Monday Afternoon, October 19, 2015

Advanced Surface Engineering
Room: 212A - Session SE+EM+EN-MoA

Thin Film Technologies for Energy Storage, Conversion and Harvesting
Moderator: Michael Stueber, Karlsruhe Institute of Technology, Andrey Voevodin, Air Force Research Laboratory

2:20pm SE+EM+EN-MoA1 Properties of Zinc Oxide Thin Films Grown on Silicon Wafers by Pulsed Laser Deposition, *Yilu Li, J.W. Wrobel, M.K. Michael*, University of Missouri-Kansas City
Pulsed ultraviolet light from a XeF excimer laser was used to grow thin films of zinc oxide on (111) p-type silicon wafers within a versatile high vacuum laser deposition system. Pressure, target temperature and distance from the target to the substrate can be adjusted in the system. Scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction spectroscopy and ellipsometry had been used to analyze the structures and properties of ZnO thin film products.

3:00pm SE+EM+EN-MoA3 Synthesis of Crystallized and Nanostructured TiO_2 Thin Films by Reactive Magnetron Sputtering for Application as Photoanode in Dye Sensitive Solar Cells, *J. Dervaux, P.-A. Cormier, S. Konstantinidis,* Université de Mons, Belgium*, P. Moskovkin, S. Lucas,* University of Namur, Belgium*, **Rony Snyders**, Université de Mons, Belgium
Nowadays, the efficient use of renewable energies, and more specifically of solar energy, represents a major economic and environmental issue. Among the potential solutions, the Dye Sensitive Solar Cells (DSSC) present many advantages. In order to improve the efficiency of DSSC, TiO_2 nanoparticles, which are usually used as photo-anode, could be replaced by nanostructured TiO_2 thin films. Indeed, a photo-anode of ordered porous nano-columnar TiO_2 would provide large surface area for dye absorption, fast electron transfer path, enhanced light trapping, and tight interfaces to conducting electrodes and contributes to a high fill factor and an overall higher cell efficiency. In view of this application, the anatase phase of TiO_2 is usually the preferred polymorph as electron acceptors in DSSCs even if a synergistic effect exists between anatase and rutile with an optimal rutile content of around 13 wt%.

In this work, nanostructured and crystallized TiO_2 thin films are synthesized by reactive magnetron sputtering combined with Glancing Angle Deposition (GLAD). The substrate temperature, the substrate bias voltage and the rotation speed were varied in order to determine the best experimental conditions leading to (nano-)porous films with anatase TiO_2 columns. The chemical composition, the crystalline structure and the microstructure of the films were analyzed by XPS, XRD, SEM and TEM, respectively while the surface area is evaluated by the BET method.

It is demonstrated that many type of microstructures (tilted columns, straight pillars, chevrons,…) are obtained by combining the GLAD parameters and the sputtering conditions. On the other hand, depending on these growth conditions, the phase constitution can be tuned from amorphous to pure rutile or anatase phases including mixtures of both polymorphs. The surface area of the synthesized layer strongly depends on the experimental conditions and on the associated microstructure. The highest obtained value is of ~ 140 m^2/g for a tilted columnar amorphous/anatase sample which is significantly better than the values reported for TiO_2 nanoparticules systems (~ 60 m^2/g). On the other hand, a clear correlation between the surface area and the dye absorption is demonstrated revealing a good impregnation of the layer. It is also demonstrated that this impregnation behaviour is depending on the size of the dye molecule revealing different populations of pores as a function of their size. This is supported by TEM and modelling data using NASCAM, a 2D-3D Kinetic Monte Carlo code for the simulation of deposition, diffusion, nucleation and growth of films on a surface.

3:20pm SE+EM+EN-MoA4 Silver-Carbon-Nanotube Metal Matrix Composites for Metal Contacts on Space Photovoltaic Cells, *Omar K. Abudayyeh*, *C. Nelson, S.M. Han,* University of New Mexico*, N. Gapp, D.M. Wilt*, Air Force Research Laboratory
The advanced solar cells used in space vehicles today are rapidly moving towards thin-film-based inverted metamorphic multijunction (IMM) solar cells mounted on flexible substrates. However, the IMM cells are more prone to cracking than state-of-the-art triple junction cells. The cell cracking can lead to metal contact failure on IMM cells, compromising the power generation. To mitigate the power loss and increase the lifetime of IMM cells, silver metal films imbedded with carbon nanotubes (CNTs), otherwise known as metal matrix composites, have been developed and investigated for the reinforced mechanical strength against stress-induced cracking. We have primarily focused on (1) surface functionalization of CNTs to make their surface more hydrophilic and wetting to metals, (2) optimization of a cyanide-free electrochemical deposition of silver, (3) electrochemical deposition, drop casting and nanospreader technique to control the composite microstructure, and (4) mechanical and electrical characterization of the composite films. We observe that carboxylation of CNTs produces a stable, homogeneous suspension of negatively charged CNTs at pH > 6. Lustrous-mirror-finish silver films are also successfully deposited, using a commercial cyanide-free silver-plating solution with precise control of current density. Currently, one of the microstructures being explored is a silver-carbon-nanotube layer-by-layer structure, where the surface coverage of CNTs is an important parameter that directly affects the CNT packing fraction and metal intercalation through the CNT network. We quantify the CNT surface coverage as a function of different deposition variables by digitally analyzing scanning electron microscopy images. In this presentation, we will further discuss how this surface coverage correlates to the mechanical and electrical properties of the MMC films. We characterize the mechanical properties, using nanoindentation and strain failure tests. The initial nanoindentation analysis reveals that the composite film has a lower elastic modulus (10 GPa) than pure silver (73 GPa) or CNT (1000 GPa). The lower elastic modulus is attributed to the electroplating process of silver, in which hydrogen is incorporated and trapped within the composite. Our finite element analysis also corroborates this speculation, where the elastic modulus near 10 GPa is predicted with approximately 4% void fraction. While the composite elastic modulus is lower than that of pure silver, the strain failure tests show that carbon nanotubes can bridge 20 to 50-mm-wide microcracks, maintaining electrical conductivity of the composite.

3:40pm SE+EM+EN-MoA5 Laser Liftoff of Single Crystal GaAs Thin Films and Energy Conversion Devices, *Bruce Clemens, G. Hayes, V. Parameshwaran, A. Jan, J.B. Reeves*, Stanford University **INVITED**
GaAs and related III-V sphalerite materials offer a wide array of tunable characteristics that lend themselves to many advanced device technologies. However, the cost of GaAs substrates limits their use, specially for photovoltaics. Separating epitaxially-grown layers from a growth substrate can reduce costs, however the current approach, which uses an acid to laterally etch an epitaxial sacrificial layer, is slow and can damage other device layers. Here, we demonstrate laser lift-off as a new approach that is orders of magnitude faster, and that enables more freedom in the selection of other device layers. We grow a structure with a spatially-tuned optical absorption coefficient by growing a small-band-gap, pseudomorphic layer between the GaAs substrate and a GaAs film and device structure. By using InGaAsN with a band gap of 0.9 eV for this layer, we achieve high absorption of 1064 nm (1.17 eV) light from a Nd:YAG nanosecond laser pulse, while GaAs is essentially transparent for this wavelength. Illumination through the back of the GaAs substrate with laser fluences of about 0.7 J/cm^2 achieves transfer of the GaAs layer to a flexible polymer substrate. Transmission electron microscopy and x-ray diffraction show that the initial InGaAsN layer is coherently strained to match the GaAs substrate, and that the GaAs film is strain-free and free of dislocations, both before and after lift-off. Thermal modeling shows only modest heating outside of the InGaAsN layer, so that the film or device above the InGaAsN layer experiences minimum thermal exposure. Examination of the lift-off interfaces shows evidence of melting and re-solidification. We demonstrate a process using additional InGaP etch layers that allow for quick and easy clean-up of this melted region, resulting in restoration of the original GaAs wafer surface to a condition suitable for re-use. Thus our process can transform the GaAs substrate from a consumable to a manufacturing tool. Device performance and material properties of lifted-off devices will be reported.

4:20pm SE+EM+EN-MoA7 Optical and Structural Properties of Metal-dielectric Composite Films, *Lirong Sun, N.R. Murphy, J.G. Jones, J.T. Grant*, Air Force Research Laboratory
In this work, the metal - metal oxide composite films were prepared in multilayer stacks. A medium layer of silver or a mixture of silver and oxide (SiO_2, Al_2O_3, ZnO and ITO) was embedded between the host (SiO_2, Al_2O_3, ZnO and ITO) materials. The mixture of silver and oxide was deposited by co-sputtering the silver target and one oxide target in pure argon simultaneously using DC and pulse DC magnetron sputtering techniques. The optical constant of composite films was tailored by varying deposition time of the medium layer, deposition conditions and host material. The

absorbing spectral peaks were influenced by silver content, silver particle sizes and oxide matrix. The *in situ* spectroscopic ellipsometry data was performed in real time during film growth to derive film thickness and optical constants. The dispersion results were further correlated with absorption spectra, film density, grain sizes and surface morphology by UV-Vis-NIR spectra, X-ray diffraction, X-ray reflectivity and scanning electron microscope measurements.

5:00pm SE+EM+EN-MoA9 Atomic Layer Deposition of Alumina and Titania Passivation Layers in Microchannel Reactors for Coke Suppression, *Hao Feng*, Xi'an Modern Chemistry Research Institute, China

Alumina and titania thin films are deposited inside the channels of stainless steel tubes by atomic layer deposition to deactivate the metal surface for the purpose of coke suppression. The ALD equipment is modified to incorporate the high-aspect-ratio metal tubes into the flow path. Experiment parameters are adjusted to ensure complete and uniform coverage of the internal surface areas of the metal tubes. The thicknesses of the passivation layers are precisely controlled by adjusting the number of ALD cycles. In coking experiments the passivated metal tubes are used as reactors for thermal cracking of a hydrocarbon fuel composed of C_{12}-C_{16} paraffins. The lifetime of the experiment system passivated by ALD alumina films can be up to 5 times longer compared to the system using bare metal tubes as the reactor. By analyzing the tested metal tube samples it is discovered that the ALD alumina film remains intact after the coking experiment so that the metal catalyzed filament coke formation can be completely inhibited by the alumina passivation layer. The anti-coking performances of ALD titainia passivation layers are also noticeable but not as stable. The formation of filament cokes can also be suppressed by titania passivation layers. However, the ALD titania films tend to crack during the coking experiments. This could lead to failures of the passivation layers and acceleration of coke formation.

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