-IP ZnO THIN FILMS FOR PHOTOVOLTAIC DEVICES**

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Optical (photoluminescence:PL, transmittance and reflectance) and Hall effect measurements have been carried out on thin (200 nm) polycrystalline ZnO films (both undoped and Ga-doped) deposited on a glass substrate by URT-IP (DC-arc ion-plating) method at 200 degrees C. Film properties were studied with relation to the oxygen flow rate (OFR) in the deposition chamber and Ga-doping concentration.

For undoped films, an increase of OFR (0-50 ccm) led to increase in resistivity (4E-3-1E0 ohm.cm), and decrease in electron concentration n ($1.5E20$ - $3E18$ cm⁻³) due to the decrease of oxygen vacancies. At OFR of 10 ccm, mobility was maximum (20 cm²/Vs), and intensity of the near-band-edge PL was maximum. At high OFR (more than 20 ccm), deep PL (2.2 eV) was observed. Thus, the best-quality film was obtained with OFR of about 10 ccm. As a result of the Ga-doping, resistivity decreased and n increased about one order of magnitude (resistivity: $2E-4$ - $2E-2$ ohm.cm, n : $1E20$ - $2E21$ cm⁻³). The lowest resistivity was $2E-4$ ohm.cm for OFR of 10 ccm. Increase in OFR made resistivity high and n low. The maximum mobility was 20 cm²/Vs for OFR of 10 ccm. PL peak energy was higher than that of the undoped films, due to the non-k-conserving band-to-band transition. The optimum OFR was about 10 ccm, similar to the undoped films. Transmittance was more than 90% for visible. Electron concentration dependence of infrared (1100-2400nm) transmittance and reflectance was also studied.

D/PIL44**AN INVESTIGATION ON THE EFFECTS OF AMMONIA CONCENTRATION ON CHEMICAL BATH DEPOSITED CdS THIN FILMS USING EDTA AS COMPLEXING AGENT**

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Cadmium sulphide, Ⅱ-Ⅵ compound semiconductor, both in bulk and thin film, has been attracted much attention due to its potential uses in photovoltaic. Of all the growth methods, chemical bath deposition (CBD) has been proven to be the most suitable method. In spite of many studies that have been used to CBD of CdS, questions remain about the phase structure of the films and the ammonia system has always been studied. In this paper, the optical, structural, morphological and electrical properties of chemical bath deposited CdS films have been investigated with the ammonia concentration using EDTA as the complexing agent without stirring. The reason why the structure of the CdS thin films prepared by CBD is difficult to identify is mentioned by compare the X-ray diffraction patterns (XRD) of two samples (one was gotten rid of the porous lay by ultrasonic device, the other was not) using only ammonia as the complexing agent without stirring. The structure transformation of the cubic phase to hexagonal phase and the variation of morphology were found when the ammonia concentration varied from 0.156 M to 2.07 M. The effect of ammonia concentration on the resistivity, composition and optical properties of CdS thin films have also been investigated.

D/PIL45**PULSED NON-MELT LASER ANNEALING OF CuInGaSe (CIGS)BASED THIN FILM SOLAR CELL**

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Non-melt laser annealing (NLA) is been widely used to improve the surface and the near surface region properties of silicon wafers while preserving the intentionally induced compositional gradient in the bulk. This has encouraged use of NLA to reduce surface defects in CuInGaSe by confining the mobility of the atoms to the near junction region of the device. Pulsed Non-melt laser annealing (NLA) was performed using a KrF excimer laser with a combination of different laser fluences and pulses on CuInGaSe samples deposited on Mo-glass. An X-Y-Z scanner was used for precise control of NLA. The Dual beam optical measurement (DBOM) was used to measure excessive carrier lifetimes and Hall measurements were used to analyze the carrier mobility and sheet resistance. From the DBOM measurements we found that the excess carrier lifetimes increased from 1 ns to 7.02 ns after NLA treatment. The Hall measurements showed increase in carrier mobility by 3 folds and the resistivity reduced by almost 72% after the non-melt laser annealing thus improving the conversion efficiency of the complete solar cell. Structural characterization was performed using Philips X'pert MRD system by x-ray reflectivity, x-ray diffraction and glancing incidence x-ray diffraction measurements to see changes in the composition of the thin film spatially as well as depth-wise.

D/PIL46**MATERIAL PROPERTIES OF ZnO THIN FILM FOR PHOTOVOLTAIC DEVICES GROWN BY URT-IP METHOD**

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Pressure-slope type plasma ion plating (URT-IP) is a technique for depositing a thin film on a substrate. This method offers the advantage of low-ion damage, low deposition temperature, large area deposition, a high growth rates. Ga-doped ZnO thin films were grown on glass substrates using a 6% Ga content ZnO target. ZnO thin film growth was performed at a substrate temperature of 200 degrees C. Samples were grown using argon gas for the plasma source and oxygen gas for stoichiometry control. The oxygen flow rate was varied over the range 0-30 sccm. Electrical properties were measured using Hall effect measurements. A pronounced dependence of the growth rate and resistivity on the growth rate was found. In the low oxygen flux growth regime, the growth rate was found to initially quickly increase with increasing oxygen flow rate and saturate for an oxygen flow rate of 10 sccm. At this flow rate, the minimum value of the rate of resistance and maximum value of mobility were obtained. It was observed that the oxygen flow rate corresponding to the maximum value in mobility occurred at the largest growth rate.

D/PIL47

THREE – DIMENSIONAL DEFECTS IN CDTE FILMS OBTAINED BY PULSED LASER DEPOSITION

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The quality and monocrystallinity of Cd chalcogenides epitaxial films can be enhanced seriously by applying a pulsed (electron beam or laser beam) method for ablation of targets. The structure of laser deposited CdTe layers was investigated by THEED. This method is very useful for detection two kinds of 3 dimensional structural defects: 1) inclusions of a second crystallography phase 2) twinnings. Layers investigated exhibit crystallize only in sphalerite phase and contain some number of twinnings of the type {111}. The number of twinnings depends strongly on the technological conditions (like substrate temperature, crystallisation rate etc.) of deposition process.

D/PIL48

QUASI-EPITAXIAL GROWTH OF CuInS₂ FILMS ON SAPPHIRE BY RF REACTIVE SPUTTERING

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We demonstrate the deposition of CuInS₂ thin films on sapphire by radio frequency reactive sputtering with a Cu-In alloy target and H₂S gas. The RF power was kept constant at 200 W (2.47 W/cm²) and the substrates were heated up to 500°C, while the H₂S flow was varied from 28 to 35 sccm during the sputter process. X-ray diffraction revealed that the as-sputtered films are of mainly (112)-oriented CuInS₂ phase incorporating a minor CuInS₂ phase, which may be attributed to the In-rich composition of the target used. The X-ray diffraction rocking curve measurement on the (112) peak showed a full width at half maximum of 0.1°, indicating an epitaxial-like growth of (112)-CuInS₂ films on (001)-sapphire. Six peaks show up in the phi-chi scans of X-ray diffraction, which can be grouped into two sets. Each set consists of three peaks with an equal separation of about 120°, which is expected for a single crystalline CuInS₂ layer. The two main reflection groups rotate by 180° with respect to each other, and lead to twins in the CuInS₂ layers. Transmission electron microscopy was carried out to investigate further the microstructure and orientation of the quasi-epitaxially sputtered CuInS₂ layers. The surface morphology of the films was characterized by atomic force microscopy and scanning electron microscopy. Hall effect measurements on the electrical properties of the films are currently underway.

D/PIL49

PROPERTIES OF CuInTe₂ SINGLE CRYSTALS BY PHOTOACOUSTIC SPECTROSCOPY

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The paper reports on the optical properties of the photovoltaic material CuInTe₂ (CIT) as characterised by photoacoustic spectroscopy (PAS). Measured spectra of p-conducting CIT single crystals grown by using the vertical Bridgman technique are given using a high resolution photoacoustic spectrometer of the gas-microphone type. The data is used to evaluate the absorption spectra, the band gap energy, and ionisation energies of defects that have been observed in the tail of the spectra. The obtained Results confirm the efficiency of the technique in detecting non-radiative defects known to dominate the properties of this compound. A discussion on the relation between the composition of the samples and the intrinsic defect chemistry in this compound is also given. Finally, we compare between the results we have obtained and those published in the literature.

D/PIL50

ANODIC MODIFICATION OF THE CuInS₂/CuS THIN FILM SYSTEM

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In order to achieve efficient performance of CuInS₂-CdS-ZnO photovoltaic cells, the absorber layers have to be prepared with an excess of copper which segregates to the surface and forms a binary Cu₂S compound which has to be removed before further processing. We present a new possibility to remove the deleterious segregated covellite phase by anodic oxidation of the film in a vanadium solution at room temperature. The changes in chemical composition, electronic properties and morphology at the electrode surface, induced by the electrochemical treatment, are studied by (cyclic) voltammetry and X-ray photoelectron spectroscopy (XPS). An improved solar cell characteristic in a photoelectrochemical cell and photovoltage changes upon increasing the contact potential by changing the redox potential comparable to cyanide treated absorbers are found. The method allows in principle cyanide-free processing of CuInS₂ solar cells and will be tested in solid state devices.

D/PIL51

LATTICE INTRINSIC DEFECTS AND ELECTRICAL RESISTIVITY IN PYRITE THIN FILMS

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Electrical resistivity dependence on temperature (ln r vs. reciprocal of temperature) of some polycrystalline semiconductors do not show the typical linear Arrhenius plot but they are curved. Werner (1) proposed a model in which a distribution of energy levels localised in grain boundaries cause curved Arrhenius plots. From this model a parabolic dependence of the conductivity on the reciprocal of temperature is obtained.

In this work, the electrical resistivity of pyrite (FeS₂) thin films has been measured at different temperatures in the range from 300 to 623K under a sulfur atmosphere. The obtained results are discussed using the Werner model but we have assumed that the energy levels causing the curved Arrhenius plots are created by lattice intrinsic defects. This hypothesis is based on several experimental facts: a) the resistivity values of pyrite thin films reported in the literature are in the range of 0.1-1.0 W-cm independently of the growing experimental procedure used and of the grain size. b) Pyrite thin films always show p-type conductivity. c) Composition analysis shows that pyrite thin films are highly under stoichiometric. We assume that pyrite thin films have a high lattice defects density (Fe and S vacancies) which create energy level distributions into the band gap which causes the curved Arrhenius plot. By applying this model to our experimental results we conclude that the energy level distribution near the valence band (caused by Fe vacancies) is characterised by an average energy changing from 0.09 to 0.11 eV. Our interpretation and analysis allow explaining the p-character of non-doped synthetic films and other relevant experimental facts. (1) J.H. Werner, Solid State Phenom. 37-38, 213 (1994).

D/PII.52**DEPENDENCE OF CARRIER CONCENTRATIONS ON OXYGEN PRESSURE FOR Ga-DOPED ZnO GROWN BY ION PLATING METHOD**

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We develop a technology for the fabrication of transparent conductive zinc oxide (ZnO) thin films in a large area. We grow the films by using ion plating (IP) systems with the plasma beam controller on glass substrates, which is expected as low damages for CuInGaSe₂-based photovoltaic devices.

On the basis of the analysis of both calculated data on the electronic states around the Fermi level in the conduction band obtained by an ab initio electronic-band-structure calculations and thermodynamic properties, such as dissociation pressure of oxides, we selected a gallium (Ga) species as donor dopants. Low-resistivity Ga-doped ZnO (ZnO:Ga) with a film thickness of 200nm were grown at a discharge current of 100 A. The resistivity of the thin film was about 2×10^{-4} Ω·cm in which the Ga content was about 3at%. Based on the analysis of the data on the dependence of the carrier concentrations on the oxygen pressure, we find that the carrier concentrations decrease slowly as the oxygen pressure increases at the low pressure. Based on the thermal-equilibrium theory, we conclude that the carriers are mostly generated by ionization of the Ga donors. Beyond the oxygen pressure described above, we find that there decrease very rapidly the carrier concentrations with an increase in the oxygen pressure. Considering that the Ga can only diffuse when it is near a vacancy, such as Zn-vacancy (V_{Zn}), the associate giving the proper oxygen dependence should be GaZnV_{Zn}, which will exhibit as a donor killer since the V_{Zn} can bind two electrons. This gives rise to a drastic decrease in the carrier concentrations. We will also present experimental data on the fabrication of ZnO:Ga deposited by using the IP systems in the range of width 550 × 650 mm.

D/PII.53**CONTROLLED DEPOSITION OF CIGSE SOLAR CELLS**

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A new deposition technique using pulsed channel spark ablation for producing high quality thin films of perspective solar cells of components CuIn_xGa_{1-x}Se (CIGSE) and CdS is presented. Directed energy is driven to the target for about 100 ns pulse by means of magnetically self-pinch electron beam with power density 5 10⁸ Wt/cm. Two step technology of deposition of CuIn_{1-x}Ga_xSe₂ (CIGS) polycrystalline films was developed: depositing with the help of a e-beam ablation; process at 2500C and subsequent selenization at 5000C. X-ray diffraction analysis of films showed chalcopyrite structure with stringent orientation <112>. Thin films have optical absorption coefficients in the 10⁴ cm⁻¹ range and the band gaps are 1.0, 1.4 and 1.65 eV for x = 0, 0.25, 1.0.

The method of admittance spectroscopy for determination of density of concentration of deep states (N(E)) was applied for optimization of deposition process and photovoltaic properties. The continuous distribution N(E) have been found.

D/PII.54**MORPHOLOGY AND STRUCTURE OF MBE-GROWN CHALCOPYRITE THIN FILMS ON Si SUBSTRATES**

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Thin epitaxial layers of the quaternary chalcopyrite semiconductor Cu(In,Ga)S₂ (CIGS) are grown on sulphur terminated Si substrates of various orientations using Molecular Beam Epitaxy (MBE) from elemental sources. The samples were investigated with a special emphasize on the film morphology which is well known to be crucial for the utilization of these layers in heterojunction devices. Rutherford backscattering spectroscopy (RBS) and Atomic Force Microscopy (AFM) are utilized to characterize their compositions, thicknesses, homogeneities, and film roughnesses. In situ Electron Diffraction (RHEED) gives further insight into the structural properties of the samples. The nucleation of the very first monolayers and the possibility to grow perfectly lattice matched chalcopyrite layers on Si through variation of the In/Ga-ratio and its implication on the epilayer morphology are investigated. For larger film thicknesses (up to 1.5µm) the influences of lattice mismatch, composition, surface segregation of binary phases, and substrate orientation are discussed. The parameters for growth of an optimized CIGS thin film morphology are presented and intrinsic limitations are evaluated.

D/PII.55**IN-SITU RESISTIVITY MEASUREMENTS DURING SELENIZATION PROCESS**

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The CuInSe₂ (CIS) is a very promising photovoltaic material with solar energy conversion efficiencies above 15 %. One of the most perspective techniques for its production is the selenization of metallic Cu-In precursors. A control of the conversion reaction is important in order to obtain high quality films. In this work in-situ resistivity measurements of selenized precursors are used for it.

Cu-In layers were co-evaporated on glass substrates and after selenized in flux of N₂ with Se vapours at the atmospheric pressure. For in-situ measurements a substrate holder with mechanical contacts to the film was used. The total resistance of metal layers and the contact system is 10-15 W before the reaction starts. During the selenization processes it increases to 5-15 kW, indicating the conversion of metals into CIS. The resistivity curve indicates the start and end point of the chemical reactions and main steps of conversion. The paper will present an interpretation of the in-situ resistivity measurements for different selenization processes and relates it to the structural properties of the Cu-In alloy during its conversion to CIS. This work was supported by grants from the Swiss National science fund and National academy of science of Belarus,

INVESTIGATIONS OF PHOTSENSITIVE In₂Se₃/CuInSe₂ STRUCTURES

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CuInSe₂ (CIS) is a widely investigated material for solar cell applications. However, as a rule CIS-based solar cell structures contain a CdS layer. From the point of view of improvement of their parameters and environment considerations, the replacement of CdS by other material is of great importance.

We have studied In₂Se₃/CIS/Au structures, where single crystalline plates with typical dimensions of 5×1169;5 mm² were used as the base material.

The crystals of p-CIS were grown by the vertical Bridgman method from the previously synthesized ingots. The room temperature carrier density and carrier mobility were $(1-3)10^{17}$ cm⁻³ and 20 to 50 cm²/Vs, respectively.

In₂Se₃ films on the CIS surfaces were obtained by the method of evaporation in a quasiclosed volume. The evaporation was carried out both from single crystalline In₂Se₃ and from polycrystalline one. Varying the temperatures of the evaporator and the substrate we have obtained the films of beta-, and gamma-modifications with reproducible properties.

For the prepared heterostructures we have investigated the temperature dependences of J_{sc} and C_{sc} characteristics, the spectral dependence of relative quantum efficiency. Possible charge transfer mechanisms are analyzed. For the investigated structures the reached V_{oc} is ~ 0.4 V and the I_{sc} is ~ 20 mA/cm². The comparison of the results to those for CdS/CIS/Au structures is made.

Thursday, June 12, 2003
Jeudi 12 juin 2003

Morning
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Session VI: Compounds TFSC

Session chair: R. Klenk and J.F. Guillemoles

- D-VI.1** 8:30 -Invited- STABILITY ASPECTS IN CdTe/CdS SOLAR CELLS
D.L. Bätzner, A. Romeo, H. Zogg, **A.N. Tiwari***, Thin Film Physics Group, Lab. for Solid State Physics, ETH Zurich, Technoparkstrasse 1, 8005 Zurich, Switzerland, *also Dept. of Electronic and Electrical Eng. Loughborough University, U.K.; M. Terheggen, ETH Zurich, Institute of Applied Physics, Switzerland and M. Döbeli, ETH Zurich/Paul Scherrer Institute, Institute of Particle Physics, Switzerland
The stability of CdTe/CdS solar cells depends on spatial changes of defects and impurities throughout the cell. Degradation effects are often associated with metal diffusion from the back contact of the cell which is Cu in the most cases. However, cells with stable back contact can exhibit instability as the other cell layers are potential sources of impurities which cause this instability. Cell degradation by generation of defects from external influences like particle irradiation is another reason for instability.
The development of back contacts leading finally to a stable back contact is presented. Other sources of instability in the cell are discussed with a special focus on the CdS and CdTe/CdS interface which is very sensitive to the accumulation of impurities and defects. An analysis of performance stability with respect to defect generation caused by external irradiation with high energy particles such as protons and electrons is presented. Additionally, effects of metastability and reversible performance changes as well as the capability to recover degradation by defect generation is shown. Possible characterisation methods to assess stability issues are suggested.
- D-VI.2** 9:00 -Invited- GROWTH TEMPERATURE EFFECTS ON EVAPORATED Cu(In,Ga)Se₂ THIN-FILMS FOR SOLAR CELLS
Miguel A. Contreras, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden CO 80401, USA
The effect of substrate growth temperatures $\geq 600^\circ\text{C}$ on the preparation of Cu(In,Ga)Se₂ (CIGS) polycrystalline thin-film materials and solar cells is presented. The $\sim 2.5 \mu\text{m}$ thick chalcopyrite layers are grown by co-evaporation from elemental sources following NREL's "3-stage process" and, to study elevated growth temperatures larger than 600°C we use Mo coated 7059 Corning glass as an alternative to the standard Mo coated soda-lime glass (SLG) which cannot endure a regime beyond 600°C .
Morphological, structural and optoelectronic aspects of the as-grown photon absorber layers and devices will be presented. Absorbers made following this type of processing have lead recently to two significant advancements in CIGS technology; first is the attainment of a 19.2% efficiency for a ZnO/CdS/CIGS/Mo/SLG solar cell and, second, the attainment of an 18.6% efficiency for a Cd-free device structure incorporating ZnS as an alternative buffer layer to CdS.
- D-VI.3** 9:30 EFFICIENT THIN FILM SOLAR CELL CONSISTING OF A TCO/CDS/CUINS₂/CUGAS₂ STRUCTURE
H. Goto, Y. Hashimoto and K. Ito, Department of Electrical and Electronic Engineering, Shinshu University, Wakasato 4-17-1, Nagano 380-8553, Japan
In an effort to introduce a wide bandgap electron mirror into thin film CuInS₂ solar cells, the formation of a thin CuGaS₂ intermediate layer between the p-type CuInS₂ absorber layer and a Mo-coated soda lime glass substrate has been found beneficial to improve their efficiencies. As a first step, a Cu/Ga stacked precursor layer with the Cu to Ga ratio of 1.0 and the total thickness of 250 nm was vacuum-evaporated onto the Mo electrode. It was then sulphurised in an Ar/H₂S mixture gas at 530°C. The sulfide layer thus formed was treated in a KCN solution. In the next step, a Cu/In stacked precursor layer of about 1,000 nm thickness was deposited onto its surface. It was again sulphurised and treated as above. A chemical bath deposited CdS layer was used as a buffer, and an RF sputtered In₂O₃ layer as a TCO (transparent conductive oxide) electrode. When a Cu to In ratio of the precursor was 1.7, a 13% efficiency cell was obtained: the open circuit voltage was 690 mV, the short circuit current density 27.5 mA/cm², the fill factor 0.68. However, the efficiency of the cell whose absorber layer was prepared from the precursor with a Cu to In ratio of 1.0 was comparatively low (up to 9%) due to a decrease both in fill factor and short circuit current density.

- D-VI.4** 9:45 **CuGaSe₂ THIN FILMS PREPARED BY A NOVEL CCSVT TECHNIQUE FOR PHOTOVOLTAIC APPLICATION**
M. Rusu, S. Wiesner, D. Fuertes Marrón, A. Meeder, W. Bohne, S. Lindner, P. Schubert-Bischoff, Th. Schedel-Niedrig, M.Ch. Lux-Steiner, Hahn-Meitner Institut, Glienicker Strasse 100, 14109 Berlin, Germany and Ch. Giessen, AIXTRON AG, Kackerstr. 15-17, 52072 Aachen, Germany
 A novel chemical close-spaced vapour transport (CCSVT) technique has been developed for the growth of the CuGaSe₂ (CGSe) thin films on areas as large as 10 x 10 cm². Cu precursors deposited on clean and Mo-coated soda lime glass (SLG) substrates are thermally and chemically treated under gaseous GaCl₃/H₂Se atmosphere in the CCSVT cell. The Ga₂Se₃ employed as source material is stoichiometrically volatilised at 550°C by a controlled amount of HCl/H₂ agent at a certain pressure. Single phase CGSe layers are prepared with a growth rate of 230-240 nm/min by using a single stage process. A two stage process is applied for the fine tuning of the CGSe composition and electronic properties appropriate for the solar cells preparation.
 Film characterisation including X-ray diffraction (XRD) measurements, scanning electron microscopy (SEM) observations, transmission electron microscopy (TEM) studies, X-ray fluorescence analysis (XRF) and elastic recoil detection analysis (ERDA) has been carried out and results are reported in this contribution. By means of ERDA method, high depth homogeneity of the deposited CGSe layers was observed. Na is found as major contaminant. First solar cell devices consisting of Mo/CGSe/CdS/ZnO heterostructures show under AM1.5 conditions a total area efficiency of 6.6% with Voc = 761 mV and Jsc = 15.17 mA/cm².
- D-VI.5** 10:00 **CD-FREE CIGS SOLAR MODULES ON LARGE AREA OF 30X30 CM² WITH IN₂S₃ BUFFER LAYER BY ALCVD**
S. Spiering, D. Hariskos, M. Powalla, Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW) Baden-Württemberg, Industriestrasse 6, 70565 Stuttgart, Germany and N. Naghavi, D. Lincot, Centre National de Recherche Scientifique, Laboratoire d'Electrochimie et de Chemie (LECA-CNRS), 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
 The development of Cadmium-free buffer layers by vacuum process for CIGS solar modules becomes ever more interesting regarding environmental aspects and the implementation in industrial production. Already excellent results have been achieved with In₂S₃ as buffer layer on small areas (record cell efficiency of 15.7 %). The In₂S₃ is deposited by the Atomic Layer Chemical Vapour Deposition (ALCVD) technique. This work presents the latest results on the module area of 30x30 cm². An efficiency of η=12.9 % (VOC=27.8 V, FF=72.6 % , ISC=0.457 A, aperture area: 714 cm² and a number of 42 cells). The measurement was certificated by the TÜV Immissionsschutz und Energiesysteme GmbH in Köln, Germany. The result shows that In₂S₃ is a promising alternative for CdS buffer layer. Investigations of the buffer layer interfaces are performed for a better understanding of the new buffer material.
- 10:15 **BREAK**

Session VII: Organics

Session chair: G. Gobsch and V. Dyakonov

- D-VII.1** 10:30 -Invited- **MOLECULES AND NANOSTRUCTURED MATERIALS FOR POLYMER PHOTOVOLTAICS**
René Janssen(a), Martijn Wienk(a), Paul van Hal(a), Jeroen van Duren(a), Waldo Beek(a), Joop Knol(b), Kees Hummelen(b), Wiljan Verhees(c), Sjoerd Veenstra(c), Lenneke Slooff(c), Jan Kroon(c), (a)Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands, (b)Stratingh Institute and MSC, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, (c)ECN, PO Box 1, 1755 ZG Petten, The Netherlands
 In this contribution new materials for polymer/fullerene and polymer/hybrid photovoltaic cells will be presented. The new materials for polymer/fullerene solar cells have been designed to improve light absorption. The new materials provide a considerable enhancement of the short circuit current and give energy conversion efficiencies over 3% under standardized AM1.5 conditions. Using a combination of ultrafast spectroscopic (fluorescence and pump-probe) and morphological studies (AFM, TEM, and SIMS) it will be shown that the morphology of the active layer has a crucial role in determining the overall energy conversion efficiency. For hybrid solar cells, new methods and materials will be described that allow mixing of conjugated polymers with metal oxides into nanostructured films that show promising behavior when used in a photovoltaic device.
- D-VII.2** 11:00 **MORPHOLOGICAL DEPENDENCE OF CHARGE GENERATION AND CHARGE TRANSPORT IN BLENDED POLYFLUORENE PHOTOVOLTAIC DEVICES**
Henry J. Snaith, Ana C. Arias, Arne C. Morteani, Carlos Silva and Richard H. Friend, Cavendish Laboratory, Department of Physics, University of Cambridge, U.K.
 We present a compositional analysis of the phase separation, nano-structure and electrical performance of blended hole-accepting and electron accepting polyfluorene related materials, in films and in photovoltaic devices. Using fast spectroscopy we show that photoluminescence quenching is insensitive to blend composition but the photovoltaic quantum yield is strongly composition dependent. This indicates that charge transport, and not charge generation, is the factor limiting device performance. We demonstrate that a meso-length scale phase separation is necessary in order to optimise charge transport properties.

- D-VII.3** 11:15 METHOXY-SUBSTITUTED PCBM'S: FINETUNING THE Voc OF 'PLASTIC' SOLAR CELLS
Minze T. Rispens, Floris B. Kooistra, Joop Knol, Alexander B. Sieval, Lacramioara M. Popescu, Anthony F. England, Harry T. Jonkman and Jan C. Hummelen, Stratingh Institute and Materials Science Centre, Groningen University, Groningen, The Netherlands
 Fullerenes have interesting properties that can be utilised in bulk-heterojunction organic photovoltaic devices. An essential parameter of these thin film photovoltaic devices is the built-in potential (Voc). To systematically investigate the critical parameters that influence the Voc of these solar cells, a series of highly soluble fullerene derivatives with varying acceptor strength (E1/2,red) was synthesised and the Voc of the devices as a function of E1/2,red was analysed.
- D-VII.4** 11:30 -Invited- PREREQUISITES AND PROPERTIES OF LOW BAND GAP MATERIALS TOWARDS PHOTOVOLTAIC APPLICATIONS
D. Vanderzande (a,b), P. Wagner(a), M. Nicolas(b), A. Heckens(a), I. Polec(b) and L. Lutsen(b), (a)Limburgs Universitair Centrum, Instituut van Materiaal Onderzoek (IMO), Universitaire Campus, Bld. D, 3590 Diepenbeek, Belgium, (b)IMEC, Division IMOMECE, Universitaire Campus, Bld. D, 3590 Diepenbeek, Belgium
 Development and evaluation of new materials, which can be used as active component in organic or polymeric photovoltaic devices, stays an important activity in this research domain. Although substantial progress has been achieved and efficiencies above 3% have been demonstrated, still much effort is needed. For issues as, achieving sufficient mobility of charge carriers, resolving the spectral mismatch, improving the stability of materials used and progress towards alternative electron acceptors, a satisfactory solution is still to be found if efficiencies close to 10% must be realised. Low band gap polymers should allow to contribute in achieving a solution for the spectral mismatch. In this presentation an overview will be given on their properties, their synthesis and their potential for solar cell applications. Also an outlook towards future progress in this material class will be given.
- D-VII.5** 12:00 -Invited- PORPHYRIN AND FULLERENE-BASED ARTIFICIAL PHOTOSYNTHETIC MATERIALS FOR PHOTOVOLTAICS
Hiroshi Imahori, Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, PRESTO, JAPAN Science and Technology Corporation (JST), Sakyo-ku, Kyoto 606-8501, Japan
 Artificial photosynthesis has attracted enormous interest, motivated by desires to address basic mechanistic problems on energy transfer (EN) and electron transfer (ET) chemistry as well as to develop artificial photosynthetic systems for light energy conversion. We have proposed and demonstrated that a combination of porphyrins with fullerenes is an ideal system because of the small reorganization energies of ET, which make it possible to realize photosynthetic ET without a special environment. Along this line a variety of porphyrin-fullerene linked molecules have been prepared to reveal a long-lived charge-separated state (up to seconds) with an extremely high quantum yield (up to 99%) in frozen matrix as well as in solutions. Unidirectional arrangements of such porphyrin-fullerene linked molecules on gold and ITO electrodes have been attempted to convert light energy into chemical and electrical energies in a macroscopic quantity. In particular, mixed self-assembled monolayers of antenna and reaction center molecules on the gold electrode have established a cascade of photoinduced EN and multistep ET, leading to the production of photocurrent output with the highest quantum yield ever reported for photocurrent generation at monolayer-modified metal electrodes using donor-acceptor linked molecules. Porphyrin monolayer-modified gold clusters have been prepared successfully to develop the artificial photosynthetic materials as well as photocatalysts and sensors.
- D-VII.6** 12:30 MODELING OF OPTICAL ABSORPTION IN CONJUGATED POLYMER/FULLERENE BULK-HETEROJUNCTION PLASTIC SOLAR CELLS
H. Hoppe, N.S. Sariciftci, Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, 4040 Linz, Austria, N. Arnold, Angewandte Physik, Johannes Kepler University Linz, 4040 Linz, Austria, D. Meissner, University of Applied Sciences, Roseggerstr. 12, 4600 Wels, Austria
 To determine the actual absorption in the photoactive layer of a plastic solar cell (for example consisting of blend of poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene) (MDMO-PPV) and a methanofullerene, [6,6]-Phenyl C61 - butyric acid methyl ester (PCBM)), a matrix formalism for the light propagation in this multi-layer system is applied. This calculation results in an upper limit for the incident photon to collected electron (IPCE) conversion efficiency for a given internal quantum efficiency. Comparisons with experimental results as well as conclusions for the optimal layer thickness are drawn.
- 12:30 **LUNCH**

Thursday, June 12, 2003
Jeudi 12 juin 2003

Afternoon
Après-midi

14:00-15:30

POSTER SESSION III Si based TFSC
Chair: A. Slaoui and J. Poortmans

D/PIII.01

ROLE OF *i* LAYER DEPOSITION PARAMETERS ON THE V_{oc} AND FF OF AN a-Si:H SOLAR CELL DEPOSITED BY PECVD AT 27.13MHz

L. Schönbächler, S. Benagli, C. Bucher, U. Kroll, A. Shah, Institut de Microtechnique, Neuchâtel, Switzerland, J. Ballutaud, EPFL/CRPP, Lausanne, Switzerland, A. Büchel, Unaxis Display, Trübbach, Switzerland

The *i* layer plays a key role in the p-i-n a-Si:H solar cell, not only because it is the active part of the cell where the carriers are generated, but also for economical reasons : With a typical thickness of 3000Å, its deposition rate has a large impact on the manufacturing costs. High *i*-layer deposition rates are, thus, highly desirable, but increasing the deposition rate often leads to poor layer quality and large cell degradation by light soaking. Another disadvantage that is often observed is powder formation.

With the PECVD technique, the pressure, the power and the SiH₄:H₂ dilution ratio can easily be varied in order to increase the deposition rate. In this work, we have tried to isolate the effect of these different parameters on the *i*-layer quality, and on the initial and stabilized (after degradation) performance of the cell. This was achieved with the help of a DOE (Design Of Experiment) by keeping the deposition rate at a constant value of around 2Å/s, while changing the deposition recipes, one of the 3 parameters being increased, the 2 others being maintained at a low value, to compensate for the increase of the first parameter. The experiments show that the power tends to reduce the porosity of the *i* layer (measured by Ellipsometry and FTIR), while the pressure has the opposite effect. It was clearly demonstrated that cell degradation is related to the porosity of the *i*-layer, whilst initial performance of the cell seems more related to *p/i* interface.

D/PIII.02

PECVD OF HYDROGENATED SILICON THIN FILMS FROM SiH₄+H₂+Si₂H₆ MIXTURES

A. Hammad, E. Amanatides, D. Mataras and D. Rapakoulias, Plasma Technology Laboratory, Dept. Chem. Engineering, University of Patras, P.O.Box 1407, 26500 Patras, Greece

The composition of the gas mixture fed in rf discharges used for the deposition of either amorphous or microcrystalline silicon thin films is of primary importance for obtaining the required deposition rates and film quality. In addition, a successful recipe would be one leading to the required deposition rates under dust free conditions and with reasonable process costs.

In this direction, we report a systematic study of the effect of a small addition of Si₂H₆ on the properties of highly diluted SiH₄ in H₂ discharges. Namely, deposition experiments were performed in a capacitively coupled parallel plate reactor, operating at 27.12 MHz and a total pressure of 1 Torr. Two kinds of experiments were performed: a) Si₂H₆ fraction in the SiH₄/H₂ mixture was maintained constant (0.6%) while varying SiH₄ partial pressure from 6% to 9%. b) SiH₄ fraction in the mixture was kept constant at 6% while Si₂H₆ fraction was varying from 0% to 0.6%. The deposition rate was measured in situ using laser interferometry while spatially resolved emission, mass spectrometry and electrical measurements were also performed for further analysis of the discharge. The results reveal that a small addition of disilane in the gas mixture leads to a deposition rate increase of about 90% while an equivalent increase of SiH₄ results to an enhancement up to 13%. The spectacular Si₂H₆ effect is attributed to the change of the relative importance of secondary gas phase reactions and on the contribution of higher radicals to the film growth.

D/PIII.03

MORPHOLOGY OF Si:H SOLAR CELLS PREPARED BY PECVD

F. Edelman, A. Chack, R. Weil and R. Beserman, Technion-Israel Institute of Technology, Solid State Institute, 32000 Haifa, Israel, P. Werner and N. Zakharov, Max-Planck Institut für Mikrostrukturphysik, 05120 Halle, Germany, T. Roschek, B. Rech and W. Beyer, Institut für Photovoltaik, Forschungszentrum Juelich GmbH, 52425 Juelich, Germany

Silicon solar cells prepared by plasma-enhanced chemical vapor deposition in the p-i-n structure on ZnO-covered glass substrates were studied by transmission electron microscopy (TEM) and micro Raman spectroscopy. The structures of the *i*-layers, which were prepared under various deposition conditions; e. g., silane concentration [SiH₄]/[H₂], deposition pressure (pdep), lead to different solar cell efficiencies (2-8 %). One factor leading to a low efficiency was an increased amorphous volume content in the *i*-layer. Two different effects induced this increase in amorphous phase. The first effect is a miss adjustment of the deposition parameters (e. g. an increase of pdep or [SiH₄]/[H₂]), leading to a transition to amorphous growth in an otherwise well-suited regime for the deposition of high performance solar cells. The other case is the deposition in a regime where even optimized growth conditions do not lead to highly crystalline material because of high energy ion bombardment. The size of the polycrystalline grains embedded in the amorphous layer was found by TEM to vary in a wide range from 2-3 to 200-500 nm, weakly depending on [SiH₄]/[H₂] and pdep. The grain shape is either columnar or tree-like. The amorphous area size and its in-depth distribution was found crucially sensitive to [SiH₄]/[H₂] and pdep. The non-uniform distribution of amorphous Si:H areas analyzed by TEM could be the reason for non-uniform Raman spectra obtained by Raman microscopy. In samples deposited with different pdep the crystalline to amorphous ratio passes through a maximum near 8 Torr, which correlates with the solar cell efficiency. Acknowledgement: this research was supported in part by the Israel Ministry of Science, Culture and Sport.

D/PIII.04**A-SiC:H TANDEM SOLAR CELLS: CHARACTERIZATION AND NUMERICAL SIMULATION**

A. Fantoni, P. Louro, D. Brida, I. Rodrigues, A. Maçarico, and M. Vieira, Electronics Telecommunications and Computer Dept, ISEL, Lisbon, Portugal

Stacked a-Si:H pin/pin diodes are known to be more stable with respect to the light induced degradation than the conventional single junction pin structure. We present a study, based on a numerical simulation, about the behaviour of an a-SiC:H pin/ a-Si:H pin monolithic tandem solar cells and we compare it with the characteristics of a tandem solar cell with the same features. The obtained results show that an accurate engineering of the internal n/p interface, related to optical gap and band banding control, can improve the solar cell efficiency. The interface band bending can be managed to create a monolithic tandem solar cell working almost as two cells connected in series. The importance of a well balanced photogeneration between the two sub-cells has also been outlined, aiming to indicate the need to determine an optimal configuration of the absorber layers (optical gap and thickness) in order to take advantage of the local fields created by the band discontinuities at the internal n/p interface.

Transport and optical modelling give insight into the internal physical process. Considerations about conduction band offsets, electrical field profiles and inversion layers will be taken into account to explain the optical and voltage bias dependence of the spectral response.

D/PIII.05**OPTICAL CHARACTERISATION OF GERMANIUM THIN FILM GROWN BY LOW ENERGY PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION FOR GAAS/GE SOLAR CELL APPLICATIONS**

R. Ginige, M. Modreanu and B. O'Looney, NMRC, Lee Maltings, Prospect Row, Cork, Ireland, M.E. Murtagh and P.V. Kelly, OMI, Cork Airport Business Park, Kinsale Road, Cork, Ireland, G. Isella and D. Chrastina, Politecnico de Milano, Polo Regionale di Como, Via Anzani 52, 22100 Como, Italy

We report the optical quality of germanium (100%) thin films (1 μ m) grown using Low Energy Plasma Enhanced Chemical Vapour Deposition (LEPECVD) on a silicon substrate with a graded SiGe intermediate layer. With the high cost of optoelectronic material compared to silicon and also due to size limitation of the available III-V optical graded substrates, there is much interest in growing high optical quality epitaxial layers on large size silicon substrates. Such a Si/SiGe/Ge substrate would form a virtual substrate for GaAs solar cells and also allows one to combine optoelectronics with microelectronics. We have investigated such substrates using UV-Visible spectroscopic ellipsometry (SE) and modulated photoreflectance (PR) techniques.

The optical interband transitions observed from analysis of the complex dielectric function of Ge thin films (obtained from SE) and from PR spectra are in good agreement with (100) 6° off towards [111] Germanium substrates used for GaAs/Ge solar cells.

D/PIII.06**INTRINSIC AMORPHOUS SILICON FILMS DEPOSITED BY A CONTINUOUS METHOD**

L. Raniero(a), E. Fortunato(a), L. Pereira, I. Ferreira, H. Águas R. Martins(a), (a)Departamento de Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa and CEMOP, Campus da Caparica, 2829-516 Caparica, Portugal

This work reports a detailed study on the role of the deposition parameters of amorphous silicon films obtained by plasma enhanced chemical vapor deposition using a continuous method, for photovoltaic applications. The continuous method consists in starting the plasma ignition using a neutral gas such as hydrogen or helium and after that the carrier gas containing the species to be deposited (silane based mixtures) is introduced, followed or not by stopping the ignition gas.

Following this procedure, no surface damages are induced in the first deposited layers and so, a more compacted and stable film is produced, when compared with amorphous films grown by conventional methods, as required for device applications. Apart from that, the electro-optical properties of the films are improved, minimizing also the polymers formation when the deposition process takes place close to the so-called gama-regime (high growth rates, as required by the industry). In this work we present the electrical and optical performances of the films produced and how they are correlated with density of states, the hydrogen content and films compactness, determined respectively by Constant Photocurrent Method, infrared spectroscopy, and spectroscopic ellipsometry. Apart from that, results concerning optimized pin structures will be also presented.

D/PIII.07**THE EFFECTS OF RF PLASMA EXCITATION FREQUENCY AND DOPING GAS ON THE DEPOSITION OF POLYMORPHOUS SILICON THIN FILM**

V. Suendo, A.V. Kharchenko and P. Roca i Cabarrocas, Laboratoire de Physique des Interfaces et des Couches Minces (UMR 7647 CNRS), Ecole Polytechnique, 91128 Palaiseau Cedex, France

Polymorphous silicon (pm-Si:H) is a nanostructured material which has attracted much attention due to its unique structure and electronic properties which make of it an excellent alternative to a-Si:H for photovoltaic applications. In this study, we present the effects of the plasma excitation frequency (13.56, 27.12 and 40.68 MHz) and of dopants on the formation of clusters in the plasma and correlate it to the optical and electronic properties of the films. While previous studies have focused on films incorporating crystallites and clusters with sizes of 1-2 nm, the analysis of the roughness by in situ spectroscopic ellipsometry suggest that the best films result from the incorporation of agglomerates with sizes up to 10 nm. Moreover, the increase of the excitation frequency does not enhance the deposition rate, but it only shifts the maximum value of deposition rate to the lower deposition pressure. These films are currently applied to PIN solar cells.

D/PIII.08**EFFECT OF THE DISCHARGE FREQUENCY ON THE PROPERTIES AND GROWTH RATE OF POLYMORPHOUS SILICON**

H. Águas, L. Raniero, L. Pereira, E. Fortunato, R. Martins, Departamento de Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa and CEMOP, Campus da Caparica, 2829-516 Caparica, Portugal

Polymorphous silicon (pm-Si:H) has been proved to be an excellent material for the production of solar cells due to their improved transport properties and stability when compared to the standard amorphous silicon material. Nevertheless, so far the pm-Si:H deposition by PECVD for solar cells has been concentrated in using a discharge frequency of 13.56 MHz at deposition rates $< 1 \text{ \AA/s}$.

This work presents a study performed concerning the deposition of pm-Si:H at excitation frequency of 27.12 MHz, since the increase of the excitation frequency increases the dissociation in the plasma and reduces the energy of ion bombardment, allowing the deposition of superior grade and compact material at higher growth rates. The plasma impedance, that allows the monitor of particle formation in the plasma, essential to pm-Si:H deposition was correlated to the films properties, characterised by spectroscopic ellipsometry, infrared and Raman spectroscopy and hydrogen exodiffusion experiments, which are techniques that permit the structural characterisation of pm-Si:H. Conductivity and density of states measurements were also performed. The set of data obtained show that by using the 27.12 MHz excitation frequency the hydrogen dilution needed to produce pm-Si:H can be reduced by more than 50%, and the r.f. power density can also to be reduced. Growth rates above 3.1 \AA/s were obtained, being the films more dense and chemical stables, with improved transport properties than the usually ones obtained with the standard 13.56 MHz.

D/PIII.09**POLYSILICON AND PHOTOVOLTAIC SOLAR CELLS : 2D NUMERICAL ANALYSIS**

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Polysilicon material is now under study for weak cost photovoltaic solar energy conversion. Here, we study the effect of the device structure (nip or pin) as well as of the polysilicon parameters (grain size, defect density at grain boundaries). on the under light characteristics.

A two dimension numerical resolution of transport equations in semiconductors (Poisson's equation and the two equations of continuity of electrons and holes) under AM1.5 is used. The photovoltaic parameters (short circuit current, conversion efficiency, open circuit voltage and fill factor) are shown to be strongly linked to the grain orientation and size, and to the grain boundaries defects. Moreover the high defect density, usually present in the low temperature polysilicon deposition, is found to constitute a real drawback in the photovoltaic application of this material.

D/PIII.10**VHF PECVD MICROCRYSTALLINE SILICON: FROM MATERIAL TO SOLAR CELLS**

P. Delli Veneri, L.V. Mercaldo, C. Minarini, ENEA, Portici Research Center, Località Granatello, 80055 Portici (Napoli), Italy

Microcrystalline silicon is an interesting material as absorber layer in solar cells. Rather thick layers (1-3 μm) are needed to collect solar radiation, therefore high deposition rates are necessary for large scale production. VHF PECVD technique allows to grow device quality material within a short fabrication time. Intrinsic microcrystalline silicon has been deposited by this technique at two different frequencies, 90 and 100 MHz. Different gas mixtures of silane and hydrogen were utilized, while keeping the substrate temperature at 220°C and the chamber pressure at 950 mTorr. In particular, the effect of the plasma power has been investigated at both frequencies in the range 20 - 40 W. The material was characterized in terms of structural, electrical and optical properties. The optimised material was inserted in pin and nip solar cells. Different types of doped materials, deposited by PECVD technique, were utilized in the devices. Since the properties of thin p-layers (~20 nm) strongly affect the solar cell performance, a particular care was directed to the structural and electrical characterization of this material. Preliminary results on the solar devices are encouraging: Efficiency of about 4.5 % was reached.

D/PIII.11**DEPOSITION OF MICROCRYSTALLINE SILICON-CARBON FILMS BY PECVD**

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Hydrogenated microcrystalline silicon-carbon ($\mu\text{c-SiC:H}$) prepared by standard PECVD systems has a higher conductivity, optical transparency and dopant activation as compared with the amorphous counterpart because of the presence of silicon crystallites. For these properties $\mu\text{c-SiC:H}$ is a very interesting material for high efficiency solar cells, TFT and LEDs. In this work the effects of deposition conditions (power density, hydrogen dilution and substrate temperature) on the structural and electrical properties of $\mu\text{c-SiC:H}$ samples deposited by RF-PECVD from silane + methane gas mixtures highly diluted in hydrogen have been investigated. Films have been grown keeping constant the fraction $\text{CH}_4/(\text{CH}_4+\text{SiH}_4)=0.5$ and varying the RF power from 5 to 50 W, H₂ dilution ($\text{H}_2/(\text{H}_2+\text{SiH}_4+\text{CH}_4)$) from 49 to 250 and substrate temperature from 200 to 400 °C. The film characterizations have been performed by UV-VIS-NIR, FTIR, Raman and Rutherford backscattering spectroscopies, X-ray diffraction, dark conductivity and photoconductivity (100 mW/cm², AM1 condition). From a preliminary data analysis it has been obtained that $\mu\text{c-SiC:H}$ alloys with higher dark conductivity ($>10^{-2} \text{ S/cm}$) contain silicon and carbon (3R graphite) crystallites, having average grain size of 200 Å. Furthermore the decrease of the RF power causes the increase of the Si crystallite grain size and a decrease in carbon incorporation. Finally at low RF power values mc-Si-C:H alloys can be deposited at 200°C

D/PIII.12**DEPOSITION OF HIGHLY CONDUCTIVE BORON-DOPED MICROCRYSTALLINE SILICON-CARBIDE(p-mc-SiC:H) THIN FILM BY RF-PECVD**

S.W. Kwon(b), J.C. Lee(a) , S.K. Kim(a), S.Y. Myong(b), K.S. Lim(b), K.H. Yoon(a), J. Song(a) and I.J. Park(a), (a)Korea Institute of Energy Research, 71-2, Jang-Dong, Yusong-Gu, Daejeon 305-343, Korea, (b)Korea Advanced Institute of Science & Technology, Gusong-Dong, Yusong-Gu, Daejeon 305-701, Korea

Boron-doped hydrogenated microcrystalline silicon-carbide (p-mc-SiC:H) films have been used as a p-type material in hydrogenated amorphous silicon (a-Si:H) based solar cell because they have higher electrical conductivity, optical transmittivity, carrier mobility, and dopability than conventional p-type layers. Boron-doped microcrystalline silicon-carbide (p-mc-SiC:H) films were fabricated by RF plasma enhanced chemical vapor deposition method using silane (SiH₄), hydrogen (H₂), diborane (B₂H₆), and methane (CH₄) as a carbon source. From the Raman and FTIR spectrum measurements, the p-mc-SiC:H film was revealed to be composed of nano-sized crystal silicon embedded in a hydrogenated amorphous silicon-carbide matrix. A dark conductivity as high as 10⁻¹ S/cm, with an optical bandgap of 2.0eV, and a crystal volume fraction of 50% were obtained. We are trying to use p-mc-SiC:H films as a window layer of amorphous silicon and microcrystalline silicon solar cells.

D/PIII.13**CRYSTALLINE SILICON FILMS AND SOLAR CELLS BY HOT-WIRE CHEMICAL VAPOR DEPOSITION**

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The polycrystalline (or microcrystalline) silicon (poly-Si or mc-Si:H) films have been promising thin film materials for photovoltaic applications because of their advantages of abundance, non-toxic, high stability compared to a-Si:H, and high efficiency potential. These high potentials of poly-Si thin films have motivated a variety of study in this field. The most important issues, not or partially solved until now, are to deposit device quality poly-Si films at substrate temperature less than 600°C. Among the various deposition methods, Hot-Wire CVD has been considered to be very promising method for fast deposition of crystalline thin films on large substrate for opto-electronic applications like solar cells and thin film transistors, etc.

In this paper, crystalline silicon films with different grain size ranged from several nanometers (fine-grained) to micrometers (large-grained) are deposited at low temperature substrate by Hot-Wire CVD method. The silane (SiH₄) gas flow rate {F(SiH₄)} is a critical parameter both for deposition rate and for crystalline properties. The poly-Si films with moderate deposition rate (about 3mm/hr) deposited at low F(SiH₄) have superior crystalline properties with crystalline volume fraction exceeding 90%. The as-deposited films also have textured surface that is strongly recommended in thin film solar cells in order to obtain high current density by increasing incident light trapping. The effects of intrinsic thin film properties, e.g. grain size and defect passivation, on the performance of solar cells are systematically discussed in this paper.

D/PIII.14**SILICON-TETRACHLORIDE BASED MICROCRYSTALLINE SILICON FOR APPLICATION IN THIN FILM SILICON SOLAR CELLS**

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Microcrystalline silicon films were prepared using PECVD (13.56 MHz excitation frequency) with mixtures of silicontetrachloride and hydrogen as process gas and compared to silane-based material. Application of silicontetrachloride could be attractive as it tends to be less dangerous and less expensive than silane gas usually employed for preparation of thin film silicon. Low substrate temperatures (≤ 300°C), a relatively high pressure (4 mbar) and a high RF power (60 W) were applied for deposition and deposition rates exceeding 3 Å/s were achieved. Microstructure, optical and electrical properties were investigated by using a combination of techniques such as infrared, Raman and optical spectroscopies, electrical conductivity and SIMS measurements. Increasing the flow ratio of silane to hydrogen, the transition from the crystalline to the amorphous state occurs at a similar flow ratio (3-5 % for undoped films) as in silane-based material and is similarly steep. Next to the transition, the lowest porosity is observed. Porosity, void-related microstructure and chlorine content decrease with increasing substrate temperature (TS = 200°C - 300°C). Undoped material shows a room temperature conductivity near 10⁻⁷ (Wcm)⁻¹. Upon boron doping, conductivity values exceeding 50 (Wcm)⁻¹ were achieved. Silicontetrachloride-based boron-doped material was incorporated as a p-layer into microcrystalline pin silicon solar cells. Similar solar cell efficiencies as for solar cells using a silane-based p layer were obtained.

D/PIII.15**TRANSPORT PROPERTIES OF MICROCRYSTALLINE SILICON FILMS DEPOSITED BY HOT-WIRE CVD AT LOW SUBSTRATE TEMPERATURE**

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It has been shown recently for the microcrystalline silicon (μ -Si:H) films deposited by RF plasma-enhanced chemical vapor deposition (PECVD) that hydrogen can passivate surface dangling bonds and oxygen-related donors when lowering the growth temperature down to 250°C or less. We have used a similar approach for μ -Si:H films deposited by hot-wire chemical vapor deposition (HWCVD), a technique having the potentiality of high deposition rates and for which the generation of atomic hydrogen is considered as very efficient. In this work, fixing the filament temperature at 1570°C and the total gas pressure at 5.5Pa, we have investigated several series of HWCVD μ -Si:H deposits by selecting values of dilution of silane in hydrogen, defined as $\{F(H_2)/[F(SiH_4)+F(H_2)]\}$, in the vicinity of the amorphous – microcrystalline phase transition (50% dilution). For each series, the average substrate temperature versus time, measured with a platinum resistance and controlled both by a heater placed behind the substrate holder and by the filament, was varying between 170°C and 250°C. In order to couple, for each sample in a series, the transport properties with the structural data, Raman spectroscopy and UV-visible ellipsometry on one hand and time-resolved microwave conductivity (TRMC) on the other hand, have been conducted. It has been shown that the TRMC mobility (transport parallel to the surface) increases rapidly with the layer thickness up to 100nm and then stabilizes. It has been observed that the real substrate temperature increases with deposition time, which may explain the first results. Finally mobility has a maximum value versus average substrate temperature near 200°C, attributable to oxygen-related donor passivation. Some high efficiency μ -Si:H p/i/n solar cells have been realized by combining HWCVD

D/PIII.16**PHOTOLUMINESCENCE ENERGY AND OPEN CIRCUIT VOLTAGE (V_{oc}) IN MICROCRYSTALLINE SILICON SOLAR CELLS**

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Photoluminescence (PL) properties of thin film microcrystalline silicon solar cells in p-i-n deposition sequence with solar cell efficiencies above 9.0% were studied. The intrinsic absorber layers were deposited by Hot Wire Chemical Vapour Deposition (HW-CVD) at various silane concentration (SC) and low $T_s=185^\circ\text{C}$. Previous work showed that the open circuit voltage (V_{oc}) increases with increasing silane to hydrogen ratio (for the preparation of the i-layer). Particularly high V_{oc} up to 600mV were obtained for HW cells. We found continuous increase of the photoluminescence energy (E_{pl}) and V_{oc} for increasing SC and generation rate. This can be qualitatively understood by assuming a reduction of tail states and reduction of the defect density due to hydrogen passivation and structural relaxation. By monitoring V_{oc} and E_{pl} as a function of temperature and optical generation rate we investigated the effect of the tail states on the splitting of the quasi-Fermi energies.

A strong decrease of V_{oc} with increasing temperature and a weaker influence of the temperature on E_{pl} was found. This can be interpreted as follows: at low temperatures the quasi-Fermi energies are close to the band edges i.e. close to or within the carrier distributions. Therefore the difference between E_{pl} and V_{oc} is small. With increasing temperature the quasi-Fermi energies are shifted to lower energies, whereas the carrier distributions in the band tails changes only weakly, thus the difference between E_{pl} and V_{oc} increases.

D/PIII.17**RELAXATION OF PHOTOEXCITED CHARGE CARRIER CONCENTRATION AND MOBILITY IN mc-Si:H**

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In mc-Si:H solar cells the detail nature of charge carrier transport and recombination is still not fully clear. We have investigated these features by the methods of equilibrium and photoexcited charge carrier extraction by linearly increasing voltage, because, due to high conductivity of mc-Si:H layers, the time-of-flight method is difficult to use. It has been obtained that the relaxation time of the photoexcited charge carriers in mc-Si:H is much longer than that of a-Si:H. Moreover, in mc-Si:H the mobility of charge carriers decreases with the delay time after photogeneration. From experimentally estimated density of equilibrium charge carriers it follows that the Debye radius is smaller than the sample thickness, thus, energy conversion efficiency of mc-Si:H solar cells is controlled mainly by the charge carrier diffusion instead of the carrier drift.

D/PIII.18**INTEGRATED OPTICAL AND ELECTRICAL MODELING OF THIN-FILM SILICON SOLAR CELLS**

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Current amorphous and microcrystalline silicon solar cells use textured substrates for enhancing the light absorption and buffer and graded layers in order to improve the overall performance of the cells. The resulting solar cell structures are very complex and for understanding the role of these layers and for further optimization of the solar cell structures computer modeling is a useful tool. In this article we describe some of the new features of the ASA (Advanced Semiconductor Analysis) device simulator developed at Delft University of Technology, including models describing crystalline semiconductor materials, and demonstrate its applications to a-Si:H based solar cells.

Simulated results of dark and illuminated I-V characteristics obtained using the ASA program are compared to experimental results in order to give insight into the behaviour of the internal parameters of the solar cells, such as generation rate profile, internal electric field, recombination rate and trapped charge. Improved understanding of the role of band gap grading of the intrinsic a-SiGe:H layer in a single junction a-SiGe:H solar cell on the cell's external parameters will be presented.

D/PIII.19**OPTICAL MODELLING OF THIN-FILM SOLAR CELLS DEPOSITED ON TEXTURED SUBSTRATES**

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In thin-film solar cells light trapping techniques are used to enhance optical absorption in thin absorber layers in the solar cell. The efficient light trapping is based on light scattering at rough interfaces which are introduced into solar cells by using substrates with textured surface. For the solar cells in the superstrate configuration surface-textured SnO₂ and ZnO are used as the front transparent conductive oxide (TCO) contact usually. Recently, realisations of high-haze TCO (HHT) have been reported enabling further enhancement of light trapping in thin-film solar cells. Haze parameters and angular distribution functions of scattered light are measured for the SnO₂:F Asahi U and ZnO:Al substrates. Scattering parameters are imported in our optical model developed for simulation of thin-film solar cells. The simulation results of the external quantum efficiencies of single-junction a-Si:H solar cells deposited on SnO₂:F and ZnO:Al substrates with different scattering properties will be presented and verified. The effects of enhanced light scattering in thin-film solar cells using hypothetical HHTs will be discussed.

D/PIII.20**POLYCRYSTALLINE SILICON THIN FILMS ON GLASS SUBSTRATE**

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The formation of high-quality polycrystalline silicon (poly-Si) on different substrates has important applications in the development of thin film transistors, solar cells, image sensors, etc. In this study, we present the results of an investigation of poly-Si films on glass, formed by aluminum induced crystallization (AIC). The process is based on isothermal annealing at temperatures between 440° and 520°C of co-sputtered Al + Si or sputtered a-Si films on glass, with and without thermally evaporated Al. The poly-Si films were investigated by Raman spectroscopy, optical microscopy, scanning electron microscopy (SEM) and X-ray photoelectron microscopy (XPS). Films of a-Si with Al (deposited by co-sputtering of Si and Al) crystallize entirely but form a porous structure. Those consisting of a-Si with Al on Al coated glass substrates form a thin continuous polycrystalline layer with the thickness of the Al sublayer. The substrate temperature of the deposited films is an important parameter for aluminum induced crystallization. A lower limit of the Al concentration for co-sputtered films exists, which determines the process of AIC.

D/PIII.21**EPITAXIAL SI THIN FILMS BY HIGH-TEMPERATURE CVD**

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Epitaxial Si thin films deposited on low-cost Si based substrates at high-temperature are the promising alternative to the amorphous and microcrystalline silicon films deposited at low temperature on foreign substrates. Epitaxial thin film solar cell concept has several advantages: first of all, it provides a high quality active layer resulting in a high efficiency of solar cell and secondly, the concept employs the same cell structure as conventional bulk Si solar cells and therefore can be easily implemented into industrial production without attracting additional efforts on research and development of new processes.

Short overview of the results obtained on epitaxial thin films grown by high-temperature CVD in a commercial ASM-Epsilon 1 reactor using DCS and TCS as a Si precursor is presented. Three kind of low-cost substrates are investigated: highly doped p-type multicrystalline-Si (mc-Si SILSO), ribbon grown on substrate (RGS) and upgraded metallurgical grade Si (UMG-Si). Two different solar cell processes are applied: lab-cell process (13.5-14.0%) and industrially compatible screen printed technology (12-13.2%). In order to improve the current cell efficiencies and decrease the thickness of deposited layer the concept for light confinement using reactive ion etching (RIE) and electrochemical etching is presented. It is shown that combination of the RIE-textured surface with a porous Si back side reflector might form a very efficient light trapping scheme in ultra-thin epitaxial cells. So far, the efficiency of 12% and 11% obtained on mono- and mc-Si with porous Si back reflector. All results point out that epitaxial Si thin film solar cells are a promising candidate to replace the existing industrial multicrystalline Si solar cells.

D/PIII.22**COMPARATIVE STUDY OF LPE AND VPE SILICON THIN FILM ON POROUS SACRIFICIAL LAYER FOR TRANSFERRED SOLAR CELLS**

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Thin film single crystal silicon on foreign substrate is an attractive way to realize cheap and efficient photovoltaic devices. In this paper we will compare epitaxial growth of silicon thin film on double porous sacrificial layers obtained by Liquid or Vapor Phase Epitaxy (LPE or VPE). Porous silicon is elaborated by electrochemical anodisation of monocrystalline silicon in a HF/ethanol solution. VPE is achieved in an atmospheric pressure chemical vapor deposition (APCVD) reactor under H₂ atmosphere. Growth rate is in between 0,5-3 µm/min. LPE is realised in a graphite sliding boat using Indium as main solvent. Growth rate is in the range 0,1-1 µm/min depending on the temperature and the cooling rate.

We discuss the substrate orientation, temperature, growth rate, layer homogeneity and electrical properties of the epilayers for both growing techniques. Diffusion length and mobility are measured respectively with LBIC and Hall effect technique. The values obtained for p-type ($\mu > 100$ V/cm²/s and $L_n > 130$ µm) allow the realisation of solar cell using interdigitated technology on the top of this layer which is detached and transferred onto mullite substrate.

D/PIII.23**TEMPERATURE DEPENDANT IBIC STUDIES OF POLYCRYSTALLINE SILICON**

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Ion beam induced charge (IBIC) collection technique can provide interesting and straightforward information about the semiconducting materials and different electronic device characteristics. This nuclear microprobe technique was used for the qualitative analysis of charge collection efficiency spatial distribution in several types of poly-Si material. We studied the influence of light impurities (oxygen, carbon) present in material on electrical activity of extended defects. It is shown that oxygen segregating close to structural defects influences their electrical activity, while for carbon we did not observe the same effect. We demonstrated that the temperature dependant IBIC technique could provide additional information about the electrically active defects, and/or their activation or deactivation during subsequent processing.

D/PIII.24**IMPACTS OF SPACIALLY REDUCED GRAIN BOUNDARY RECOMBINATION REGIONS ON POLYCRYSTALLINE SILICON SOLAR CELLS PERFORMANCES**

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In this work, we investigate the impacts of grooving grain boundaries (GBs) of polycrystalline silicon on the performances of the related solar cells. GBs like defects may be easily grooved using Porous Silicon (PS). We then used these interesting properties to try reducing the area of these highly recombinant regions. To reach this objective a thin porous silicon (PS) layer was formed at both front and back sides of the polycrystalline material. After removing the PS films, conventional phosphorus diffusion was achieved. Grooved GBs enable deep penetration of phosphorus and metallic contacts. As a result, we found an improvement of the I-V characteristics under the dark and at AM1.5 illumination. Light-beam-induced-current (LBIC) measurements showed an increase of the short-circuit current (I_{sc}) of about 25% and an improvement of the bulk minority carrier diffusion length (L) and the GB recombination velocity (V_r). The internal quantum efficiency was also found to be enhanced of about 15% in a rather wide spectral range approximately between 650 nm to 950 nm. These results are discussed referring to solar cells based on untreated polycrystalline silicon substrates.

D/PIII.25**LIFETIME MEASUREMENTS OF POROUS SILICON AND POROUS Si-Ge STAIN ETCHED AND HYDROGEN PASSIVATED**

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Porous silicon layers stain etched in low nitric acid concentrations, and formed only in some tens of seconds, exhibits surprising low reflectance values (< 4%) in the whole 300 - 1100 nm spectral range. This property can be useful to apply this kind of layers on top of silicon-based photodetectors and solar cells. Consequently, the quantum efficiencies of these devices can be increased with respect to conventional antireflection layers on top of silicon. However, the surface states induced by this porous layer on the silicon wafer act as high velocity recombination centres. Then, it is necessary to efficiently passivate the porous layers to reduce this detrimental effect.

In this work we present the first micro-wave photo-conduction decay measurements for porous silicon and porous Si-Ge stain etched and hydrogen-passivated. These technique measures the lifetime of the charge carriers photogenerated, and it is extremely useful to characterise the surface recombination properties of the silicon-based photodetectors. We also study the time evolution of the carriers lifetime for samples exposed to ambient conditions. We observe a decrease of the carrier lifetime for porous layers with respect to the silicon substrate before stain etching. However, when the samples are hydrogen-passivated, the lifetime for the porous layers increases to larger values than the silicon substrate before stain etching.

D/PIII.26**PHOTOVOLTAIC STRUCTURES BASED ON POLY-SI THIN LAYERS - DESIGN AND PROCESSING**

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The design of a photovoltaic p-i-n structures based on thin poly-Si layers together with technological process and their characteristics are presented. A thin polysilicon layer of 1 μ m was deposited by LPCVD method at 610 $^{\circ}$ C over a SiO₂ layer of 150 nm grown at 1100 $^{\circ}$ C by wet thermal oxidation on silicon wafers. This first poly-Si layer was n⁺-type doped by phosphorus diffusion from POCl₃ source at 920 $^{\circ}$ C for 45 min. The second undoped poly-Si layer of 2.5 μ m was deposited over the n⁺-doped layer as the active i-type layer of the p-i-n structure where the light absorption takes place. A shallow junction (0.3-0.4 μ m) was obtained by boron diffusion from BN at 1000 $^{\circ}$ C for 30 min. The preparation is completed by deposition of an silicon dioxide AR coating of 800 nm. An etching process of poly-Si for back contacting of the structure is applied. Ti (400 Å) and Al (5000 Å) were deposited by evaporation under ultrahigh vacuum (5 $\times 10^{-7}$ torr) and patterned using photolithography. The photovoltaic structures can be connected in series by the mask for the contacts. The structures characterisation reveals the possibility to work in photovoltaic and photoconductive regime.

D/PIII.27**ELECTRIC FIELD EFFECT OF METAL INDUCED CRYSTALLIZATION OF AMORPHOUS SILICON**

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Anomalous crystallization behavior has been found for a metal induced crystallization (MIC) of the amorphous silicon (a-Si). The Ni density of 3.05×10^{13} atoms/cm² was deposited uniformly over whole a-Si layer and then the 2nd Ni layer was selectively deposited on the a-Si using a shadow mask with Ni density of 3.65×10^{14} atoms/cm². The a-Si films were annealed for 30 minutes at 500 $^{\circ}$ C under DC electric field that was applied to the a-Si by means of two metal bar electrodes. The crystallization started at first in the high Ni density (3.65×10^{14} atoms/cm²) region as a result of MIC in an electric field and then the a-Si in low Ni density (3.05×10^{13} atoms/cm²) region was laterally crystallized. However, the lateral crystallization proceeded in radial direction from the high Ni density region, forming disk-like grains, even though a parallel bias-field (DC electric field) was applied, then, the crystallization speed increased with the electric field strength. The lateral crystallization speed was shown an exponential relationship with the electric field as $r = r_0 e^{\alpha E}$ with constant r_0 and α of 44.73 mm²/V \cdot h. The dependence appears to be due to the reduction in the activation of Ni diffusion in an electric field.

D/PIII.28**Me-INDUCED Si FILMS CRYSTALLIZATION**

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In [1] the method of the low-temperature crystallization of Si amorphous films with using of 3d-metal silicide crystal seeds (PdSi₂, in particular) is proposed. By this, as its known, the catalyst effect of 3d-metal silicide which reduces the temperature and time of amorphous Si crystallization is used. However, the continuous (>2h) thermic annealing of Me-Si-composition and relatively small size of poly-Si microcrystallites (300nm) are defects of this and similar methods. The micro-crystallites size must be not less 500nm for numerous photovoltaics applications. Our method is based on separation of poly Si seeding and crystallization processes on glasses and SiO₂. By this, crystallization is coming through Sn liquid layer (Sn-isovalent to Si metal). The operations is following: - Me-sublayer (Pd, Ni, Er, etc.) deposition on substrate, - vacuum evaporation according to the method [2] of thin layer am. Si (0,1 μm), - thermic annealing of the composition by 400C during 1 hour (formation of the silicide seeds), - thermic evaporation of Sn film (0,1...0,2 μm), - heating of composition to 270...300C and evaporation Si onto the surface of Sn liquid film by [2]. By this Si crystallizes according with steam-liquid mechanism. The layers were homogeneous. Contents of Si amorphous phase less than 10% vol.

[1] G.Liu, J.Fonash/ Appl.Phys.Lett., 1993, v.62, p.2554.

[2] N.D.Vasilenko, V.A.Krasnov, B.I.Sushko/ Cryst.Prop.and Prep., 1991, v.32-34, p.39

D/PIII.29**ENHANCEMENT OF METAL-INDUCED CRYSTALLIZATION IN SiGe/Ge/Ni/SiO₂ LAYERED STRUCTURE**

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Low temperature (<550 oC) formation of high quality poly-SiGe films on glass substrates has been expected to realize high efficiency solar cells and system-in-displays. To achieve this, we examined metal induced lateral crystallization (MILC) of a-SiGe/SiO₂. In the experiment, a-Si_{1-x}Ge_x layers (50 nm thickness) and Ni films (5 nm) were deposited on SiO₂ films. Then, Ni films were patterned by using photolithography. Finally, they were annealed at 550 oC in a nitrogen ambient. For samples with high Ge-fractions (x>0.4), dendrite growth of SiGe was found around the Ni-patterns. However, for samples with low Ge-fractions (x<0.35), plane growth was obtained. Growth velocity was estimated to be 0.7 mm/hr (x=0) and 1 mm/hr (x=0.3). Such enhancement by Ge-doping was attributed to enhanced Ni-migration in locally strained a-SiGe films. To use Ge-doping effect effectively, we examined MILC in a layered structure, i.e., a-Si_{0.7}Ge_{0.3}(50nm)/ a-Ge(30nm)/ Ni-pattern/ SiO₂. Significant high growth velocity (~3 mm/hr) of SiGe was achieved. As a result, poly-Si_{0.7}Ge_{0.3} with large grains (30 μm) was obtained. Raman spectroscopy measurements showed that grown layers were completely strain free. Mechanisms of the enhanced growth velocity have not been clarified yet; however, present combination of MILC and SiGe layered structure is a useful way to realize large poly-SiGe films on glass substrate. This should be used for low-cost and high-efficiency solar cells.

D/PIII.30**ALUMINIUM-INDUCED CRYSTALLIZATION OF AMORPHOUS SILICON: GROWTH PROCESS VS SI DEPOSITION METHOD**

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Aluminum-induced crystallization (AIC) technique can lead to the formation of large grains polycrystalline silicon films on glass substrates, which is desirable for thin-film solar cells. It is based on the overall layer exchange of adjacent Si and Al films during the formation of amorphous to polycrystalline Si. Here, we present results of AIC on thermally oxidized Si (t-SiO₂) and mullite ceramic substrates. The aluminum layer was deposited first onto the substrates by electron beam evaporation. The amorphous Si layer was deposited by different methods including plasma enhanced-CVD (PECVD), hot wire-CVD (HWCVD) and sputtering. Different Si deposition methods led to different crystallinity and hydrogen content in the Si layer.

We have studied the Si nucleation rate versus the annealing parameters (T,t) and the a-Si nature. The Al and Si exchange was performed during annealing at temperatures in the range 450 ? 550 °C and for durations of 30min to 20h. The resulting poly-Si films were analyzed by optical and scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction (XRD). The Al content in the layer was determined by secondary-ion-mass spectroscopy (SIMS). During annealing, the dissolved atoms crystallize within the aluminium. The Si grain grows vertically between the substrate and the a-Si/Al interface. Dendritic growth is observed. It seems that hydrogen present in the a-Si layer can increase the nucleation rate and influence the final grain size. Grains as large as 25 μm, uniformly distributed, values up to 40 μm were however reached on non pre-heated samples. Preferential orientation of the grains as well as the crystallographic structure vs Si deposition method will be shown and discussed.

D/PIII.31**POLYCRYSTALLINE SILICON OBTAINED BY METAL INDUCED CRYSTALLIZATION USING DIFFERENT METALS**

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The aim of this paper is to study the role of different metals in inducing crystallization on films produced by LPCVD at high and low temperature processes and, to compare the structural, morphological, optical and electrical properties of the various films produced. This work envisages the use of the most suitable conditions that lead to the production of films for optoelectronic applications such as solar cells.

The suitability of different metals such as gold, aluminium, molybdenum, nickel and titanium to achieve good electronic quality polycrystalline silicon thin films was studied, before and after heat treatment. Some of the metals above referred such as nickel and aluminium have been extensively used on silicon crystallization rather than others, like molybdenum. The results that we have already achieved show that the use of molybdenum as metal coating of the substrate has a great influence on the crystallization process, by inducing a preferential growth through the <111> planes, which leads to more compact and dense films, as shown by XRD, spectroscopic ellipsometry and SEM data. The corresponding role of molybdenum when deposited over or laterally on the silicon films (amorphous or polycrystalline) will be also presented. Apart from that, the data also show that the films grown on molybdenum-coated substrates have improved electrical properties, where the hopping conduction contribution for the conductivity is reduced, as demonstrated by the electrical conductivity measurements.

- D/PIII.32** HIGH TEMPERATURE CRYSTALLIZED POLY-SI FILM ON THE METAL SHEET SUBSTRATE FOR PV CELL APPLICATIONS
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 Polycrystalline silicon thin films are very useful in the solar cell applications for low cost photovoltaic cells. However, it was very difficult to fabricate high performance poly-Si at a temperature over 600°C for glass substrate because of the limitation of temperature. The conventional process technologies like solid phase crystallization (SPC) of amorphous Si require high temperature (600-1000°C) process. The objective of this paper is to grow poly-Si on flexible metal substrate such as molybdenum, stainless steel for the PV application using a rapid thermal crystallization (RTC) of amorphous silicon (a-Si) layer. And we can reduce the crystalline temperature with the seeding layer. For the high temperature poly-Si crystallization, we deposited the a-Si film on the metal sheet having a thickness of 150 nm. For crystallization, the heat treatment was performed in a RTC system. The experimental results show the grain size larger than 0.5 μm and conductivity of 10-5 S/cm. The a-Si:H was crystallized at 1050°C within 3min and improved crystal volume fraction of 92 % by RTC. In this paper, we exhibit the properties of high temperature crystallized poly-Si films on metal sheet substrate.
- D/PIII.33** INFRARED STUDY OF a-SiC_xH and a-SiC_xNy:H FILMS FOR c-Si SURFACE PASSIVATION
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 Amorphous silicon carbide (a-SiC_xH) and carbonitride (a-SiC_xNy:H) films deposited by PECVD from SiH₄/CH₄ and SiH₄/CH₄/N₂ mixtures have been shown to provide excellent electronic passivation of p-type and n-type c-Si. We have reported effective surface recombination velocities (Seff) lower than Seff < 11 cm s⁻¹ for a-SiC_xH films on p-type c-Si (3.3 ohmcm) [1, 2] and Seff < 16 cm s⁻¹ for a-SiC_xNy:H films on n-type c-Si (1.5 ohmcm) [3]. From the analysis of the injection level dependency of Seff determined by the quasi-steady-state photoconductance method results that the good electronic passivation is due to field-effect passivation created by a strong band bending at the c-Si surface. Our studies of the dependency of Seff on CH₄/SiH₄ gas flow ratio (Y) indicate a minimum of Seff for a certain Y for p-type c-Si and n-type c-Si, and lower Seff for higher deposition temperature.
 In this work we will present a comprehensive study of the composition of these films determined from infrared transmission spectra. We will relate the compositional data to Seff and film properties like electrical conductivity, optical band gap or refractive index. Interestingly, addition of N₂ to the CH₄/SiH₄ gas mixture not only results in nitrogen incorporation into the films, but also results in higher carbon incorporation.
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- D/PIII.34** GROWTH AND ELECTRONIC PROPERTIES OF THIN a-Si:H(n) EMITTER LAYERS
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 Ultra-thin films (down to 5 nm) of hydrogenated amorphous silicon (a-Si:H) are used as emitter heterojunction solar cells. To reach an optimum efficiency, the films must be compact and void-free. Non-compact films lead to shunting problems between crystalline silicon (c-Si) substrate and the transparent conducting oxide (TCO) in a TCO/a-Si:H(n)/c-Si(p) solar cell. Our samples are prepared in a standard Plasma Enhanced Chemical Vapor Deposition (PECVD) reactor and characterized for structural and electronic properties.
 By means of atomic force microscopy (AFM), the initial nucleation stage of the film growth, the topography and the surface roughness of the layers are monitored. The dependence of the work function, gap state density, position of Fermi-level and Urbach-energy on the thickness and the doping level of the a-Si layers has been analysed by ultraviolet photoelectron spectroscopy (UPS). It has been found, that the variation of the doping level from 0 to 20000 ppm PH3 addition results in a saturation of the Fermi level at EC-EF = 0.27 eV, while the Urbach energy increases from 51 meV to 101 meV. Surface photovoltage (SPV) and Photoluminescence (PL) spectroscopy are used to determine the quality of the a-Si films and a-Si/c-Si interface.
- D/PIII.35** INVESTIGATION OF a-Si:H/c-Si HETEROJUNCTION SOLAR CELLS INTERFACE PROPERTIES
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 Amorphous/crystalline silicon heterojunctions are very promising structures for high efficient solar cells fabricated at low temperature. However, interface defects can enhance the recombination of photogenerated carriers and limit the cell efficiency. Thus, the determination and control of interface properties are a major step in the development of a-Si:H/c-Si heterojunction devices. The interface properties of solar cells fabricated with different pretreatments of p-doped c-Si wafers and different thickness of n-doped a-Si:H layers were investigated by capacitance and luminescent measurements. Correlations between capacitance versus temperature (C-T) and capacitance versus voltage (C-V) curves in the dark, and current-voltage (photo I-V) curves under illumination were observed. For the structures having the highest efficiency, no step in the C-T curve is observed and the photo I-V curves show no S-shape even down to 100 K. Heterostructures showing a step on the C-T curves (accompanied by local maximum of conductivity) also show S-shape I-V curves under illumination and have lower efficiency. These features are also correlated to photoluminescence properties of these cells.

D/PIII.36**SILICON HETEROJUNCTION SOLAR CELLS WITH P NANOCRYSTALLINE THIN EMITTER ON MONOCRYSTALLINE SUBSTRATE**

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The heterojunction structure which involves the use of a p-type nanocrystalline Si (nc-Si) emitter grown by VHF-PECVD on (100) c-Si, at 170 °C, was studied. The aim of the experiment was to use the specific properties (optical gap) of nanocrystals to increase the built-in potential and consequently the Voc of the device. Our experimental data demonstrate that the p nc-Si / i a-Si:H / c-Si heterojunction solar cells exhibit Voc values higher than the (p+i) a-Si:H / c-Si heterojunctions. On flat devices, including a totally amorphous passivating i-layer and a non optimized p nc-Si layer, we obtained Voc up to 640 mV and efficiencies as high as 14 %. The deposition of a thin p nc-Si layer on the ~ 5 nm thick i a-Si:H buffer layer is critical. The nanocrystalline growth in VHF condition requires high hydrogen diluted plasmas, that can etch or recrystallize the underlying thin a-Si:H layer. To improve the device efficiency it is important to preserve the continuous thin i a-Si:H layer at the heterojunction (passivating the c-Si surface) and to control the thickness and crystallinity of the p nc-Si emitter. In the case of these very thin emitters deposited on c-Si, the long range effects of H atoms in the plasma can only be evidenced by performing the optical measurements and high resolution TEM cross section observations on the p nc-Si / i a-Si:H double layers. Our results on the optimization of that heterojunction microstructure, resulting both by the simulation of optical spectra and by the HRTEM observations, are reported and correlated with the corresponding solar cells characteristics.

D/PIII.37**COMPARISON OF AMORPHOUS/CRYSTALLINE HETEROJUNCTION SOLAR CELLS BASED ON n AND p TYPE CRYSTALLINE SILICON WAFERS**

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In this work we investigated the difference and the potentiality of the two kind of heterojunctions for photovoltaic application: p-type a-Si:H / n-type c-Si; n-type a-Si:H / p-type c-Si.

Devices based on p-type crystalline silicon were optimized by an effective back surface field, obtained by screen printed Al diffusion step on the back side of the wafer and introduction of intrinsic buffer layer between amorphous emitter and crystalline absorber after dry cleaning of silicon surface. 17% conversion efficiency on 2cm² samples was reached. Devices based on n-type crystalline silicon were fabricated by two heterojunctions: p-type a-Si:H / n-type c-Si on the front side and n-type c-Si / n-type a-Si:H on the back side of the wafer. In both depositions an intrinsic buffer layer was introduced as indicated in the SANYO process [1]. Experimental comparison of performances in dark AC and DC regime and under AM1.5G condition were performed and discussed. In particular, with the aid of a numerical model, able to solve AC and DC problem in multilayer structure we evaluated the transport mechanism and the defect behavior at the junction for both kind of solar cell heterostructures. Difference in the technological steps needed to device formation have been considered for high efficiency solar cell. Finally an explanation of the difference in the role played by the defect density at the heterojunction for both kind of structure has been proposed.

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D/PIII.38**CHARACTERISATION OF C-SI(P)/A-SI(N), A-SI(N)/TCO, C-SI(P)/A-SI(N)/TCO HETEROJUNCTIONS BY MEANS OF SPECTRAL DEPENDANT SURFACE PHOTOVOLTAGE SPECTROSCOPY**

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We use thin films (5-50 nm) of n-doped hydrogenated amorphous Silicon a-Si:H(n) as emitter layers for amorphous/crystalline silicon heterojunction solar cells, Al/c-Si(p)/a-Si(n)/TCO. The two heterojunctions, c-Si(p)/a-Si(n) and a-Si(n)/TCO play a decisive role for efficient solar energy conversion. We investigate these heterojunctions by means of spectral dependant surface photovoltage spectroscopy (SPV). By specific generation of excess carriers within the a-Si:H(n) emitter only (i.e. at 532 nm) or within the c-Si(p) absorber only (i.e. at 904 nm) band bending within the emitter due to the TCO/a-Si(n) contact can be distinguished from band bending in the absorber. Effective emitter and absorber lifetimes can be extracted. It is shown that (1) the TCO/a-Si contact leads to a depletion of the emitter, (2) if the emitter is thin enough (~5 nm), the TCO/a-Si contact affects the band bending within the absorber. These results are supported by additional IV, CV and work function measurements. In order to analyse the SPV signals the band bending resulting from steady-state SPV has been numerically simulated for all the above cited heterojunctions.

D/PIII.39**DETERMINATION OF THE INTERFACE CHARGE IN THE a-Si/c-Si STRUCTURE BY HIGH FREQUENCY C-V MEASUREMENTS**

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Recently the structure hydrogenated amorphous silicon-crystalline silicon (a-Si:H/c-Si) has been studied actively since it is attractive for application in solar cells and in position sensitive detectors[1,2].

In this work we present a method for estimation the density of charged traps in the a-Si:H based on high frequency C-V measurements. Intrinsic a-Si layers with different thicknesses are deposited on the top of p-type crystalline Si by PECVD at two frequencies - 13.56 and 27.12 MHz. After Al metallization capacitor structures are formed. Due to the high dark resistivity of the intrinsic a-Si the structure Al/a-Si:H/c-Si can be considered as a MIS capacitor. In this case, in depletion mode the 1/C² dependence on the applied voltage (Va) is linear: 1/C² = A + Bx. The parameter A depends on the a-Si:H thickness, charged traps in the a-Si:H, charged traps in the interfacial region a-Si:H/c-Si and the work function difference between the Al and c-Si. The fitting of the dependence - parameter A vs. a-Si:H thickness - with a second order polynomial gives information about the density of the net charge trapped in the a-Si:H and its location. The results from the C-V measurements will be compared with the results measured on the same samples by the constant photocurrent method (CPM).

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D/PIII.40**EFFECT OF THE TUNNELLING OXIDE THICKNESS AND DENSITY ON THE PERFORMANCE OF MIS PHOTODIODES**

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In this work metal-insulator-semiconductor (MIS) photodiodes with a structure: Cr/a-Si:H(n+)/a-Si:H(i)/oxide/Au was studied, where the main objective was to determine the influence of the oxide layer grown by different techniques on the performance of the devices. The results achieved show that the photodiodes performances are a function of both oxide thickness and oxide density and that similar results are achieved when thin $< 20\text{Å}$ dense oxides or thicker $> 20\text{Å}$ porous oxides are used. Anodic oxidation, H₂O₂ oxidation, evaporation of SiO₂ by electron gun, and chemical deposition of SiO₂ by plasma of HMDSO were investigated.

The experimental data show that the thickness of the oxide is easily controlled with the hydrogen peroxide oxidation technique, which is also the easiest and cheapest known technique. By proper control of the oxide thickness it was possible to achieve photodiodes exhibiting an open circuit voltage of 0.7V and short circuit current density under AM1.5 illumination above 11 mA/cm², with a response times less than 1 ms, a diode quality factor of about 1 and a ratio of 107 between forward and reverse currents. The ideal oxide thickness, determined by spectroscopic ellipsometry was estimated to be in the range of 5 to 30 Å, depending on the oxidation technique used, which determines the degree of the oxide density. In this work it is also presented a method for reducing the saturation current of the diodes by burning small short-circuits by applying to the devices a controlled reverse voltage.

D/PIII.41**PROPERTIES OF Si:H NANOCRYSTALLINE UNDOPED AND DOPED FILMS PRODUCED BY HWP-CVD TECHNIQUE**

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Nanocrystalline undoped and doped Si:H films have been produced by combining the hot wire chemical vapour deposition (HW-CVD) and plasma enhanced chemical vapour deposition (PECVD) techniques which we call hot wire plasma assisted chemical vapour deposition (HWP-CVD). The energy delivered to the gas dissociation is determined and correlate to the films properties. We show that using HWP-CVD technique we obtain at high growth rate compact and stable intrinsic films and high conductivity doped films with a smooth surface and compact structure. These films are used to produce glass/ZnO/nc-p-SiC:H/i-Si:H/nc-nSi:H/Al structures and the behaviour of the individual layer thickness in the short circuit current and open circuit voltage is presented.

D/PIII.42**NANOCRYSTALLINE SILICON FILMS ON PLASTIC SUBSTRATES FORMED BY PULSE LASER CRYSTALLIZATION OF THIN a-Si FILMS**

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The thin nanocrystalline silicon films were manufactured on polyimide substrate with Si₃N₄ buffer layer using XeCl excimer laser crystallization of a-Si films deposited with the use of low-temperature low-frequency plasma enhanced deposition technique. The thickness of Si films were 100 nm. The polyimide (temperature of plasticity up to 200 °C) was chosen as substrate due its good dielectric and mechanical properties. The structural properties of the films were studied using Raman scattering and high resolution electron microscopy (HREM). Several regimes of pulse laser crystallization were used, the average size of obtained Si nanocrystals were modified from 2.5 up to 10 nm depending on crystallization regime. The sizes of nanocrystalline grains were estimated from Raman scattering data using approach of effective folding of optical vibration states in nanocrystals. The estimated from data of Raman scattering size of nanocrystals were in good agreement with direct data of HREM. The possibility of scanning laser treatments was shown. The obtained results are actual for manufacturing of polysilicon on plastic substrates structures for giant microelectronic applications (active matrixes of thin film transistors et. c.)

D/PIII.43**MICROSTRUCTURE AND OXYGEN CONTAMINATION IN NANOCRYSTALLINE SILICON FILMS GROWN BY RADIOFREQUENCY MAGNETRON SPUTTERING**

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Nanocrystalline hydrogenated silicon films were grown by radiofrequency magnetron sputtering in an Argon/Hydrogen (30%/70%) plasma. For some series Helium or Nitrogen was added to the gas mixture. The films were grown at 250°C for different pressures varying from 5 to 15 Pa. The crystalline fraction increases with pressure from 85% to 93% but at the same time porosity increases from 11% to 19% for the films in the Ar/H plasma. This relatively high porosity leads to an important post-growth contamination of oxygen as revealed by IR absorption spectroscopy and nuclear reaction analysis (NRA) and can explain the low stress observed in these films. The Electron spin resonance (ESR) performed at 35 GHz indicates the presence of oxygen in the surroundings of the paramagnetic defects. The spin density is of the order of some 10¹⁷ cm⁻³, independent of the growth pressure and in agreement with photothermal deflection measurements. From the IR spectroscopy and NRA one can deduce that most of the oxygen in the films is bound to silicon. The introduction of He at 5 Pa in the plasma tends to reduce the porosity and the oxygen contamination in the film but above 30% He dilution, the crystalline fraction decreases. When nitrogen is introduced into the plasma during growth, the films become amorphous, even for very small partial pressures of N (0.01 Pa).

D/PIII.44**INFLUENCE OF SURFACE TREATMENTS ON NANOCRYSTALLINE SILICON**

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Free standing porous silicon (PS), which is a form of nanocrystalline silicon (nc-Si), prepared by anodizing B-doped c-Si wafers shows red photoluminescence (PL). PS samples are characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM). The as prepared PS rinsed in ethanol show a PL peak at 800nm when excited by a He-Ne laser (632nm) and a XRD peak at $2\theta = 68.87^\circ$ using CuK α line (1.5405Å), gives a change in lattice parameter $\Delta a = 2.95 \times 10^{-3}$ in the nc-Si state, as compared to the c-Si value. High resolution AFM images depict the presence of nc-Si of sizes 2.7nm, 3.4nm, 4.6nm and higher. Upon rinsing PS in deionized water, the PL peak blue shifts to ≈ 744 nm and no PS peak is found in XRD. AFM shows nc-Si of size 2.7nm are still present, but those of sizes between 3.4nm and 4.6nm are removed by water. Upon dipping in pentane, toluene and acetone show no significant changes in XRD and AFM data. No change in PL data is found, but in acetone, where PL intensity reduces by about 50%. The quantum confinement model [1] can explain satisfactorily the PL results in all cases using AFM data, but in acetone. A large increase in dark current (DC) is observed upon exposure to above ambients. But a layer of Se decreases DC, suggesting that besides quantum confinement, charge transfer at the surface of nc-Si plays an important role.

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D/PIII.45**NANOCRYSTALLINE SILICON THIN FILMS BY PECVD: ACTIVE LAYER OF SOLAR CELLS**

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Nanocrystalline silicon (nc-Si:H) thin films have been deposited by plasma enhanced chemical vapor deposition (PECVD) technique, using silane diluted with hydrogen as source gas. Hydrogen dilution, chamber pressure and substrate temperature have been varied to achieve optimized condition for the deposition of nc-Si:H films. Mainly the amorphous to microcrystalline transition region has been probed for this purpose. Presence of nanometer-sized (<10 nm) crystalline grains are observed in the films from X-ray diffraction analysis and the grains are supposed to be embedded in the amorphous matrix as observed in transmission electron microscopy. The dark conductivity of the films remain within the range from 10^{-9} S/cm to 10^{-8} S/cm. The photosensitivity (i.e. photoconductivity/dark conductivity) of the films show quite higher value ($10^2 - 10^3$) than that ($10^0 - 10^1$) of highly microcrystalline films. Interestingly, these films degrade much less than typical amorphous films. Compared to microcrystalline films, less microstructural defects have been found for nc-Si:H film in FTIR studies. Optical absorption studies in the UV-VIS-NIR range, estimates wide band gap (~1.9 eV) for these films and the absorption profile is close to that of amorphous films. Thus, the nc-Si:H films could be potential materials as active layer, even to replace the top amorphous i-layer of tandem solar cells in micromorph configuration.

D/PIII.46**FABRICATION AND CHARACTERIZATION OF NANOCRYSTALLINE SILICON USING PLATINUM-NANOMASK**

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Nano-structured semiconductors are most promising materials for the future device application because of its various quantum effects and the possibility to realize a new-functional device. In this study, we have investigated the novel and easy technique to fabricate Si nano-crystals. The SiO_x/a-Si/SiO_x films were sequentially deposited on the p-type Si(100) substrate by r.f magnetron sputtering deposition method. And then, nano-sized Pt particles were deposited onto this structures by d.c sputtering deposition method. These nano-sized Pt particles play a role as masks to be used for the anisotropic dry etching process. The average diameter and the density of Pt particles were 8~12nm and $6.5 \times 10^{11} \text{cm}^{-2}$ respectively. After the formation of SiO_x/a-Si/SiO_x columns by utilizing the reactive ion etching process, the 10nm-thick gate oxide, SiO₂, layer was deposited on the top of samples. The formation of Si nano-crystals was performed by the rapid thermal process. Si nano-crystals having diameters ranges between 5 and 8nm were clearly observed from the cross-sectional image of transmission electron microscopy. The intensive blue emission near 460nm was observed in the low temperature luminescence spectrum. It is well understood that the emission from the region around 450nm is attributed to the emission from Si nano-crystals. After the fabrication of metal-oxide-semiconductor capacitor embedding Si nano-crystals, Al/SiO₂/nc-Si/SiO₂/p-Si, finally, we have evaluated the electrical property. The hysteresis behavior was observed in the measurement of capacitance-voltage relationship and the flat-band voltage shift was 326mV.

D/PIII.47**SILICON NANOCRYSTALS AS LIGHT CONVERTOR FOR SOLAR CELLS**

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Involving nanostructures in solar cell could be a way to increase their efficiency. We have investigated silicon nanocrystals (Si-nc) embedded in silica matrix as a light converter in a conventional silicon based solar cell. The high energetic photons are absorbed by the Si-nc and transformed via photoluminescence (PL) to red ones which are then absorbed much efficiently in the cell and in principle increase the collection probability. Increase in external quantum efficiency is observed in the region of Si-nc excitation. In the present contribution we first present the fabrication of Si-nc ex-situ of the silicon dioxide host matrix. Two different methods were used: pulverising of porous silicon and ball milling. Second, we investigate and compare the optical properties of Si-nc versus the preparation method. Such a Si-nc were embedded into a spin-on-glass matrix and then spun onto a standard silicon solar cells. The solar cell performances (spectral response, current voltage characteristic, efficiency) with and without presence of Si-nc are compared and the results are discussed.

D/PIII.48

INFLUENCE OF LOW-TEMPERATURE MBE GROWTH AND ARSENIC FLUX ON OPTICAL PROPERTIES OF ANNEALED 1.3- μ m GaInNAs / GaNAs / GaAs QUANTUM WELL STRUCTURE

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The quaternary alloy InGa_xNAs was challenged for realization of laser and solar cell applications in the long wavelength range. In spite of progress in the device fabrication based on InGaAsN with nitrogen in dilute limit, the optical quality of as-grown GaInAsN is significantly poorer than that of InGaAs, partly, due to relatively low temperatures used for InGaAsN fabrication. The annealing step is unconditional for obtaining high-quality devices.

In this work we studied the influence of the growth temperature and arsenic flux on the emission properties of InGa_xNAs single quantum well structure (SQW) subjected to post-growth annealing. The strain-compensated GaInNAs / GaNAs / GaAs quantum wells (QW) were grown by solid source molecular beam epitaxy at temperatures from 410 to 470 °C. The set of samples was grown under different arsenic flux at 450 °C. The samples were characterized by HRXRD and room temperature photoluminescence spectroscopy. It has been found that an improvement of the optical quality and alloy stability under annealing can be governed with the optimal growth conditions. The optical quality of the samples grown at lower temperature degraded as annealing temperature increases from 650 °C to 700 °C, whereas photoluminescence samples grown at 450 °C and 470 °C systematically improved. The enhancement of the emission intensity and peak wavelength blue shift (BS) upon annealing appeared to be suppressed by lowering in arsenic flux. Our results confirm that improvement of the optical quality occurs most likely due to homogenization of the alloy at atomic scale, which may occur via group III diffusion process in the GaInNAs QW and in the GaInNAs / GaNAs barrier.

D/PIII.49

DIRECT ENTROPY PRODUCTION CALCULATIONS AND CHEMICAL POTENTIAL CONSIDERATIONS IN ILLUMINATED III-V PHOTOVOLTAIC MULTI-QUANTUM WELL NANO-STRUCTURES

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Multiple quantum wells in the intrinsic regions of p-i-n photovoltaic devices, under illumination, offer remarkable probes for the study of carrier confinement and subsequent escape and transport. An incident flux of (solar) photons is expected to cause an entropy production and a chemical potential shift in relation with the layer interfaces. On these grounds, we propose a direct method of calculating thermodynamic properties of photovoltaic nanostructures, via the partition function method. The latter is a well established way by which eventually all thermodynamic parameters of an electron system can be derived, and especially the entropy function of the nanostructure under both dark and illumination conditions. For any quantum well in a nanostructure, we proceed as follows: (a) emphasize the difference between illuminated and "dark" partition functions by including the effect of the incident photon flux in the initial Z-function (b) derive the entropy change ΔS of the confined electron gas in the quantum well, due to illumination and dark conditions, and finally (c) determine chemical potential shift relative to adjacent layers in the nanostructure, under both dark and illumination.

D/PIII.50

MULTI-QUANTUM-WELL PHOTODIODE WITH LATERAL P-N-JUNCTIONS

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The purpose of this paper is to theoretically investigate the quantum efficiency of novel lateral photodiode consisting of vertically stacked multiple wells (QWs) formed by narrow gap layers sandwiched between relatively thick wide-gap undoped barrier layers. A half of each QW is doped by donors while another one is doped by acceptors so that several parallel two-dimensional (lateral) p-n-junction are formed. When photons with energy between energy gaps of the QW and barrier layers, are incident perpendicular to the QW planes the uniform photogeneration of electron-hole pairs occurs only in QWs. The main potential advantages of such lateral junctions photodiode are associated with a large breakdown voltage and wider depletion region because of weakness of contact electric field screening by two-dimensional carriers. At large bias voltage the total area between the n+ and p+ contact regions can become depleted serving as a photosensitive active region. A strong lateral electric field given by surface density of ionized impurities acts to sweep out the carriers generated in the depletive regions of QWs before they can recombine so that the photocurrent is equal simply to the number of photons absorbed in QWs. For total absorption of the light and, hence, strong output photocurrent the structure must contain a sufficiently large number of parallel QWs. Such photodiodes will have nearly unity quantum efficiency and can be integrated with other optical and electrical devices.

D/PIII.51

PHOTOIONIZATION OF CORE/SHELL TYPE QUANTUM DOTS

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The process of carrier photoexcitation from bound state to continuum and quasi-discrete states in ordinary spherical quantum dots and quantum dots covered by thin semiconductor layer with wider band gap (core/shell type) has been investigated theoretically. The influence of confining potential of quantum dot on the wave function of ejected electron has been taken into account for correct estimation of photoionization threshold and position of spectral maximum of absorption coefficient. On the other hand the replacement of the wave function of continuum with the pure plane wave function of free particle make the latter non-orthogonal to wave functions of discrete spectrum, which can lead to serious mistakes in calculations of photon cross section.

The presence of thin covering layer leads to the appearance of pronounced quasi-discrete levels in the positive energy range of quantum dot. Due to the finite width of quasi-discrete levels the dipole transition matrix element has remarkable value in narrow range of energy which leads to the same behavior of absorption coefficient. Thus the use of core/shell quantum dots allows to govern effectively the shape and threshold of absorption curve, which can be used for detection of infrared photons.

D/PIII.52**A MONTE CARLO SIMULATION OF EXCESS PHOTOGENERATED AND THERMIONICALLY ESCAPING CARRIERS IN THIN III-V MULTI- QUANTUM WELL PHOTOVOLTAIC NANOSTRUCTURES**

Argyrios Varonides and Andrew Berger, Physics & Electrical Engineering Dept, University of Scranton, Scranton PA 18510, USA

Excess photogenerated carriers trapped in single and multiple quantum well nanostructures of direct bandgap intrinsic semiconductors are carried out in detail. Two main mechanisms of recombination are included in the diffusion equation, which is solved analytically via the Green's function method: the Auger and the Radiative recombination respectively. The general profile of these excess carriers is calculated for a range of thin quantum well widths, and under several levels of incident solar photon fluxes, and at different surface recombination velocities. The solar photons distribution is (assumed to be of a black body radiation) abiding by the Boltzmann-Einstein statistics and the connection between incident radiation and photo-generated carriers is carried out via a Monte Carlo simulation method. It is shown that, by starting from a specific photon flux, the concentration of the net (after recombination losses have been taken out) excess carriers, is at least one order of magnitude greater than the dark carrier population, already in the minibands of the quantum wells.

D/PIII.53**TUNNELING PHOTOCONDUCTIVITY OF MULTI-QUANTUM WELL P-I(NANO)-N PHOTOVOLTAIC NANOSTRUCTURES BY MEANS OF THE CAUSAL GREEN'S FUNCTION**

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The generalized Kubo-Greenwood formula for photo-induced conductivity, due to photo-excited carriers escaping via tunneling from quantum wells in crystalline nanostructures is used for an explicit calculation of the along-the-growth-direction AC-conductivity of mainly (but not restricted to) III-V photovoltaic (PV) nanostructures. The method is based on the causal form of the Green's function and relates the conductivity with the nanostructure parameters, such as repeat distance, energy mini-bands and bandwidths, electronic self-energy, and especially the chemical potential EF (Fermi level). Specifically, at AC conditions, the photoconductivity is expressed explicitly as a function of incident wavelength range or photon energies from 1.4 to 2.6 eV. A nanostructure, consisted of multiple layers of two kinds of lattice-matched materials with two different bandgaps respectively, replaces the intrinsic region of a p/i/n PV device, with potential barriers lightly doped. For a InP-InGaAs multilayer {40 repeat periods, 2.5nm (InP-layer width) -7nm (InGaAs-layer width) 80 degrees Kelvin}, photoconductivity values are predicted at levels vary from 900 S/cm to 3,000 S/cm for photon range from 2.6eV to 1.4eV (InP energy gap 1.35eV) indicating powerful performance for near-earth space applications.

D/PIII.54**SILICON SOLAR CELL WITH QUANTUM WELLS**

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Nowadays, the technology of quantum well solar cell (QWSC) is considered as promising way to enhance the solar cell efficiency. In present work we analyse the influence of parameters of quantum wells on the photovoltaic processes in thin film solar cells. The Schottky- type barrier structure on thin n-Si film has been chosen both for device simulation and cell manufacturing. Such cells are forming by the typical processes of electrochemical silicon etching in HCl:H₂O:C₂H₅OH solution followed by the semitransparent metal film deposition. The layers of nanocrystalline silicon (the porosity is 60%, E_g=1.9 eV) formed at etching current I= 20 mA/cm² are used as bulk material in QWSC. The layers of quasi single crystalline silicon (the porosity is less than 10%, E_g=1.1 eV) formed at small etching currents are used as well material in QWSC. One-dimensional device simulator, SimWindows was used for cell simulations. Current-voltage characteristics were calculated as function of cell thickness, well geometry, doping concentration, and number of wells. The location of the single QW within the device is simulated too. QWSC with Schottky barrier (barrier height 0.7 eV, N_d= 1E15 1/cm³, cell thickness 5E-7 m) shows that the introduction of 10 QWs results in the increase of the circuit current I_{sc} from 4.4 mA/cm² to 6.2 mA/cm². I_{sc} depends also on the well localisation in depletion region and well width. The maximal value of I_{sc} is observed at different number of quantum wells in dependence of cell thickness and well geometry. The method and setup for QWSC forming by electrochemical etching of Si is presented.

D/PIII.55**THIN FILM SOLAR CELLS WITH INTEGRATED LIGHT COUPLER GRATING**

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Amorphous (a-Si:H) and microcrystalline (μc-Si:H) silicon thin film p-i-n diodes require effective light trapping schemes to achieve efficient absorption. Hence, textured transparent conductive oxides (TCO) with a randomly distributed surface morphology are widely employed. As an alternative approach periodic light coupler gratings of ZnO were prepared by different photolithography, etching and lift-off processes and used as substrates for solar cells. The periods and the groove depths were adjusted independently from each other and vary between 1 to 4 μm and 100 to 600 nm, respectively. The thickness of the i-layer was chosen to 450 nm for the a-Si:H and to 1 μm for the μc-Si:H p-i-n diode.

The effect of the grating on light scattering and the optoelectronic properties of solar cells with integrated gratings was investigated. The measured diffraction angles of the rectangular grating show a wavelength dependence in accordance to the grating formula. The angular distribution of the scattered light depends strongly on the grating period and groove depth. However, for the realized solar cells with a-Si:H or μc-Si:H i-layer the short circuit current, I_{sc}, shows no significant influence of the grating period whereas I_{sc} increases with elevating groove depths. In comparison with cells on smooth substrates, the spectral response in the long wavelength region is enhanced. However, I_{sc} is smaller compared to diodes deposited on substrates with a randomly distributed texture. Based on a detailed study of the grating parameters we will evaluate the applicability of periodic light coupler structures in solar cells.

D/PIII.56**EMISSION PROCESSES OF OPTICALLY INDUCED CHARGES IN STACKED Ge/Si QUANTUM DOTS**

C.J. Park(a), D.Y. Kim(a), T.W. Kang(a), H.Y. Cho(a), Y.H. Lee(b), J. Liu(c), S. Tong(c), K.L. WANG(c), (a)Quantum-functional Semiconductor Research Center, Dongguk University, Seoul 100-715, Korea, (b)Department of Information and Communication, Dongguk University, Kyungju 780-714, Korea, (c)Electrical Engineering Department, University of California at Los Angeles, Los Angeles CA 90024, USA

Hole emission processes of optically induced charges have been investigated on 10 stacked Si/Ge quantum dots (QDs) using optically assisted capacitance-voltage (CV) and deep level transient spectroscopy (DLTS) measurements. 10 period Ge QDs on the n-type Si buffer layer (300 nm) were grown through the self-assembled method by using molecular beam epitaxy (MBE), and the PIN structure with QDs for IR detectors was fabricated with the p-Si layer (100 nm). The QDs shape and size were identified using transmission electron micrograph (TEM) and secondary ion mass spectroscopy (SIMS), and the height and width are 7 nm and 80 nm, respectively. A peak of photoluminescence, which is responsible for the confined state of Ge QDs, was observed at 0.85 eV. From the 77K-CV measurement under an optical illumination, it is found that QDs in the fully depleted intrinsic layer can have the charges optically induced through an e-h generation and then the confined hole densities are about $1 \times 10^{18} \text{ cm}^{-3}$ at 77K. From the optical DLTS measurement for QDs, the peaks related to the valence band offset can be classified distinctly, and especially the peak for the band offset is about 10 ~ 100 times higher than that for the defect in intensity. The signal related with the ground state in the valence band offset appears near 95 K, and the activation energy is calculated to be $E_v + 128 \text{ meV}$. As the bias voltage increases, the peak related to the excited state shifts to low temperatures, and the shift is thought to be due to the effect of the hole emission by a tunneling. Especially, the optical efficiency of the Ge QD detector will be discussed in view of the confined QD state and the density of state, which are obtained from the above results.

D/PIII.57**POLARISED RAMAN SPECTROSCOPY OF MULTILAYERED Ge/Si(001) QUANTUM DOT HETEROSTRUCTURES**

A.V. Baranov, T.S. Perova, S. Solosin and R.A. Moore, University of Dublin, Trinity College, Dublin 2, Ireland and V. Yam, Vinh Le Thanh and D. Bouchier, Institut d'Électronique Fondamentale, Bât. 220, Université Paris XI, 91405 Orsay, France

In recent years, considerable attention has been paid to self-organised Ge quantum dots both for fundamental physics studies and potential application. Polarised Raman spectroscopy in backscattering geometry has been applied here for investigation of Ge/Si(001) quantum dot multilayers (ranging from 1 to 20) grown by Stranski-Krastanow technique. The characteristic Raman spectra of Ge dots has been obtained by cross-referencing the Raman spectra of a sample with dots and a Si reference substrate, both registered with the same polarisation in the scattering channel. We found that Raman spectra of Ge dots obtained in such a manner are strongly polarised, in particular for Si-Ge (at $\sim 413 \text{ cm}^{-1}$) and Ge-Ge (at $\sim 295 \text{ cm}^{-1}$) vibrational modes. This behaviour deviates substantially from the behaviour of polarised Raman spectra of Si_{1-x}Ge_x alloys with different Ge contents, where these lines are depolarized. The dependence of peak intensity and peak position for Si-Ge and Ge-Ge modes have been studied on a number of layers with Ge dots. These dependencies, as well as some other investigations on different samples with Ge dots, lead us to conclude that the Raman lines under discussion are a feature of the dots and not of the wetting layer, and can be used for quantum dot characterization. The strong polarization of the Si-Ge Raman lines indicates an alignment of the Si-Ge bonds, most likely on the surface of the Ge dots.

D/PIII.58**COMPUTER SIMULATION OF THE PHOTOCURRENT COLLECTION COEFFICIENT IN SOLAR CELLS BASED ON THE TEXTURED THIN-FILM Al_xGa_{1-x}As-GaAs HETEROSTRUCTURE**

O.Yu. Borkovskaya, N.L. Dmitruk, V.G. Lyapin, A.V. Sachenko, Institute of Semiconductor Physics of the National Academy of Sciences of Ukraine, 45 prospect Nauki, 03028 Kiev, Ukraine

Using the geometrical optics approximation, we determined optical losses due to light reflection for two cases (angles of 90 and 60°) of V-like grooves at the illuminated surface. It is shown that surface texturing generally leads to growth of photocurrent losses resulting from increase of charge carrier recombination in a thin Al_xGa_{1-x}As layer. At the same time the photocurrent losses resulting from recombination in the GaAs bulk decrease. The possibilities for minimisation of photocurrent losses in the Al_xGa_{1-x}As layers are analysed. We took into account a contact grid-related heterogeneity (as regards the value of the effective surface recombination velocity) of the front surface of solar cells based on the heterostructure discussed. It is shown that peak of the photocurrent collection coefficient can be achieved, by varying the Al_xGa_{1-x}As layer thickness, as a result of compromise between decrease of the effective surface recombination velocity (as this thickness increases) and increase of the photocurrent losses due to recombination in the above layer. An analysis is made of the effect of texturing features on the photocurrent losses.

D/PIII.59**ELEMENTARY BANDS IN THE COMPLEX "RED" PHOTOLUMINESCENCE SPECTRUM OF THIN POROUS SILICON LAYER**

Z. Swiatek, E. Bielanska, R. Ciach, W. Maziarz, W. Baliga, Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 30-059 Krakow, 25 Reymonta Str., Poland, F. Krok, Regional Laboratory for Physicochemical Analyses and Structural Research, Jagiellonian University, 30-060 Krakow, 3 Ingardena Str., Poland, I.M. Fodchuk, Chernivtsi State University, 274012 Chernivtsi, 2 Kotsyubynsky Str., Ukraine

The photoluminescence mechanism in thin porous silicon (PS) layer formed on the n+-type, (111)- oriented Si wafer have been studied. This complex and broad ($\sim 550 - 750 \text{ nm}$) photoluminescence spectrum is composed from four elementary bands. The morphology and microstructure of PS layer were investigated using transmission electron microscopy and non-contact atomic force microscopy (AFM) measurements.

On the basis of the results obtained, the mechanisms of the four elementary bands in photoluminescence spectra are discussed.

D/III.60**THIN SILICON FILMS DEPOSITED AT LOW SUBSTRATE TEMPERATURES STUDIED BY SURFACE PHOTOVOLTAAGE TECHNIQUE**

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Investigation of microcrystalline silicon ($\mu\text{-Si:H}$) thin films for solar cells deposited at low substrate temperatures is motivated by further reduction of the energy budget and a possibility to use practical polymer substrates. We have applied the surface photovoltage (SPV) technique in expanded spectral region to study transport properties of $\mu\text{-Si:H}$ thin films deposited at substrate temperatures between 35 and 200°C. The application of the SPV technique revealed new phenomena of low-temperature $\mu\text{-Si:H}$ growth (e.g. formation of bottom barrier for deposition temperatures below 100°C, presence of defective layer for deposition temperatures 75-200°C) without performing any additional measurements. Good separation of top and bottom space charge region was detected even for the sample thicknesses less than 0.5 μm . While increasing the deposition temperature, the transition from the amorphous to microcrystalline growth was crossed. However, it seems not to be sharp - the experimental data indicate at least three different growth regimes.

15:30

BREAK**Session VIII: Si based TFSC & Advanced solar cell concepts**

Session chair: J. Nelson, J. Poortmans

D-VIII.1 16:00 -Invited-**PRESENT STATUS OF INTERMEDIATE BAND SOLAR CELL RESEARCH**

A. Luque, **L. Cuadra**, A. Martí, C. Tablero, P. Wahnón, N. López, P. Palacios and J. Fernández, Instituto de Energía Solar-UPM, ETSIT de Madrid, Ciudad Universitaria sn, 28040 Madrid, Spain

The Intermediate Band Solar Cell (IBSC) is a novel device that, thanks to the existence of an intermediate band located within what in conventional semiconductors constitutes its bandgap, is capable of absorbing not only high energy photons that cause transitions from the valence band to the conduction band but also sub-bandgap photons. Furthermore, due to carrier concentration in each band is described by its own quasi-Fermi level, this device is able to deliver a photocurrent higher than that of a conventional single-gap solar cell without degrading its open-circuit voltage.

This paper reviews, first, the basic operation of the IBSC and continues describing our own research about the topic. This includes, for example, the engineering of the IBSC by means of quantum dots, and the research on material science aimed to the direct synthesis of a suitable intermediate band material. Research carried out world-wide about the intermediate band concept is also briefly reviewed.

D-VIII.2 16:30**TRANSPORT LOSSES DUE TO QUANTUM WELL-SCATTERING OF THERMIONICALLY ESCAPING PHOTO-EXCITED CARRIERS IN III-V MULTIQUANTUM WELL PHOTOVOLTAIC NANOSTRUCTURES**

Argyrios Varonides, Physics & Electrical Engineering Dept, University of Scranton, Scranton PA 18510, USA

In this communication, interest is focused in the transport of photogenerated carriers that have already escaped from quantum wells, by thermionic emission. In such a case, thermally escaping excess electron concentrations (out of a quantum well), once in the energy continuum above the edge of the quantum well, are expected to diffuse towards and be collected at the n-region of the p-i-n device. During this process, trapping and reflection due to nearest-neighboring quantum wells are highly probable, thus leading to overall reduction of final current density values. In this study, a quantum mechanical method of counting for losses due to trapping and reflection is proposed, namely, (a) current density values of thermionically escaping net (after recombination losses) photogenerated electrons are evaluated and (b) reduction of current density values due to quantum well scattering is included. This is done in two steps: first, the net excess photogenerated carrier concentration and its corresponding current density are derived, by directly solving the diffusion equation, secondly, accounting for quantum size effects, carrier scattering (trapping and reflection) is included, thus leading to overall reduction of current density values. Initial computations show that thermionic carrier current density values drop by 30 to 40% due to scattering, namely, for a 6nm width (GaAs-AlGaAs) undoped quantum well at room temperature, current densities are expected to drop from 0.4 mA/cm² down to a range of 0.24 mA/cm² to 0.28 mA/cm².

- D-VIII.3** 16:45 FABRICATION OF SOLAR CELL WITH STACKED GE ISLANDS FOR ENHANCED ABSORPTION IN THE INFRARED REGIME
N. Usami, A. Alguno, K. Fujiwara, T. Ujihara, G. Sazaki, K. Nakajima and Y. Shiraki, Institute for Materials Research (IMR), Tohoku University, Sendai, Japan, and *Dept. of Appl. Phys., The University, Tokyo, Japan
 We report on the performance of Si-based solar cell with stacked Ge islands, which shows improved quantum efficiency in the infrared regime. The stacked Ge islands with 10 to 100 repetitions were epitaxially grown using the Stranski-Krastanov growth mode on p-type Si(100). Then, pn junction was formed through thermal diffusion of P atoms for characterizations of solar cell performance. The quantum efficiency in the infrared regime, 1.2 to 1.4 microns, was found to be improved with increasing number of the stacking. This demonstrates that photocarriers absorbed in the Ge islands contributed to the increase of the current. However, no response was observed with illumination of further longer wavelength. Possible reasons are the deformation of the Ge islands during formation of pn junction and/or recombinations of carriers in Ge. The former was indicated by photoluminescence measurements, in which the photoluminescence from the Ge islands was quenched after annealing the sample. By lowering the processing temperature, more improvement of the solar cell performance is expected.
- D-VIII.4** 17:00 OPTICAL ABSORPTION OF THIN FILMS CONTAINING SPHERICAL PARTICLES FOR INTERNAL LIGHT SCATTERING
Heiko See and Rolf Brendel, Bavarian Center for Applied Energy Research, ZAE Bayern, Am Weichselgarten 7, 91058 Erlangen, Germany
 A thin film containing light scattering particles shows an enhanced optical absorption. Here we consider light scattering spheres of arbitrary size distribution and random position in the film. We present an analytical model that coherently calculates the optical absorption spectrum. The main constituents of the model are coherent light propagation of non-scattered light in the thin film, Mie scattering at the spherical particles, and Lambertian light trapping of the scattered light. For an experimental verification of this model we fabricate 1 to 4 μm thick films of sintered porous Si. These monocrystalline Si films contain almost spherical voids that are 10 to 130 nm in diameter. We evaluate the void size distribution by scanning electron microscopy and then apply our optical model. The model does not contain any free parameters for fitting the experimental results. Simulated and experimental absorption spectra agree to better than 10% in the spectral range from 250 to 1500 nm. Our model may also be applied to other film systems such as low temperature-deposited Si films or organic solar cells containing small light scattering spheres of arbitrary material.
- D-VIII.5** 17:15 -Invited- SEMICONDUCTING BLOCK COPOLYMERS FOR SELF-ASSEMBLED PHOTOVOLTAIC DEVICES
Georges Hadziioannou, Ecole de Chimie et des Polymères, Strasbourg, France
- D-VIII.6** 17:45 -Invited- HYBRID SOLAR CELLS BASED ON INORGANIC NANOCLUSTERS AND SEMICONDUCTIVE POLYMERS
Elif Arici (a), Dieter Meissner(b), N. Serdar Sariciftci(a), (a)Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University, Altenberger Str. 69, 4040 Linz, Austria, (b)Fachhochschule Wels, Roseggerstr. 12, 4600 Wels, Austria
 We investigated blends of semiconducting polymers with copper indium diselenide (copper indium disulfide) nanocrystals, for photovoltaic applications [1,2,3]. Depending on the synthesis, the particles are shielded by different organic surfactants. Different concentrations of these nanoparticles were suspended in the polymer solutions and spin cast onto ITO glass covered with PEDOT as a transparent conductive front contact. Solar cells were then produced by evaporation of different metallic back contacts. Optical, electrical and morphological investigations of this new prototype of composite solar cells will be presented.
 [1] E. Arici, H. Hoppe, A. Reuning, N. S. Sariciftci, D. Meissner, 17th European Photovoltaic Solar Energy Conference, Proceedings of the International Conference held in Munich, Germany 2001.
 [2] E. Arici, N. S. Sariciftci, D. Meissner, Molecular Crystals Liquid Crystals vol. 383 pp. 129-136, 2002
 [3] E. Arici, N. S. Sariciftci, D. Meissner „ CIS-Polymer Composite Solar Cells “ (in print Adv. Func. Mat.)

DIFFRACTION GRATINGS AND BURRIED NANO ELECTRODES - ARCHITECTURES FOR ORGANIC SOLAR CELLS

Michael Niggemann, Markus Glatthaar, Andreas Gombert, Andreas Hinsch and Volker Wittwer, Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstr.2, 79110 Freiburg, Germany

One promising concept for an organic solar cell is the bulk heterojunction of a donor-type conjugated polymer and acceptor molecules (PCBM, a C60-derivative). A widely used cell architecture is planar with a photoactive layer spin coated on a hole selective PEDOT/ITO electrode and an evaporated aluminium counter-electrode. The reported efficiency under AM 1.5 illumination is 3%. A small film thickness due to weak charge carrier mobility and a small bandwidth of the absorptance spectrum cause an incomplete absorption of the incident light. The presented work focuses on the extension from the one dimensional planar device architecture to a two dimensional structure. Microlithography based on holographic exposure techniques allow the generation of periodic micro- and nano-structures down to dimensions of 200nm on large areas. Two approaches of implementing microstructures into cell architectures are pursued. Light trapping with surface relief gratings is one method to increase the absorptance in a distinct range of the solar spectrum. The potential of this approach is evaluated by calculations of the optical near field inside the device. The second approach is based on vertical micro electrodes. The planar, semi-transparent electrode is substituted by comb-like electrode array embedded in the photoactive polymer blend. The potential of this approach is discussed and initial experimental results are presented.

Friday, June 13, 2003
Vendredi 13 juin 2003

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Session IX: Hybrid solar cells

Session chair: D. Vanderzande and C.J. Brabec

- D-IX.1** 8:30 -Invited- HYBRID-NANOROD POLYMER SOLAR CELLS
A. Paul Alivisatos, University of California, Berkeley, Depart. of Chemistry and Lawrence Berkeley National Laboratory, Materials Sciences Division, USA
This talk will describe our recent work related to the fabrication of solar cells, based upon blends of inorganic semiconductor nanorods with semiconductor polymers, such as P3HT. Such blends offer the possibility of paint-on type cells that combine high electron and hole mobilities, but require the development of methods to reliably control the dispersion of the two materials on the nanometer scale. Several approaches will be described, including the incorporation of so-called tetrapods, branched four armed inorganic nanocrystals that spontaneously align on a substrate.
- D-IX.2** 9:00 NANOPOROUS TiO₂ SOLAR CELLS SENSITISED WITH A FLUORENE-THIOPHENE COPOLYMER
Punniamoorthy Ravirajan(a,c), Saif A. Haque(b), Dmitry Poplavskyy(a), Emilio Palomares(b), James R. Durrant(b), Donal D.C. Bradley(a) and Jenny Nelson(a), Centre for Electronic Materials and Devices, Departments of (a)Physics and (b)Chemistry, Imperial College, London SW7 2BZ, U.K; (c)Department of Physics, University of Jaffna, Sri Lanka
Composites of nanostructured metal oxides with conjugated polymer are promising material combinations for efficient solar energy conversion. However, performance of such combinations is normally limited by the low interfacial area of planar structures and poor mobility of the polymer. In this study we focus on TiO₂ with a high hole-mobility polymer, poly(9,9'-dioctylfluorene-co-bithiophene) (F8T2). Transient optical spectroscopy confirms that efficient photoinduced electron transfer occurs from F8T2 to TiO₂ in both planar TiO₂/F8T2 structures and in high surface area, porous TiO₂ / F8T2 structures. Recombination between the positive polaron in the polymer and electron in the TiO₂ is remarkably slow (~ms) in both cases. The influence of layer thickness and surface morphology on cell performance of ITO / TiO₂ / porous TiO₂ / F8T2 / Au devices was examined. The best cell was made with reduced layer thickness and increased surface morphology and offered a quantum efficiency of 11.5 % and monochromatic power efficiency of 1 % at 440 nm. This cell produced an open circuit voltage VOC of 0.80 V and a short circuit current density about 300 microAcm⁻² under simulated AM 1.5 illuminations. However, the power conversion efficiency is limited by poor fill factor, which is tentatively attributed to an energy barrier at the polymer/metal interface. We investigate this using alternative polymer and top contact metals, and independent measurements of the built-in potential.
- D-IX.3** 9:15 ALIGNMENT OF ENERGY STATES AT SEMICONDUCTOR/DYE HETEROINTERFACES
U. Weiler, F. Säuberlich, G. Liu, T. Mayer, A. Klein, W. Jaegermann, Institute of Materials Science, Darmstadt University of Technology, Petersenstr. 23, 64287 Darmstadt, Germany
For organic solar cells using dyes or organic semiconductors as absorber layers the alignment of its energy states to the valence and conduction band states of the contact phases is of similar importance as for inorganic devices. So far there are only limited numbers of studies to study the electronic structure of inorganic/organic interfaces used in photovoltaics. We present first investigations of dye/inorganic semiconductor interfaces using photoelectron spectroscopy as characterisation technique. As dyes phthalocyanin and polypyridine dyes with different metal cores have been used. As substrates TiO₂ and ZnO thin films, H terminated Si and layered chalcogenides have been used. The results show that detailed information on interface interactions as well as on the electronic structure can be obtained. An interesting but so far not understood effect is a change in band alignment depending on the chemical interaction at the phase boundary. Evidently the electronic alignment at the phase boundary depends on changes of the electronic double layers at the phase boundary.
- D-IX.4** 9:30 IMPROVED ITO THIN FILMS ON POLYMERS FOR PHOTOVOLTAIC APPLICATIONS WITH A THIN ZnO:Al LAYER BY SPUTTERING
J. Herrero and C. Guillén, Departamento de Energías Renovables, C.I.E.M.A.T., Av. Complutense 22, 28040 Madrid, Spain
Indium-tin-oxide (ITO) films have shown high transparency, near 80% on the 400-1100nm spectra range, and conductivity, $\sigma > 10^3$ (W-cm)⁻¹, on polymer substrates, that make them useful as photovoltaic solar cells. A rf-magnetron sputtering system was used for the deposition of ITO films on polymer substrates, polyethylene (PET) and polyimide (Kapton KJÓ) and onto glass as reference, at room temperature. We also try to improve the quality of ITO films by applying a ZnO:Al buffer before the ITO deposition in the same run of sputtering. Very good texture ITO films can be grown on glass with ZnO buffer because of the small lattice mismatch (3%) between the neighboring oxygen-oxygen (O-O) distance on the closest-packed (111) plane of ITO and (001) plane of ZnO. We present a study on the electrical, optical and morphological properties of ITO and ITO on ZnO:Al buffered films on polymer substrates by rf sputtering using oxygen-argon mixtures at room temperature and we also compare them with those deposited on glass. Owing to the importance of the polymer thermal stability during the TCOs growth effect of the deposition at room temperature without heating during sputtering and different process temperature even post-deposition annealing will be discussed and presented during the conference.

D-IX.5 9:45

BULK HETEROJUNCTIONS BASED ON POLYMER BLENDS AND HYBRID POLYMER/INORGANIC SEMICONDUCTORS

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In polymer based bi-layer photovoltaic cells, the short exciton diffusion length of the conjugated polymer limits the efficiency, as only the first 5-20 nm at the interface is active in these devices. Bulk heterojunctions (BHJ) that have a phase separation between the donor and acceptor phase with dimensions in the order of the exciton diffusion length can improve the cells. We will discuss two different approaches towards BHJ. In the first concept, a polymer/polymer BHJ is formed by spin coating a solution of a blend of electron donating and electron accepting polymers. During the spin coat process, an interpenetrating polymer network is formed. The device characteristics strongly depend on the morphology of the thin polymer film. It will be shown that devices can be improved substantially with thermal annealing after the device fabrication. The second concept uses a new, simple procedure for preparing BHJ hybrid organic-inorganic solar cells, in which a continuous interpenetrating network of TiO₂ is created inside a thin conjugated polymer film. The BHJ cells were spin coated from a mixture of titanium(IV) isopropoxide and polymer. Photoluminescence quenching and photoinduced absorption measurements will be shown as well as device characteristics for several polymer:TiO₂ ratios.

10:00

BREAK

Session X: Si based TFSC & Hybrid solar cell concepts

Session chair: A. Luque and A. Slaoui

D-X.1 10:30 -Invited-

ELECTRODEPOSITION OF ZINC OXIDE / DYE HYBRID THIN FILMS AND THEIR APPLICATION TO DYE-SENSITIZED SOLAR CELLS

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Cathodic electrodeposition from dye-added aqueous solution of zinc salt results in a self-assembly of sponge-like crystalline zinc oxide (ZnO) thin films colored with dyes. The deposited ZnO/dye hybrid thin films perform as highly efficient dye-sensitized photoelectrodes which achieve an incident photon to current conversion efficiency of 90%, thanks to the high crystallinity and nano-porous structure of the material, which are usually difficult to be achieved at the same time. Since the process does not require any heat treatment at high temperatures, the materials can be processed directly onto a conductive plastic substrate for the realization of a flexible dye-sensitized solar cell. The photoelectrode material can also be furnished in various colors by choosing the dye to load, thus setting a new goal in solar cell research to develop fashionable film-type solar cells in all color variations, "rainbow cells".

D-X.2 11:00

NANOSTRUCTURED TiO₂-CuInS₂ BASED SOLAR CELLS

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In last decade the photovoltaic properties of nanocomposite thin films have been stimulating the interest of many. Dye-sensitized solar cells and polymer /C60 cells are indeed very promising concepts for cheap and efficient energy conversion. Here we introduce a completely new all solid-state solar cell based on a 3-dimensional architecture. Light is absorbed by CuInS₂, which is applied inside the pores of nanoporous TiO₂ (2 micron thick), which comprises of 10 to 50 nm particles. To grow CuInS₂ inside a nanoporous matrix, Atomic Layer Deposition (ALD) is used. In this gas-phase deposition technique the reactants are supplied sequentially, which avoids clogging of pores. Growth takes place at a reactor pressure of 2 mbar and a temperature of 4000 C. CuCl, InCl₃, H₂S as used as precursors. The quality of the films can be improved by the post deposition treatments. Annealing in sulphur atmosphere at 5000 C and 1 bar improves the stoichiometry and the defect concentration. We also apply buffer layers of CdS or Al₂O₃, the latter being a tunnel barrier. The photovoltaic properties of this all solid-state 3D solar cell are quite good. Already an energy conversion efficiency of 2% has been reached. Further optimisation will bring a significantly better performance within reach.

- D-X.3** 11:15 **SUBSTANTIAL EFFICIENCY IMPROVEMENT OF CIS-BASED ETA SOLAR CELLS BY THE USE OF AL₂O₃ TUNNEL BARRIER COATINGS**
F. Lenzmann(a), M. Nanu(b), O. Kijatkina(c), A. Belaidi(d), (a)Solar Energy Department, ECN, Westerduinweg 3, 1755 ZG Petten, The Netherlands, (b)Laboratory for Inorg. Chemistry, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands, (c)Tallinn Technical University, Materjalitehnika Instituut, Ehitajate tee 5, 19086 Tallinn, Estonia, (d)Hahn-Meitner Institut, Abt. Heterogene Materialsysteme (SE2), 14109 Berlin, Germany
 The recent success of ultrathin insulator oxide coatings on mesoporous TiO₂ films (such as Al₂O₃ and MgO) with regard to the efficiency of solid state dye-sensitized solar cells [1] has received substantial attention [2,3].
 While the physical origin for the beneficial effect of these coatings (referred to as tunnel barrier coatings in this text) is still under discussion, it is certainly accompanied by a decrease of the interface recombination rate [2]. These findings inspired us to investigate the effect of tunnel barrier coatings in the ETA solar cell concept. This recently introduced concept is based on Extremely Thin inorganic Absorber layers (such as CuInS₂) at the interface of a transparent nano- or microstructured p-n heterojunction (such as n-TiO₂/p-CuSCN) [4]. Interface recombination appears to be a particularly dominant problem in this type of solar cells and the idea to quench it by means of a tunnel barrier coating therefore appeared to be very appealing. In this contribution we report on the substantial enhancement of the photocurrent density of the TiO₂/CIS interface using an Al₂O₃ tunnel barrier (TiO₂/Al₂O₃/CIS) by a factor of up to 50. These findings lead for the first time to the practical realization of an ETA solar cell with a current density well above 5 mA/cm², which can be considered a first major breakthrough for this type of solar cells.
 [1] K. Tennakone et al., Physica E 14 (2002), 190-196
 [2] E. Palomares et al., Chemical Communications, 14 (2002): 1464-1465
 [3] A. Kay et al., Chemistry of Materials, 14/7 (2002): 2930-2935
 [4] I. Kaiser et al., Solar Energy Materials and Solar Cells 67(2001) 89
- D-X.4** 11:30 **HOMO-EPITAXIAL Si ABSORBER LAYERS GROWN BY LOW-TEMPERATURE ECRCVD**
B. Rau, B. Selle, I. Sieber, S. Brehme, U. Knipper, S. Gall and W. Fuhs, Hahn-Meitner-Institut Berlin, Silizium Photovoltaik, Kekuléstr. 5, 12489 Berlin, Germany
 We report on a study of homo-epitaxial growth of Si absorber layers at low temperatures by electron-cyclotron resonance chemical vapor deposition (ECRCVD). We grew epitaxial Si films at temperatures from 420 °C to 560 °C on (100)-, (111)-, and multicrystalline Si-wafers to optimize the growth conditions for large-grained polycrystalline Si thin film solar cells on glass. Both substrate temperature and orientation have a pronounced influence on the structural quality. Above 510 °C good epitaxial growth was observed on Si(100) substrates with growth rates of 15 to 18 nm/min. With increasing film thickness the crystal quality of the films worsens only very slightly up to 2 µm. We observed an increase of local high defective regions with increasing thickness but no classical breakdown of the epitaxy connected with the formation of amorphous Si. Below 480 °C the disorder in the films increases significantly with decreasing temperature starting right at the interface. On Si(111)-wafers films grew always microcrystalline. Using multicrystalline substrates the quality of the films is related to the orientation of the particular grain. We observed different degrees of disorder from excellent epitaxy to pure microcrystalline growth. Furthermore we discuss the electrical properties of these intentionally undoped films in view of a solar cell application. The results show, that (100)-oriented seed layers are advantageously for the fabrication of polycrystalline Si thin film solar cells on glass following the seed layer concept.
- D-X.5** 11:45 **CHARACTERIZATION OF FREE-STANDING THIN CRYSTALLINE FILMS ON POROUS SILICON FOR SOLAR CELLS**
C.S. Solanki(a), R.R. Bilyalov(a), J. Poortmans(a), J. Nijss(a,b) and R. Mertens(a,b), (a)IMEC vzw, Kapeldreef 75, 3001 Leuven, Belgium, (b)Katholieke Universiteit Leuven, Electrotechnical Department, 3000 Leuven, Belgium
 A promising cost-effective way of converting sun light into electricity could be a solar cell realized in a thin monocrystalline silicon film, due to its potential to achieve cell efficiencies of more than 20% in a 20 µm thick film. Layer transfer techniques based on porous silicon (PS) is being developed to get a high quality thin silicon film on a foreign substrate. The PS serves two purposes. Firstly, it allows separation of the epitaxial layer from the starting substrate and transfer to a foreign substrate. In this way the starting silicon wafer can be used again, aiming for cost-reduction. Secondly, it allows the growth of a high quality epitaxial layer on it if sintered in H₂ at temperature above 1050°C. Deposited epitaxial layer is used as an active layer for device fabrication. Based on this concept we have developed a process known as FMS (Freestanding Monocrystalline Silicon) for thin film solar cell fabrication and achieved a solar cell efficiency of more than 10% in a 20 µm thick film. This work presents the characterization of the film at different steps of FMS process. Characterization has been carried out using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Ellipsometric Porosimetry (EP), X-ray Diffraction (XRD), Raman Spectroscopy (RS) and Atomic Force Microscopy (AFM). TEM, XRD and RS reveals the high monocrystalline quality of silicon epitaxial film deposited on PS, suitable for high efficiency thin film silicon solar cells.

D-X.6 12:00

THE INFLUENCE OF HYDROGEN DILUTION, SUBSTRATE TEMPERATURE AND FILM THICKNESS ON THE PROPERTIES OF NANOCRYSTALLINE SILICON THIN FILMS GROWN BY HOT-WIRE CVD

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Nano and microcrystalline silicon films have recently been receiving special attention due to their lower production cost than crystalline silicon, and the fact that they do not exhibit the degradation problems of amorphous silicon. Furthermore, because of their bandgap, they can be used in tandem cells with a-Si. Among the deposition methods, hot-wire CVD has the advantage of higher deposition rates when compared to other deposition techniques, such as plasma-enhanced CVD.

In this work, we deposit these films at different temperatures (200° - 400°C) and dilution ratios between hydrogen and silane (10-100), and study the relationship between these two parameters, and their influence on the properties of the films. We also study the effects on the film morphology and crystallinity of using a very thin seed layer deposited with high concentration of hydrogen. Further, the effects of the substrate (glass versus Si) and film thickness are investigated. The films are characterized using several techniques, such as: atomic force microscopy, grazing-angle incidence X-ray diffraction, and high-resolution transmission electron microscopy. We will correlate the growth conditions with film properties such as crystallinity, surface morphology, the ratio between crystalline and amorphous phases, and the evolution of the microstructure from the substrate/film interface to the film surface.

D-X.7 12:15

REVIEW ON EUROPEAN TECHNOLOGIES TO REALIZE THIN SILICON SOLAR CELLS

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For a long while, wafer and thin-film technologies have evolved as competing options for photovoltaic application for which the solutions to the technical problems could have come out from only one of these two research lines. Further possibilities have arisen at today by new hybrid technological approach applied to processing of thin wafers obtained by techniques like edge-defined film-fed growth (EFG), string ribbon silicon, Silicon Film™, dendritic web growth or, alternatively, by high deposition rate of silicon on insulator or metallic substrates obtained by HW, VHF or RF-PE CVD. The thermal degradation of the substrate and/or of the minority-carrier lifetimes associated with high-temperature processes typical of conventional wafer technology, requiring innovative technological solutions and new architectures. These requirements are added to other factors such as the search for automatic module-assembly approach by using environmentally friendly ones, the need to lower costs by simplifying technology and spending less energy have led to the development of a relative and environmentally friendly new PV sub-field bonded to low-temperature processes (<250°C) not only cost-effective by itself, but to also allow the use of low-cost substrates sensitive to temperature damage. A review of state of art on European RTD activity applied to thinner silicon for photovoltaic applications is depicted. Particular emphasis is reserved to silicon-heterojunction cells. Remarkable work was done by ENEA-Rome University to produce solar cells with 17.1% 2cm² net area on p-type CZ cSi for photovoltaic applications, one of the best worldwide results until now reached on p-type base.