Electronic Materials and Processing
Room: 314 - Session EM+NS+TF-FrM

Transparent Electronics
Moderator: Lisa M. Porter, Carnegie Mellon University

9:00am **EM+NS+TF-FrM3 Transparent Amorphous Oxide Semiconductors: Interfacial Chemistries and New Applications**, ***Gregory Herman***, Oregon State University **INVITED**

During the past decade research in the area of transparent amorphous oxide semiconductors (TAOS) has increased substantially due to the ability to fabricate thin film transistors (TFT) at relatively low processing temperatures while still maintaining large electron mobilities. The primary applications for these materials include active matrix displays with the possibility for integration onto flexible polymeric substrates. More recently potential applications have expanded to include non-volatile memory, sensing, and memristive neurological networks. We have studied amorphous zinc tin oxide (ZTO) and indium gallium zinc oxide (IGZO) that have been deposited by both vacuum and solution based approaches. The electrical characteristics of the films have been evaluated in both TFT and metal-insulator-metal memristive devices. Excellent device characteristics have been obtained, however we have found that surface impurities can strongly affect device stabilities. We have found that the chemistry of absorbed species on the back-channel strongly influences the bias stress stabilities of ZTO and IGZO TFTs, while reactions at the Al/ZTO interface leads to the resistive switching characteristics of memristors, and post annealing leads to interfacial reactions and modifies the Schottky barrier for Pt/IGZO diode structures. To better understand the role of interfacial reactions on TFT and memristive devices we have developed methods to prepare clean well defined surfaces for ZTO and IGZO, and further characterized there surface and interface properties with X-ray photoelectron spectroscopy and secondary ion mass spectrometry.

9:40am **EM+NS+TF-FrM5 HMDSO/O_2-Plasma-Deposited Organic-Inorganic-Hybrid Materials as Gate Dielectrics for MgZnO Thin Film Transistors and Encapsulation Layers for Solar Cells**, *Y.S. Li, C.H. Tsai, I.C. Cheng*, ***Jian-Zhang Chen***, National Taiwan University, Taiwan, Republic of China

Organic-inorganic hybrid materials can be deposited from hexamethyldisiloxane (HMDSO) diluted with oxidants using plasmas technology. The properties of the deposited material can be controlled by varying the dilution ratio of the oxidants. The chemical compositions can vary from polymer-like (organic-like) to SiO_2-like (inorganic-like) depending on the oxidant dilution ratio and the process power. In this paper, we report two applications of HMDSO/O_2-plasma-deposited organic-inorganic-hybrid materials developed in our group: (1) as gate dielectrics of MgZnO TFTs, and (2) as the encapsulation layers for organic-inorganic hybrid solar cells.

The inorganic/organic component ratios in hybrid films were tailored by varying the process power and the O_2/HMDSO flow rate ratio. The FTIR analysis and contact angle measurement show that higher deposition power and/or larger O_2/HMDSO flow rate ratio result in more SiO_2-like films. For rf-sputtered MgZnO TFTs, a more organic-like film affords a better interface to the MgZnO active layer and higher dielectric constant, leading to a smaller threshold voltage and a steeper subthreshold slope; while an inorganic-like film has lower leakage currents, resulting in a larger on/off current ratio in the transistors. The TFT with an organic-inorganic-hybrid gate dielectric deposited at an O_2/HMDSO ratio of 40 and process power of 30 W exhibits a threshold voltage of 6.8 V, a subthresold slope of 0.48 V/dec, an on/off current ratio of $>10^7$ and a linear mobility of ~60 $cm^2V^{-1}s^{-1}$, respectively. We also have demonstrated that this O_2/HMDSO-plasma-deposited organic-inorganic material can be used as an efficient single-layer encapsulation technique for organic photovoltaic cells. Calcium test was used to evaluate the water vapor transmission rate (WVTR) of the barrier film deposited on a polyimide foil. A water vapor transmission rate of 3.6×10^{-6} g/m^2-day was obtained for a 1.5 um-thick single permeation layer. Inverted type organic photovoltaic passivated by the hybrid material was used to evaluate the effectiveness of this encapsulation. Efficiency decay was not observed in the cell coated with this encapsulation layer after 3000-hour exposure to the air; on the contrary, the un-encapsulated counterpart cell degraded rapidly and completely failed after 120-hour exposure to the air. The result shows that this single-layer hybrid material encapsulation can enhance the stability of organic photovoltaic cell. The cell life time is greatly improved.

10:00am **EM+NS+TF-FrM6 Solution Processed Oxide Semiconductor and Dielectric Thin Films: Towards High Performance, Low Temperature ZnO Field-effect Transistors with Low Operation Voltage**, ***Yu Liu***, *H. Katz*, Johns Hopkins University

Solution processing is a preferred method for manufacturing large-area low-cost electronic devices. High performance metal oxide semiconductor-based field-effect transistors can be fabricated in this manner. For applications of flexible electronics, a low processing temperature is required to avoid overheating of the substrate material. It is a challenge to fabricate a dense impurity-free oxide semiconductor film at low temperature. A water-based ZnO precursor with ammine-hydroxo complex was introduced to decrease the processing temperature. However, repeated time-consuming centrifugation and decantation steps are required in this process.

To simplify the processing steps we discovered a new strategy to prepare aqueous ZnO precursor. Based on this precursor, ZnO FETs with a benchmark dielectric SiO_2 have been fabricated at 200 °C. The transistors exhibited promising performance with a saturation field-effect mobility of 0.7 $cm^2\cdot V^{-1}\cdot s^{-1}$ and a typical on/off current ratio on the order of 10^4. To prepare the precursor, zinc nitrate hexahydrate and acetylacetone were dissolved in ammonium hydroxide with a concentration of 0.6 M. As prepared precursor was then filtered and dilute it with DI water. A similar strategy was applied in the preparation of aqueous zinc tin oxide precursor with tin fluoride as tin source.

Based on a redox chemical reaction between fuel and highly exothermic oxidizer, a combustion processing method has been found to be promising for decreasing the annealing temperature of oxide semiconductor thin films. In this study, combustion processing strategy was used in preparing high capacitance ion-incorporated alumina dielectrics at 200 °C by using urea as the fuel and aluminum nitrate nonahydrate as oxidizer.

Both zinc tin oxide and sodium-incorporated alumina low temperature precursors showed strong exthothermic reaction peaks at temperatures lower than 200 °C. This suggests a conversion from ammine-hydroxo/combustion precursor to solid zinc tin oxide/sodium incorporated alumina thin films at a temperature lower than 200 °C. A sharp (002) peak is shown in the XRD pattern of 200 °C processed ZnO thin film, which demonstrates a wurtzite crystal structure.

The high-k dielectrics exhibited a good compatibility with our low temperature ZnO precursor and excellent transistor performance has been achieved in these devices. With this, we are able to fabricate low temperature low voltage transistors on plastic substrates such as polyimide. This low temperature ZnO precursor could also be applied to fabricate flexible inverters in combination with p-type solution processed polymer semiconductors, such as PBTTT and TIPS-pentacene.

10:40am **EM+NS+TF-FrM8 Metal Oxide Conductors and Semiconductors: From Materials to Device Applications**, ***Elvira Fortunato***, *R. Martins*, FCT-UNL and CEMOP-UNINOVA, Portugal **INVITED**

Transparent electronics has arrived and is contributing for generating a free real state electronics that is able to add new electronic functionalities onto surfaces, which currently are not used in this manner and where silicon cannot contribute [1,2]. The already high performance developed n- and p-type TFTs have been processed by physical vapour deposition (PVD) techniques like rf magnetron sputtering at room temperature which is already compatible with the use of low cost and flexible substrates (polymers, cellulose paper, among others). Besides that a tremendous development is coming through solution-based technologies very exciting for ink-jet printing, where the theoretical limitations are becoming practical evidences. In this presentation we will review some of the most promising new technologies for n- and p-type thin film transistors based on oxide semiconductors and its currently and future applications.

[1] E. Fortunato, P. Barquinha, and R. Martins, "Oxide Semiconductor Thin-Film Transistors: A Review of Recent Advances," Advanced Materials, vol. 24, pp. 2945-2986, Jun 2012.

[2] P. Barquinha, R. Martins, L. Pereira and E. Fortunato, Transparent Oxide Electronics: From Materials to Devices. West Sussex: Wiley & Sons (March 2012). ISBN 9780470683736.

11:20am **EM+NS+TF-FrM10 Influence of Oxygen Diffusion in Transparent $In_{0.9}Sn_{0.1}O_x$ Film on Effective Work Function Change**, ***Toshihide Nabatame***, NIMS, Japan, *H. Yamada*, Shibaura Institute of Technology, Japan, *A. Ohi*, NIMS, Japan, *T. Oishi*, Shibaura Institute of Technology, Japan, *T. Chikyo*, NIMS, Japan

The $In_{0.9}Sn_{0.1}O_x$ (ITO) films is widely used as transparent electrodes in optical and optoelectronic devices. The work function (WF) of the ITO film was generally evaluated by optical measurements such as ultraviolet photoemission spectroscope and Kelvin probe. However, the optically measured WF differs from the effective work function (EWF) estimated by electrical measurement. The influence of oxygen diffusion in ITO film on EWF change has not been also understood. In this paper, we systematically investigate EWF change of ITO film by oxidation and reduction annealing. We also examine oxygen diffusion coefficient (D) of ITO film, using isotope ^{18}O tracer, to discuss influence of oxygen diffusion of ITO film on EWF change.

The ITO films were prepared under an Ar/O_2 by sputtering using an $In_{0.9}Sn_{0.1}O_x$ target. The ITO-gated metal-oxide-semiconductor (MOS) capacitors with HfO_2 and SiO_2 gate insulators were fabricated to estimate EWF value of ITO film. The ITO (150 nm)/SiO_2/Si films were annealed at 300 – 500 °C for 30 min under 10^4 Pa of ^{18}O isotope (99%) gas to obtain D value.

The resistivity of ITO film, which consists of cubic structure, shows an almost same value regardless of oxidation and reduction annealing temperatures. The EWF of ITO-gated MOS capacitors significantly changes from 4.4 to 5.2 eV as the oxidation annealing temperature increases from 250 to 350 °C. The EWF change is saturated at 350 °C. On the other hand, the EWF value decreases in reduction annealing temperature ranging from 200 to 350 °C. This must be due to oxygen introduction and removal in ITO film during oxidation and reduction annealing, respectively. To understand the mechanism of oxygen transfer in the ITO film, we examine D behavior of ITO film. The ITO film has a large D value of about a 1.1X10-20cm2/s at 300 °C and a small activation energy (Ea) of about 1.4 eV. We found that the D and Ea values are similar to those of grain boundary in monoclinic ZrO_2. This results indicate that oxygen diffusion of ITO film occurs even at low temperature of 300 °C and affects to the EWF change during oxidation and reduction annealing at around 300 °C.

11:40am **EM+NS+TF-FrM11 Transparent Conducting Films from Ultraporous Aerogels of Single-Walled Carbon Nanotubes / PEDOT:PSS Composites**, ***Xi Liu***, *L.M. Porter*, *M.F. Islam*, Carnegie Mellon University

In this study we report on the fabrication and characterization of ultralight (>99% porosity) aerogels based on single-walled carbon nanotubes (SWCNTs) and poly(ethylene dioxythiophene) : poly(styrene sulfonate) (PEDOT:PSS), that are electrically conducting and highly stretchable. The aerogels were created by critical-point drying of aqueous elastic co-gels of individually dispersed SWCNTs mixed with PEDOT:PSS to yield either free-standing films or thin films supported on flexible (PET) or glass substrates; the nanotubes substantially reduce the percolation threshold of PEDOT:PSS. These transparent conductors with sheet resistance of 35 ohm/sq and 60% transparency (at 550 nm) also proved to be highly flexible – they can be repeatedly stretched to 20% with < 1% change in resistivity. The electrical, optical, mechanical, and microstructural properties of these materials will be presented, along with their application in devices.

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