

# Monday Morning, October 18, 2010

## Thin Film

Room: Pecos - Session TF+EN-MoM

### ALD: Energy Applications

Moderator: S.M. George, University of Colorado at Boulder

8:20am **TF+EN-MoM1 ALD Applications in Heterogeneous Catalysis**, *P.C. Stair*, Northwestern University & Argonne National Lab, *J. Lu*, Northwestern University, *H. Feng*, *J.E. Libera*, *J.W. Elam*, *M.J. Pellin*, Argonne National Laboratory, *H.-S. Kim*, Northwestern University  
**INVITED**

Atomic Layer Deposition (ALD) has enormous potential for the synthesis of advanced heterogeneous catalysts with controlled composition and structure at the atomic scale. The ability of ALD to produce conformal oxide coatings on porous, high-surface area materials offers the possibility to provide completely new types of catalyst supports. At the same time ALD can achieve highly uniform catalytically active metal and oxide phases with (sub-) nanometer dimensions.

Vanadium oxide species supported on high surface area oxides are among the most important catalytic materials for the selective, oxidative conversion of hydrocarbons to useful chemicals. In our laboratory ALD has been used to synthesize both the catalytic vanadium oxide and the supporting oxide on both high surface powders and anodic aluminum oxide (AAO) nanoliths. These materials have been characterized by SEM, XRF, ICP, UV-Vis absorption spectroscopy, Raman spectroscopy and evaluated for the oxidative dehydrogenation (ODH) of cyclohexane.

More recently we have studied what we call "ABC-type" ALD in which metal nanoparticles and support materials are grown sequentially in each ALD cycle. This method makes possible metal deposition at lower temperatures than conventional AB-type ALD and exceptionally small particles, ca. 0.5 nm. Using additional ALD support layers at the conclusion of the growth, the metal particles are stabilized against sintering at high temperatures and reaction conditions.

9:00am **TF+EN-MoM3 Process and Materials Optimization for Ru/RuO<sub>2</sub> ALD using a Novel Cyclohexadienyl Precursor**, *K. Gregorczyk*, *L. Henn-Lecordier*, University of Maryland, *J. Gatineau*, *C. Dussarrat*, Air Liquide, *G.W. Rubloff*, University of Maryland

Ruthenium is of particular interest to the semiconductor industry and others due to its low bulk resistivity ( $7\mu\Omega\text{ cm}$ ) and high work function (4.7eV). In addition, its complementary oxide, RuO<sub>2</sub>, can exhibit high specific capacitance (up to 750 F/g) and conductivity ( $80\text{--}100\mu\Omega\text{ cm}$ ), making it attractive for energy storage applications. We report results for Ru and RuO<sub>2</sub> ALD using a novel Ru cyclohexadienyl precursor and oxygen. This precursor is attractive because it is liquid at room temperature, stable in air and non-reactive with water, while its vapor pressure is similar to that of common ALD Ru precursors RuCp<sub>2</sub> and Ru(EtCp)<sub>2</sub>, i.e., 0.1 Torr at 60°C and 1 Torr at 100°C. ALD Ru deposition was achieved in a wafer scale (100mm), cross-flow ALD reactor. Self-limiting ALD surface chemistry is observed between 250–300°C with a growth rate of  $\sim 0.5\text{Å}/\text{cycle}$  and across-wafer uniformity >98%. Four point probe measurements show a low sheet resistance of  $16\mu\Omega\text{ cm}$ . Ru nucleation is improved compared to RuCp<sub>2</sub> and Ru(EtCp)<sub>2</sub> based processes, with no nucleation delay on SiO<sub>2</sub> or TiO<sub>2</sub>, a slight delay on Si, and a significant delay on Al<sub>2</sub>O<sub>3</sub>. Growth rates are constant with the number of deposition cycles. Conformality studies were conducted using high aspect ratio anodic aluminum oxide (AAO) thin films, using a thin TiO<sub>2</sub> nucleation layer before Ru ALD. This Ru ALD process converts to a RuO<sub>2</sub> ALD process at higher oxygen partial pressure, with an oxide conductivity of  $\sim 80\mu\Omega\text{ cm}$ . Post-process thin film characterization using XRD, XPS and AFM will be also presented.

This work was supported by the US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center.

9:20am **TF+EN-MoM4 Atomic Layer Deposition Enabled Metal-Insulator-Metal Tunnel Diode for Infrared Energy Rectifying System**, *I.-T. Wu*, University of South Florida, *N. Kislov*, NanoCVD Inc., *J. Wang*, University of South Florida

Amongst present-day renewable energy sources, solar cells have been widely considered as the most viable solution. However, the energy conversion efficiency for the solar cells is limited to 30% or below due to the device physics. Rectifying antenna (rectenna) is an ideal supplement that is able to efficiently capture the abundant infrared (IR) energy from the solar radiation in part due to IR antenna's inherent high efficiency. The

rectenna system consists of two key elements: antenna and rectifying diode. The IR antenna captures the solar radiation within the wavelength of interest to be delivered to the ultrafast diode that rectifies the received signal into usable DC power.

Rectennas operating at microwave frequencies with efficiency up to 85% has been routinely demonstrated. However, the key remaining challenge for the infrared counterparts can be ascribed to the insufficient cutoff frequency of the semiconductor-based diodes owing to their excessive depletion-induced capacitance. In order to obtain the desired response times less than 10–12seconds, metal-insulator-metal (MIM) tunnel diodes with junction area in the range of  $100\text{nm}\times 100\text{nm}$  were implemented herein to enable the coveted terahertz frequencies due to the greatly reduced junction capacitance and ultrafast quantum tunneling.

In this work, MIM tunnel diodes with sub-micron sized junction have been mass produced using CMOS-compatible processes without the need for E-beam lithography or sophisticated chemical etching. Standard photolithography and atomic layer deposition (ALD) were used to allow formation of a micrometer-wide finger in the second metal layer separated from the electrode in the first metal layer by an ALD-deposited sidewall dielectric spacer, thus forming a nm-thick vertical tunnel junction. The nano-scale junction is defined by the width of the finger and the thickness of the electrode, while the junction thickness is controlled by the ALD process.

On par to nano-scale devices, MIM tunnel diodes with micron-scale self-aligned cross-fingers have been successfully developed. Through this process, we have investigated a wide variety of metal and insulator materials such as Au, Cu, Pt, Ni, Al, Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub> to advance the performance of the MIM diode with particular focus on its efficiency. Some preliminary DC and RF characterization have been carried out to study the device characteristics such as responsivity, nonlinearity and asymmetry of I-V, and frequency responses. Ongoing research for modeling of MIM tunneling diode based on measured S-parameter data and further reduction of the device junction area will be detailed in the final manuscripts.

9:40am **TF+EN-MoM5 New Semiconductor-Insulator-Semiconductor Solar Cell Concept based on Wet Chemically Etched Silicon Nanowires: Processing and Electro-Optical Properties**, *B. Hoffmann*, *V.A. Sivakov*, *G. Broenstrup*, *F. Talkenberg*, Institute of Photonic Technology, Germany, *S.H. Christiansen*, Max Planck Institute for the Science of Light, Germany

Silicon nanowire (SiNW) ensembles with vertical geometry have been realized using wet chemical etching of bulk silicon wafers (n-Si(100)) with an etching hard mask of silver nanoparticles that are deposited by wet chemical electroless deposition on silicon surfaces.

The new concept of the solar cell is based on the semiconductor-insulator-semiconductor (SIS) layer sequence produced by Atomic Layer Deposition (ALD). A thin tunnelling oxide (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) with a thickness of 5–20 Å and a 300 nm transparent conductive oxide (Al doped ZnO or In doped SnO<sub>2</sub>) around 1D silicon nanostructures have been realized using Plasma Assisted ALD approach (Oxford Plasma, OpAL).

The first prototype reached an open-circuit voltage of 80mV and a short-circuit current density of  $23\text{mA}/\text{cm}^2$ .

The influence of the thickness and chemical nature of the tunnelling oxide will be discussed. Back side contacts of Ti/Al or Ti/Ag were realized using sputtering. From literature it is known that the planar SIS solar cell can reach an energy conversion efficiency of approx 15%. Absorption of visible and infra-red light is significantly enhanced in nanowires compared to planar layers of identical thickness. Thus, wet chemically etched silicon nanowires have the potential for even higher energy conversion efficiencies compared to the planar SIS solar cells. The morphology, crystallographic and surface structure, optical and solar cell properties will be presented and discussed in details.

10:00am **TF+EN-MoM6 Ultrathin Al<sub>2</sub>O<sub>3</sub> for c-Si Solar Cells: Differences in Passivation by Thermal and Plasma ALD-Synthesized Films**, *G. Dingemans*, *N.M. Terlinden*, *M.L.C. Adams*, *H.B. Profijt*, *M.M. Mandoc*, *M.C.M. van de Sanden*, *E.W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Ultrathin films of Al<sub>2</sub>O<sub>3</sub> synthesized by ALD at low substrate temperatures (200 °C) have recently demonstrated their potential as surface passivation material in c-Si photovoltaics enabling solar cell efficiencies up to 23.4%.

So far, the best results were obtained by plasma ALD Al<sub>2</sub>O<sub>3</sub> but recently it was shown that similar excellent results can be obtained by thermal ALD [1]. For both methods, Al<sub>2</sub>O<sub>3</sub> yield excellent lifetimes after annealing (at 400 °C) on both *p*- and *n*-type Si wafers with the best results corresponding to ultralow surface recombination velocities < 1 cm/s (for 3.5 Ohm cm *n*-type *c*-Si). However, also several striking differences have been observed in terms of the underlying passivation mechanism as will be addressed in this contribution. From capacitance-voltage (C-V) measurements, corona charging experiments and optical second harmonic generation (SHG) it was found that Al<sub>2</sub>O<sub>3</sub> deposited with thermal ALD contains a lower negative fixed charge density (~10<sup>12</sup> cm<sup>-2</sup>) than plasma ALD (> 5·10<sup>12</sup> cm<sup>-2</sup>). This indicates that field-effect passivation (i.e., shielding of one type of charge carriers from the surface) is less important for thermal ALD. On the other hand, it was observed that chemical passivation (i.e., reduction of interface defect states) is very important for both thermal and plasma ALD Al<sub>2</sub>O<sub>3</sub>. Relatively low interface defect densities *D<sub>i</sub>* of <10<sup>11</sup> eV<sup>-1</sup> cm<sup>-2</sup> were found for both methods after anneal. However, for as-deposited Al<sub>2</sub>O<sub>3</sub>, the interface defect density (and correspondingly the surface recombination velocity) is significantly poorer for plasma ALD Al<sub>2</sub>O<sub>3</sub> than for thermal ALD Al<sub>2</sub>O<sub>3</sub>. From vacuum ultraviolet (VUV) emission measurements, it has been found that the high *D<sub>i</sub>* can be attributed to plasma radiation damage by photons with an photon energy of ~9.5 eV. Furthermore, it will be shown that the difference in importance of field-effect passivation explains several differences observed in the passivation performance for thermal and plasma ALD Al<sub>2</sub>O<sub>3</sub> (e.g., the minimum thickness required for excellent passivation).

[1] G. Dingemans, M. C. M. van de Sanden, W. M. M. Kessels, *Electrochem. Solid-State Lett.*, 13, H76 (2010).

10:40am **TF+EN-MoM8 Cathodoluminescent and Photoluminescent Properties of Pulsed Laser Deposited Thin Phosphor Films**, *O.M. Ntwaeaborwa\**, *P.D. Nsimama, J.J. Dolo*, University of the Free State, South Africa, *M.S. Dhlamini*, University of the Free State and CSIR, South Africa, *E. Coetsee, J.J. Terblans, H.C. Swart*, University of the Free State, South Africa **INVITED**

Phosphors have many uses today, such as information display, medical imaging, and theft prevention. The phosphors are often used as powders, even though thin films offer higher resolution and better chemical stability. We have investigated the cathodoluminescent (CL) and photoluminescent (PL) properties of thin films of several phosphors (e.g. SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>; SiO<sub>2</sub>:PbS; Gd<sub>2</sub>O<sub>3</sub>:Tb<sup>3+</sup>; SiO<sub>2</sub>:Ce<sup>3+</sup>,Tb<sup>3+</sup> and Y<sub>2</sub>SiO<sub>5</sub>:Ce<sup>3+</sup>) that were ablation deposited onto Si (100) substrates using either conventional pulsed laser deposition (PLD) or pulsed reactive crossed beam laser ablation (PRCLA). Several deposition parameters were varied, including vacuum versus partial pressure of gas (O<sub>2</sub> or Ar), type of laser pulse, and substrate temperature using either a 307 nm XeCl or 248 nm KrF excimer laser. The CL spectrum and intensity were measured in vacuum from films irradiated with 2 keV electrons for a prolonged period of time, while PL data were collected in air under excitation by either a 325 nm HeCd laser or a monochromatized xenon lamp. Both the CL and PL intensities were strongly dependent on the deposition conditions and post-deposition annealing. Data from scanning electron microscopy (SEM) and atomic force microscopy (AFM) show that the major influence of the deposition conditions on the CL/PL intensity was through changes in the morphology and topography of the films, which affects light scattering and out-coupling. Finally, the CL intensity from the films decreased significantly during prolonged electron beam irradiation. The degraded CL intensity resulted from the formation of non-luminescent oxide layers on the film surfaces. The chemical composition and electronic states of the 'dead' layers were analyzed using x-ray photoelectron spectroscopy (XPS). The influence of the various deposition conditions on the luminescent intensities will be discussed. The mechanism leading to lower CL intensities will be concluded to be electron stimulated surface chemical reactions.

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\* Paul Holloway Award Winner

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