

## Energy Frontiers Topical Conference

Room: Pecos - Session EN+TF-TuA

### Thin Films for Photovoltaics

Moderator: L.W. Rieth, University of Utah

2:00pm **EN+TF-TuA1 Ar/H<sub>2</sub> Plasma Treatment of a-Si:H Thin Films: On the Role of Atomic Hydrogen in  $\mu$ -Si:H Thin-Film Deposition.** A.C. Bronneberg, A.M. Creatore, M.C.M. van de Sanden, Eindhoven University of Technology, the Netherlands

The transition from amorphous (a-Si:H) to microcrystalline ( $\mu$ -Si:H) silicon film growth has been ascribed to the interaction of atomic hydrogen with the (sub)surface of the growing film [1]. To gain more insight into the formation of microcrystalline silicon and to the role of atomic hydrogen, several studies have been dedicated to hydrogen treatment of a-Si:H films [2,3,4,5]. However, the observed film crystallization is often wrongly ascribed to the impinging hydrogen atoms. What tended to be overlooked, is that the counter electrode is covered with an a-Si:H film during the deposition step. Interaction of the H<sub>2</sub> plasma with the coated electrode will result in formation of molecules and radicals originating from silane [4]. Hence, the resulting plasma conditions are similar to those used for  $\mu$ -Si:H, which explains the observed crystal formation.

Here, we show that this is not only true for direct plasmas, but that also in remote plasmas the reactor wall has big influences on the growth process. By using *in situ* spectroscopic ellipsometry and *ex situ* Raman spectroscopy, we show that H<sub>2</sub> plasma treatment of a-Si:H only results in the formation of crystals when there is a source of silicon-based molecules and radicals. Together with a plasma study, comprising mass spectrometry and ion probe measurements, we address the origin and kinetics of the crystal formation and discuss the implications for  $\mu$ -Si:H growth.

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2. A. F. I. Morral, J. Bertomeu, and P. R. I. Cabarrocas, Materials Science and Engineering B-Solid State Materials for Advanced Technology **69**, 559-563 (2000).
3. A. F. I. Morral and P. R. I. Cabarrocas, Journal of Non-Crystalline Solids **299**, 196-200 (2002).
4. K. Saitoh, M. Kondo, M. Fukawa, T. Nishimiya, A. Matsuda, W. Futako, and I. Shimizu, Applied Physics Letters **71**, 3403-3405 (1997).
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2:20pm **EN+TF-TuA2 Spectroscopic Analysis of the Role of Hydrogen in Amorphous Silicon.** P. Schäfer, F. Nobis, O.D. Gordan, H. Kupfer, F. Richter, D.R.T. Zahn, Chemnitz University of Technology, Germany

Amorphous hydrogenated silicon (a-Si:H) is widely used in photovoltaic applications. The high absorption renders a-Si:H technically relevant especially for thin film solar cells. Despite lower efficiency, an amorphous silicon solar panel possesses the advantage of higher absorption rate and easier processing at lower production cost.

Here the focus lies on highly (p and n) doped amorphous silicon films. The samples are prepared using d.c.-pulsed magnetron sputtering of crystalline silicon targets. A controlled hydrogen flow is added to the sputtering plasma. Hydrogen in amorphous silicon is known to saturate dangling bonds and improves the short range atomic order [1]. To probe the influence of hydrogen in the sputtering process various spectroscopic techniques were applied for sample characterisation.

Raman spectroscopy is a technique sensitive to the morphological aspects of the film. The relaxation of quasi-momentum conservation in amorphous films results in drastically different spectra of amorphous and crystalline silicon. A broad band at  $\sim 485$  cm<sup>-1</sup> appears instead of the sharp crystalline phonon feature at 520 cm<sup>-1</sup>. Its shape and asymmetry unveils further information on the short range order like the average dispersion angle from tetrahedral conformation. With the help of Fourier transformed transmission infrared spectroscopy the concentration of hydrogen in the sample is studied. Vibrational hydrogen-silicon stretching modes in the region around 2000 cm<sup>-1</sup> are therefore assessed by a modified [2] Brodsky-Cardona-Cuomo approach [3]. Access to the optical constants  $n$  and  $k$  and therefore the complex dielectric function  $\epsilon$  of the sputtered material is granted by variable angle spectroscopic ellipsometry. Thereby important parameters like the Tauc-Lorentz band gap which is mainly determined by interband gap defects are revealed. The combination of these spectroscopic techniques provides a detailed picture of morphological, electrical, and optical parameters of the system. An in depth discussion of the degree of structural

improvement, the decrease of interband gap defects, the saturation of hydrogen content, and evolution of optical properties in correlation with the hydrogen flow will be presented.

[1] R. A. Street, "Hydrogenated Amorphous Silicon", chapter 2.3, Cambridge University Press.

[2] A. A. Langford, M. L. Fleet, B. P. Nelson, W. A. Lanford, N. Maley: Phys. Rev. B **45** (1992) 13367.

[3] M. H. Brodsky, M. Cardona, J. J. Cuomo: Phys. Rev. B **16** (1977) 3556.

2:40pm **EN+TF-TuA3 Improved Efficiency and Air Stability of Hybrid Thin Film Solar Cells with a ZnO Nanoparticle Layer.** P.H. Holloway, L. Qian, J. Yang, R. Zhou, A. Tang, Y. Zheng, J. Xue, University of Florida

INVITED

Hybrid solar cells with active and transport layers based on conjugated polymers and/or inorganic semiconductor nanoparticles are an alternative to all-organic or all-inorganic solar cells. In hybrid cells, inorganic nanoparticles complement the absorption of the organic phase and provide better charge transport properties due to higher carrier mobility, while still maintaining the ability to solution-process. These properties will be illustrated first in hybrid solar cells with a mixed active layer based on poly(3-hexyl thiophene) (P3HT) and colloidal CdSe nanospheres, and with a ZnO nanoparticle buffer layer. The CdSe and ZnO nanoparticles were synthesized using a micelle and a sol-gel method, respectively. Both the active and buffer layers were spin-coated from solution onto a poly(3,4-ethylene dioxithiophene) doped with polystyrenesulfonic acid (PEDOT:PSS) layer on an ITO/glass substrate, and finished by deposition of the Al cathode. Compared to control devices without the ZnO layer, devices with the layer showed only slight changes in open-circuit voltage and fill factor, but showed 40-70% higher short-circuit current density, depending on the size of the CdSe nanospheres. ZnO-containing devices showed a maximum power conversion efficiency of 2.5-2.8%, compared to approximately 1.6-1.9% for the best P3HT/CdSe nanosphere devices without the ZnO layer. Using a ZnO layer and a low-gap poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) to better harvest near-infrared photons, we have achieved a maximum power conversion efficiency of 3.3-3.5%. In addition to the efficiency enhancement, the ZnO layer also drastically improved the air stability of both types of hybrid solar cells. While devices without the ZnO layer degraded completely after one to three days of air exposure, devices with the ZnO layer exhibited only a modest 35% efficiency decrease after >70 days of storage in laboratory air. The mechanisms leading to higher efficiencies and reduced degradation will be discussed.

4:00pm **EN+TF-TuA7 Energy Band Alignments and Influence of Doping on Ga-doped ZnO, CuO and Si.** S.Y. Chiam, S.J. Wang, J.S. Pan, L.M. Wong, Institute of Materials Research & Engineering, Singapore, W.K. Chim, National University of Singapore

It is important to investigate new materials for thin film solar cells for 2<sup>nd</sup> generation devices. Materials extraction cost and annual electricity production considerations highlighted several potential new materials including cuprous oxide (Cu<sub>2</sub>O). In this work, we report on the growth of Cu<sub>2</sub>O and highlighted the importance of the oxygen partial pressure during growth. Namely, the partial pressure of oxygen determines the transition of Cu<sub>2</sub>O to CuO with increasing partial pressure. This is accomplished at a fixed total pressure as this may influence Cu<sub>2</sub>O formation. We then discuss about the interface energy alignments, first between between Cu<sub>2</sub>O/ZnO and then ZnO/Si. The former is of importance as inorganic thin film p-n junction that is suitable for 2<sup>nd</sup> generation solar cell devices. For the latter case, we fabricated device structure on differently doped Si, to investigate influence on doping on the transport characteristics of the hetero- pn junction. It is found that forward bias characteristics for a heterojunction, is not critically dependant on the band offsets, but rather the build-in-field at the heterojunction. If the physics is considered from the point of view of quasi-fermi level separation during light illumination, this build-in-field will also determine the V<sub>oc</sub>. In this sense, band offset measurements can only give an indication of the maximum limit of the V<sub>oc</sub> for differently doped semiconductors (non-degenerate) heterojunction solar cells. In addition, we show that under illumination, the current conduction for the ZnO/Si at zero-bias is a "forward bias" current, unlike all homojunction devices. This can be understood with a detail examination of the energy band diagrams. This work shows the importance of using measured band offsets to aid in understanding the relative Fermi-level alignment instead of using bulk electron affinity values. The work also demonstrates a whole array of

playground possible for thin film heterojunction of different materials to engineer an ideal junction for solar cell devices.

**4:20pm EN+TF-TuA8 Growing Low-Dislocation-Density Ge on Si through Nanometer Sized Voids in Chemical Oxide and Subsequent Integration of III-V Films for Multijunction Solar Cells, D. Leonhardt, J.J. Sheng, University of New Mexico, J.G. Cederberg, M.S. Carroll, Sandia National Laboratories, M.J. Romero, National Renewable Energy Laboratory, S.M. Han, University of New Mexico**

In an effort to reduce the manufacturing cost of multijunction solar cells, which currently utilize Ge substrates, we have scaled up a process to produce low-defect-density Ge films on 2-inch-diameter Si substrates. This process begins with the nucleation of over  $1 \times 10^{11}/\text{cm}^2$  Ge islands on Si through 3-to-7 nanometer diameter voids in chemical  $\text{SiO}_2$ . It is shown that upon Ge island coalescence, the Ge film primarily contains stacking faults as opposed to threading dislocations. We have found that annealing the Ge islands at an early stage of island growth removes the stacking faults, but results in the formation of  $5 \times 10^7/\text{cm}^2$  threading dislocations upon further growth. Herein, we report on a detailed investigation using transmission electron microscopy (TEM) to clarify the mechanism of the stacking fault formation in the Ge. We will also discuss the effect of annealing both on the Ge island morphology and in eliminating the stacking faults. Additionally, the origin of the threading dislocations obtained after annealing is revealed through the TEM study. Lastly, we report characterization results of GaAs-based double heterostructures integrated on the annealed Ge films, whose photoluminescence intensity over the entire 2-inch wafer is comparable to the same structures grown on commercially available GaAs and Ge substrates.

**4:40pm EN+TF-TuA9 Optimizing Heterojunctions of ZnTe/ZnSe Solar Cells: Effect of Surface Treatment and Growth Conditions, F. Fang, B. McCandless, R. Opila, University of Delaware**

II-VI direct band gap semiconductors are attractive for thin film solar cell (TFSC) applications owing to their potential flexibility in tunable optoelectronic properties and possible application in tandem cells for being band gap materials ( $E_G > 2$  eV). For the  $n$ -ZnSe/ $p$ -ZnTe heterojunction solar cell, the defect states and electronic band alignment at the ZnSe/ZnTe interface are crucial for device performance. We have employed Al-K $\alpha$  X-ray photoelectron spectroscopy as well as synchrotron source ultra-violet photoelectron spectroscopy to study the surface chemical composition and electronic structures at heterojunction interface. Scanning electron microscopy (SEM) was used to study observe the film microstructure morphology of the interface.

We used two different deposition techniques: Close Space Sublimation (CCS), a low-cost deposition method already demonstrated for high efficiency and commercial CdTe TFSC, and conventional thermal evaporation. Our preliminary results indicated that surface oxides on CCS-grown ZnSe film formed once open to air, and a significant valence band offset induced by this oxide is observed which acts like additional energy barrier for carrier transport, resulting in low open circuit voltage. Also, during sequential CSS deposition of the two stacking films, the covering ZnTe thin film layer growth damage the microstructure of the underlying ZnSe film, i.e., enlarged pores are observed in ZnSe films in the locations where partially covering ZnTe film was deposited. A degraded device performance is expected and low short circuit currents and fill factors of the cells are detected. By analogy to CdS/CdTe TFSC, we are aiming for close-packed column polycrystalline of ZnSe/ZnTe film growth. Therefore, we are exploring etching processes, annealing temperatures and ambient settings to optimize the growth conditions. Evaporation is under investigation, since we have the option of dual-sources in the self-designed chamber, sequential growth of ZnSe and ZnTe films without vacuum break is feasible. Film morphology as well as energy band alignment at the heterojunctions using evaporation growth is being studied.

**5:00pm EN+TF-TuA10 Investigation of NbSe<sub>2</sub> as Potential High Work Function Back Contact for CdTe Solar Cells, M.A. Wolak, S. Gutmann, M.M. Beerbom, C.S. Ferekides, R. Schlaf, University of South Florida**

The layered semi-metal NbSe<sub>2</sub> combines a chemically inert van der Waals surface with a high work function of about 5.8 eV. This motivated an investigation of NbSe<sub>2</sub> as Ohmic hole injection contact for CdTe solar cells. Current back contacts made from Cu suffer from interdiffusion issues leading to cell degradation. In the discussed experiments, the interface between NbSe<sub>2</sub> and CdTe was investigated using x-ray and ultraviolet photoemission spectroscopy (XPS, UPS). In these experiments CdTe and NbSe<sub>2</sub> thin films were grown in-situ in a vacuum chamber attached to the photoemission system. This enabled the investigation of the CdTe/NbSe<sub>2</sub> interface without interference by ambient contamination. After growth of a CdTe thin film, the NbSe<sub>2</sub> film was prepared in several steps. Photoemission spectroscopic characterization between each of the

deposition steps allowed the observation of the formation of the band line-up at the interface. The results of the experiments indicate that an intermixed layer forms at the interface. This layer causes the formation of an interface dipole, preventing the formation of an Ohmic contact. A Schottky-type band line-up formed instead.

**5:20pm EN+TF-TuA11 In-Rich InGa<sub>1-x</sub>N Films for Efficient Photovoltaic Devices Grown by ENABLE, T.L. Williamson, M.A. Hoffbauer, Los Alamos National Laboratory, K.M. Yu, L.A. Reichertz, W. Walukiewicz, Lawrence Berkeley National Laboratory**

The wide band gap tunability of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  thin films (0.7 eV to 3.4 eV,  $1 > x > 0$ ) makes them ideal for efficient photovoltaic (PV) devices. However, growing high-quality In-rich  $\text{In}_x\text{Ga}_{1-x}\text{N}$  films with strong photoluminescence in the green-to-red portions of the visible spectrum has faced considerable challenges due to indium phase segregation and other materials issues. These challenges have precluded the growth of both In-rich InGa<sub>1-x</sub>N and compositionally graded InGa<sub>1-x</sub>N materials, and make it difficult to grow higher bandgap Ga-rich materials on top of lower bandgap In-rich materials. Overcoming these difficulties using conventional epitaxial techniques is challenging due to the low decomposition temperatures of In-rich materials (e.g. InN ~ 550°C) and the relatively high growth temperatures for Ga-rich materials (e.g. GaN > 800°C).

Energetic neutral atom beam lithography & epitaxy (ENABLE) is a low-temperature thin film growth technology recently developed at LANL that utilizes a collimated beam of energetic neutral N atoms (kinetic energies 0.5 to 5.0 eV) to react with evaporated Ga and In metals to grow InGa<sub>1-x</sub>N. ENABLE is similar to MBE, but provides a much larger N atom flux and correspondingly high film growth rate. The high kinetic energy of the reactive N atoms substantially reduces the need for high substrate temperatures, making isothermal growth over the entire InGa<sub>1-x</sub>N alloy composition range possible at rates of >3 microns/hr with no toxic precursors or waste products.

Data on film photoluminescence, crystallinity, electrical properties, doping, and electro-luminescence of  $\text{In}_x\text{Ga}_{1-x}\text{N}$ , graded  $\text{In}_x\text{Ga}_{1-x}\text{N}$ , and GaN films grown using ENABLE over the full composition range will be presented. ENABLE-grown  $\text{In}_x\text{Ga}_{1-x}\text{N}$  films show strong photo- and electro-luminescence spanning the entire visible region of the spectrum, with reasonable carrier mobilities background carrier concentrations typically in the low  $10^{17}$  range. Evidence for p-type doping of In-rich InGa<sub>1-x</sub>N films and characterization of p/n junctions will be discussed along with the prospects for using ENABLE to fabricate efficient PV devices.

**5:40pm EN+TF-TuA12 Copper Oxide Thin Films: Preparation and Modulation of Semiconducting Properties by Electrochemical Methods, F. Caballero-Briones, CICATA-IPN/Universitat de Barcelona, Spain, A. Palacios-Padrós, Instituto de Bioingeniería de Catalunya, Spain, F. Sanz, Instituto de Bioingeniería de Catalunya/CIBER-BBN, Spain**

Copper oxide is a p-type semiconductor with a direct band gap of 2 eV, suitable for photovoltaic applications. In this work we present an electrochemical method to prepare p-type semiconducting  $\text{Cu}_2\text{O}$  films around 100 nm thick with noticeable photocurrent response. The film properties were modulated by varying different conditions such as the time at a dissolution potential and the film doping with alkaline ions. The modification of the time of exposure to the dissolution potential allows the tailoring of the crystallinity, the band gap energy and the disorder parameter  $E_0$  and also provided elements to outline the growth mechanism of the  $\text{Cu}_2\text{O}$  films that involve surface reaction, diffusion of oxygen species that react in the solid state accordingly to the point defect model, and heterogeneous deposition of  $\text{Cu}_2\text{O}$  from the  $\text{Cu}^+$  ions dissolved in a chemical bath-like fashion. On the other side, the study of the behavior of different alkaline metal ions (A: Li, Na, K, Cs) present in the electrolyte used to prepare the  $\text{Cu}_2\text{O}$  films lead to important results. It was observed that important amounts of the alkaline ion (around 1%) can be incorporated to the film and that are indeed electrically active impurities that modify the band gap energy probably by introducing states within the band gap in the case of Cs or by getting incorporated to the crystalline lattice for Na or Li. Changes in the optical absorption, thickness, density of carriers and in defects are related with the size of the employed ion. To complete the study, an electronic diagram of the  $\text{Cu}|\text{Cu}_2\text{O}|\text{Electrolyte}$  interface was prepared by using a combination of techniques including Electrochemical Impedance and Electrochemical Tunneling Spectroscopy/Microscopy.

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