

Wednesday Afternoon, October 31, 2012

Thin Film

Room: 11 - Session TF+AS-WeA

Thin Films: Growth and Characterization-I

Moderator: M.R. Davidson, University of Florida

2:00pm **TF+AS-WeA1 Studying the Microstructure of Cu₂ZnSn(S,Se)₄ Thin Film Solar Cells.** *L. Zhang, Y. Cao, D.H. Rosenfeld, M. Lu, J. Caspar, C. Chan,* DuPont Central Research and Development

To advance the next generation photovoltaic technology, the new ink-based Cu₂ZnSn(S,Se)₄ (CZTSSe) solar cells have attracted rapid growth attention in the thin film photovoltaic areas. As a potential alternative to CIGS, the CZTSSe technology offers a non-vacuum based and likely low manufacturing cost process with active area efficiency above 9%. In particular, the fact that CZTSSe utilizes only earth abundant elements enables the sustainability & renewability for future green energy demand.

The overall CZTSSe solar cell developed by DuPont scientists consists of multi-layer inorganic structures of ITO/ ZnO/ CdS / CZT(S,Se) / Mo on sodalime glass substrate. A novel synthetic method has been developed to produce the active CZTSSe layer. During the process, binary and ternary chalcogenide nanoparticles are first synthesized as starting materials, formulated into a precursor ink, applied onto a substrate, and then converted into CZTSSe upon a thermal annealing process. To aid product development for optimum efficiency, chemical and structural characterization of the active CZTSSe layer and interfaces between different layers are performed using multiple analytical techniques. For example, sputter depth profiling with XPS and Auger, and cross-section SEM/EDX helped us to visualize the structural chemistry at specific locations in the films which enabled the team to adjust ink formation as well as processing conditions for better and more efficient cell production. This presentation will cover the characterization of CZTSSe solar cells, including the study of film composition and morphology, inter-layer diffusion, and their correlation with device performance.

2:20pm **TF+AS-WeA2 Seed-Mediated Growth of 1D Pyrite (FeS₂) Structures.** *Y.J. Kwon, N. Berry, M. Law, J.C. Hemminger,* University of California Irvine

Iron pyrite is a promising semiconductor for use in solar cells due to its earth-abundance, suitable bandgap, and high absorption coefficient. Pyrite device efficiency is only about 3% due to a low open-circuit photovoltage and high dark current, possibly as a result of sulfur deficiency at the surface resulting in thermionic field emission. Although fabrication of pyrite thin films has been studied by various methods, specific details of the pyrite growth process in the presence of homogeneous nucleation sites has not been studied. In this project, the role of pyrite nucleation sites is investigated in the growth of pyrite thin films by atmospheric-pressure chemical vapor deposition (AP-CVD). The pyrite nanoparticle nucleation sites are fabricated by sulfurization of pre-deposited Fe₂O₃ grains on the step edges of highly oriented pyrolytic graphite (HOPG) using H₂S, elemental sulfur or a combination of the two annealing treatments and characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman spectroscopy. H₂S-sulfurized Fe₂O₃ nuclei coalesce to form FeS₂ nanowires containing both pyrite and marcasite phases. A subsequent elemental sulfur treatment on either H₂S-sulfurized samples or pre-deposited Fe₂O₃ samples yield pure pyrite; however, the nanowires convert to a less desirable morphology of randomly sized spherical grains as a result of this annealing treatment. Atmospheric Pressure-CVD of FeS₂ from iron-(III) acetylacetonate and *tert*-butyl disulfide was performed to grow pyrite on these seeded substrates. Initial deposition on the H₂S-annealed samples leads to only seed-mediated growth and the formation of linear arrays of polycrystalline FeS₂ nanowires. However, due to marcasite phase presence on pre-covered FeS₂ nanoparticle seeds, both marcasite and pyrite phases could be observed. Initial deposition on elemental sulfur treated samples with pure pyrite phase showed deposition occurring throughout the substrate. No preferential growth on seeded pyrite nucleation sites was observed. It is proposed that during elemental sulfur treatment, new nucleation sites form, leading to deposition covering the substrate. Further work is in process to clearly determine or identify the growth mechanism of pyrite. In this work, we will gain a greater understanding of early stages of pyrite growth process in the presence of homogeneous nucleation sites.

2:40pm **TF+AS-WeA3 Investigation of Recrystallization in Low-Temperature Grown CdTe Solar Cells in Substrate and Superstrate Configuration.** *L. Kranz, C. Gretener, J. Perrenoud, S. Buecheler, A.N. Tiwari,* EMPA, Switzerland

INVITED
CdTe solar cells and modules on glass substrates have already shown high performance and low cost. Production costs and energy payback time can be further reduced by minimizing the thermal budget of the production process, increasing the throughput and by the use of low-cost substrates. We developed a process for the conventional superstrate configuration which involves substrate temperatures below 450°C. The low temperatures enable the growth on flexible polyimide foil. Efficiencies up to 15.6% and 13.8% on glass and polyimide were achieved, respectively.

In the conventional superstrate configuration sputtered ZnO:Al/ZnO was used as transparent front electrical contact. CdS and CdTe were evaporated at low temperatures of 160 and 350°C followed by an annealing treatment in the presence of CdCl₂ at 420°C and the cells were finished with a metallic electrical back contact. The annealing treatment is essential for highly efficient CdTe solar cells as it leads to grain growth of CdTe, improves electronic properties of CdTe and leads to an intermixing between CdTe and CdS.

For the growth on opaque substrates like flexible metal foils, we developed a growth process of CdTe solar cells in substrate configuration, where light does not need to pass the substrate. It enabled efficiencies of 11.3% and 8.7% on glass and flexible steel foil, respectively.

A combination of Mo, MoO₃ and Te was deposited as back contact and in some cases Cu was added. Evaporated MoO₃ grew with low crystallinity and recrystallized during subsequent processing. CdTe was deposited by vacuum evaporation while CdS was grown by chemical bath deposition. In substrate configuration, the CdTe and CdS layers were annealed separately as a combined annealing step would lead to excessive CdS-CdTe intermixing. The annealing treatment of the CdTe layer leads to similar grain growth as in superstrate configuration. The CdCl₂ treatment after deposition of CdS was optimized, resulting in increased grain size and wurtzite structure. CdS-CdTe intermixing, which is commonly observed in superstrate configuration was less pronounced in substrate configuration. The effects of the recrystallization treatments in substrate configuration are compared to the conventional superstrate configuration.

4:00pm **TF+AS-WeA7 High Quality ZnMgO Thin Films Grown on Sapphire and ZnO Substrates by Molecular Beam Epitaxy.** *M. Wei, R.C. Boutwell, W.V. Schoenfeld,* University of Central Florida

Zinc oxide (ZnO) based material is attractive for high efficiency ultraviolet (UV) optoelectronics devices. We will report growth of high quality ZnMgO on both sapphire and ZnO substrate by plasma-assisted molecular beam epitaxy (MBE). With relatively low growth rate and optimized growth condition, we were able to achieve step flow growth of ZnO thin films. ZnO thin films grown on sapphire showed high crystalline quality, low carrier concentration, high mobility and sub-nanometer surface roughness with terrace steps, indicating suitability for UV application. Homoepitaxial ZnO films were grown on both c-plane and miscut ZnO substrates with atomically flat surface, no threading dislocation and same crystallinity as the substrate. Ga doping was demonstrated for ZnMgO films on sapphire and ZnO substrates. This work may lead to the realization of high efficient UV emitters such as Laser diodes.

4:20pm **TF+AS-WeA8 Epitaxial Growth of Zirconium Dioxide Thin Film on Ge(111) Wafer.** *C. Hubault, A. Baba, A. Fleurence, Y. Yamada-Takamura,* Japan Advanced Institute of Science and Technology

GaN-based semiconductors are widely used in optoelectronic devices. To grow these films, substrates such as sapphire, SiC and Si are used. However, recently, Lieten *et al.* [1] have proposed to grow GaN on Ge(111) substrate to have a more closely matching thermal expansion coefficient and to decrease the lattice mismatch. Despite the good quality of the film, misoriented domain and voids can be found in it. While the domains can be suppressed, the voids cannot, as they come from a diffusion of Ge atoms in the film. This is a problem for the growth of p-type or semi-insulating GaN layers.

Using ZrB₂ as a buffer layer on Ge substrate could help by providing a diffusion barrier. Moreover, ZrB₂ substrate has already been used as a conductive growth template for GaN and has proven to be interesting thanks to the low lattice mismatch and close in-plane thermal expansion coefficient [2]. Therefore, ZrB₂ has been used as a buffer layer for the growth of GaN films on Si wafer [3] and those films were shown to be promising.

It was also demonstrated that on top of ZrB₂(0001) thin film on Si(111) substrate, silicene, which has a similar structure to graphene was present

[4]. In the periodic table, C, Si and Ge are in the same column. Therefore, we can envisage the possibility of the formation of germanene in the same manner as silicene on top of the ZrB₂ layer grown on germanium substrate.

Here, we report on the epitaxial growth of ZrB₂ thin films on Ge(111) by thermal decomposition of Zr(BH₄)₄ in a dedicated UHV-chemical vapour deposition system. The growth was monitored *in situ* by RHEED, and the samples were further analysed by XRD and TEM. The film grows with epitaxial relationship of ZrB₂(0001)//Ge(111). Under slow growth conditions (substrate temperature, T_s=750°C), two types of in-plane orientations, which are rotated by 30° can be observed, while under faster growth condition (T_s=650°C), the layer is monocrystalline. The single-crystalline film has in-plane orientation of ZrB₂[11-20]/Ge[-110], similar to the case of single-crystalline ZrB₂ film on Si(111) [4], but with a different surface reconstruction of ($\sqrt{3}\times\sqrt{3}$) when cooled down under 450°C. There is a good epitaxy between the layer and the substrate with the presence of a second phase at the interface, which tends to disappear when the growth was carried out at 550°C.

- [1] R.R. Lieten *et al.*, *J. Cryst. Growth*, 314, 71 (2011).
- [2] H. Kinoshita *et al.*, *Jpn. J. Appl. Phys.*, 42, 2260 (2003).
- [3] Y. Yamada-Takamura *et al.*, *Phys. Rev. Lett.*, 95, 266105 (2005).
- [4] A. Fleurence *et al.*, *Phys. Rev. Lett.*, accepted for publication.

4:40pm TF+AS-WeA9 Effect of Growth Conditions on Cubic ZnMgO films. C. Boutwell, M. Wei, W.V. Schoenfeld, University of Central Florida
ZnMgO films were grown on MgO substrates by Plasma-Enhanced Molecular Beam Epitaxy. Epilayer morphology, stoichiometry, and crystalline orientation were investigated. Films were produced by varying cation source temperature/flux, substrate temperature, and oxygen plasma power and flow rate. Crystalline immiscibility was determined in the phase mixed cubic/wurtzite range. Growth rate varied from 30nm/hr to 175nm/hr while roughness varied from 4nm to 110nm in cubic to mixed-phase samples. Wurtzite ZnO peaks at (002) and (101) were apparent from θ -2 θ X-Ray Diffraction on phase separated films, indicating multiplanar ZnO crystallite growth on the (001) MgO substrate. Growth condition information will be useful for optimization of optoelectronic devices functional in the deep ultraviolet/solar-blind range.

5:00pm TF+AS-WeA10 Properties of Ytterium Doped Zinc Oxide Thin Films Deposited by r.f. Magnetron Sputtering. K. VanSant, T. Barnes, J. Burst, J. Duenow, T.A. Gessert, National Renewable Energy Laboratory

Transparent conducting oxides (TCOs) based on zinc oxide (ZnO) and aluminum (Al) doped ZnO (AZO) are important for many large-scale commercial applications because they exhibit good optical and electrical properties. Further, their constituent elements are non-toxic and abundant, and high-quality thin-films can be deposited at room temperature using a variety of deposition processes. These characteristics make AZO appealing for use as part of the top contact in copper indium gallium diselenide (CIGS) PV modules. Although the present generation of ZnO-based TCOs meet many of the technical requirements of present-generation technologies, it is known that the material could be much more widely applied if some of its properties were more consistent with another important TCO, In₂O₃:Sn (i.e., ITO). In this comparison, the main properties requiring improvement include increasing the mobility from ~20 to ~50 cm² V⁻¹s⁻¹ while maintaining carrier concentrations > 5x10²⁰ cm⁻³ and improving the moisture-tolerance of the films. Earlier work has already shown that AZO with mobility approaching 50 cm² V⁻¹s⁻¹ can be achieved by careful control of the sputtering ambient and the dopant concentration. This study investigates the use of the Group IIIA material yttrium (Y) as a dopant, as well as the impact it has on the optical properties of ZnO. The Y-doped ZnO films are deposited on glass by r.f. magnetron sputtering using pressed powder targets, and the Y concentration is varied by simultaneous co-sputtering from a ZnO:Y target. The films will be analyzed using a combination of Hall measurements, UV-Vis-NIR spectrophotometry, spectroscopic ellipsometry, and Auger/X-ray photoelectron spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS). Based on prior research related to the addition of zirconium (Zr) to ITO, it is suspected that the addition of Y in ZnO may lead to similar changes in the optical properties of this material. Understanding the functionality of these changes could have significant implications for device applications requiring greater control of the dielectric properties of ZnO.

5:20pm TF+AS-WeA11 Effect of Process Parameters on Molybdenum Thin Films and Development of Single Layer Molybdenum Film for CIGS Thin Film Solar Cells. S. Pethé, A. Kaul, N. Dhere, Florida Solar Energy Center, University of Central Florida

Molybdenum back contact in CuIn_{1-x}Ga_xSe_{2-y}S_y (CIGSeS) solar cells is usually deposited using DC magnetron sputtering. Properties of thin films

are dependent on process parameters. Films deposited at high power and low pressure, tend to be more conductive. However, such films exhibit poor adhesional strength since the films are under compressive stress. Films deposited at low power and high pressure tend to be under tensile stress and exhibit higher roughness and resistivity, while the films adhere very well to the sodalime glass substrate. Therefore, it has been a practice to deposit multi-layered Mo back contact to achieve properties of good adhesion and higher conductivity. Deposition of multi-layered back contact results in either increase in deposition time if a single target is used or increase in foot print if multiple targets are used resulting in increase in the total cost of production. Experiments were carried out to understand effects of working pressure, sputtering power and working distance on molybdenum film properties with the final aim to develop a process recipe for deposition of a single molybdenum film with acceptable properties of both good adhesion and higher conductivity. Experiments were carried out at a fixed working distance by varying the working pressure and keeping the sputtering power constant and then varying the sputtering power keeping the working pressure constant. The same set of experiments were repeated with varying working distance. Moreover, the effect of the relative position of the substrate with respect to the sputtering target for a moving target was studied. Adhesive tape test was performed on each film to determine the adhesional strength of the films. Moreover, the sheet resistance and the average roughness for each film were measured using a four probe measurement setup and the Dektak Profilometer, respectively. All experiments were also carried out on narrow and long glass strips in order to estimate the residual stress in the film by using the bend test method. Based on the results obtained from the experiments carried out a process recipe was developed for depositing on a moving substrate, a single layer molybdenum film with acceptable properties of good adhesion and higher conductivity.

5:40pm TF+AS-WeA12 Oxygen Reservoir Effect and its Impact on HfO₂. C. Vallee, C. Mannequin, P. Gonon, L. Latu-Romain, LTM (CNRS / UJF-Grenoble1 / CEA), France, A. Salaiin, H. Grampeix, V. Jousseau, CEA, LETI, MINATEC Campus, France

ReRAM device is a non-volatile memory based on resistive switching phenomena in a dielectric in a MIM (Metal Insulator Metal) structure. Depending on the nature of the oxide and the metallic electrode, the switching is based on a unipolar thermochemical mechanism (TCM), a bipolar valence change mechanism (VCM), as well as a bipolar electrochemical metallization mechanism (ECM). For all these devices, the choice of the oxide (nature, crystallization, density, doping, vacancies), the metal (inert electrode, its free energy formation of the oxide) as well as the interfacial layer (role of the electrode, role of the process) are impacting the operation sets and reliability of the device. For example, it has been shown that electrode reaction is one of the major factors determining the functionality of ECM cells [1].

This work is focused on HfO₂ based ReRAMs which are good candidates for embedded non-volatile memories [2-4]. For this material, forming/set and reset processes are correlated with the respective generation of oxygen vacancies and recombination of Vo²⁺ positive charges with oxygen ions (O²⁻). It has been recently proposed that during the negative reset the passivation occurs by the back-diffusion of oxygen ions stored in the oxide portion near the conductive filaments and at the electrode, which serve as oxygen reservoir [5].

With this work we propose to discuss on the reservoir effect by studying HfO₂ memories obtained with top electrodes of different chemical compositions and morphologies. The HfO₂ dielectric (10 nm) is deposited by Atomic Layer Deposition on Pt and TiN. X-ray Photoelectron Spectroscopy and Transmission Electron Microscopy characterization have been used to investigate the chemical composition, morphology and crystalline structure of the oxide and metallic layers. It is hence demonstrated that devices with gold deposited by a PVD process give better results than those obtained with gold deposited by evaporation. This can be related to a modification of oxygen diffusion through the top electrode via a difference in the electrode morphology (roughness, thickness...) induced by the process. Moreover, it is shown that alloying the gold target of the PVD process with a suitable metal considerably helps to improve the reliability of the memory. This is discussed in terms of catalytic effect and modification of the electrode morphology and reservoir effect.

- [1] I. Valov *et al*, *Nanotech.* **22** (2011) 254003
- [2] P. Gonon *et al*, *J. Appl. Phys.* **107** (2010) 074507
- [3] J.J. Yang *et al*, *Appl. Phys.* **A102** (2011) 785
- [4] Ch. Walczyk *et al*, *J. Vac. Sci. Technol.* **B29** (2011) 01AD02-1
- [5] S. Yu *et al*, *IEDM* (2011) 17.3.1

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