Transparent Conductors and Printable Electronics Focus Topic
Room: Hall B - Session TC-TuP

Transparent Conductors and Printable Electronics Poster Session

TC-TuP2 A Universal Method of Producing Transparent Electrodes Using Wide-Bandgap Materials: Direct Ohmic Contact to *p*-AlGaN, *H.D. Kim, S.W. Kim,* ***K.H. Kim****, S.J. Kim,* Korea University, Republic of Korea*, M.D. Kim,* Chungnam National University, Republic of Korea*, T.G. Kim*, Korea University, Republic of Korea

Indium-doped tin oxide (ITO) is the most popular transparent conductive electrodes (TCEs) used in flat screen displays and lighting technologies for decades. However, due to indium's limited supply and increasing cost, there has been a big push for many years to find alternatives or replacements of ITO (i.e., indium-free TCEs); many scientist and engineers have been working with zinc oxide and other metal-oxide materials but this area still remains quite challenging. Here we worked towards something different, developing new ways to give a current path between the TCEs using ordinary wide-bandgap materials and p-(Al)GaN layers via conducting filaments (CFs), which can be formed using electrical breakdown (or forming) processes, for ultraviolet light-emitting diodes (UV LEDs).

UV LED is one of the eco-friendly optical sources for different wavelengths in the UV A to C regimes (200–400 nm), useful for various applications including sterilization and high color rendering index lighting. However, currently, the external quantum efficiency of the UV LED, particularly in UV-C bands, is extremely low (3-11%). One of the primary reasons for this low efficiency is a large absorption in narrow-bandgap contact layers for ohmic contact. To fundamentally solve this problem, we should obtain a direct ohmic contact to the p-AlGaN layers using UV-transparent conductive electrodes, as depicted in the right figure below. However, with conventional ohmic methods, it is almost impossible to make such contact and therefore no report has been made so far. In this article, we present a universal method of producing transparent electrodes with high conductivity and high optical transmittance in the UV A to C regimes (as well as visible-to-infrared regimes) using electrical breakdown to form CFs providing a current path between the TCEs and the semiconductor, which leads to a large reduction in their contact resistance. As a result, we found the contact resistance between the TCEs and the p-GaN layers (or p-AlGaN layers) to be on the order of 10^{-5} $\Omega \cdot cm^2$ (or 10^{-3} $\Omega \cdot cm^2$) while optical transmittance was maintained at up to 95% for the AlN-based TCEs at 250 nm.

TC-TuP4 Bending Properties of In and Ga Doped Zinc Oxide Films Deposited on Plastic Substrates by Magnetron Sputtering, ***K. Nagamoto****, K. Kondo,* LINTEC Corporation, Japan*, K. Ishii*, Utsunomiya University, Japan

Transparent conductive oxides (TCO) on polymer substrates are prospected as a key material for next-generation devices such as flexible displays and photovoltaics. The advantages of polymer substrates include light-weight, low cost, a multiplicity of materials with tailored properties, shock absorption and highly flexibility. However, polymer substrates also have disadvantages such as low heat resistance and large thermal expansion coefficient compared with glass substrates. A main challenge for an efficient TCO on polymer substrate is not only to choose conductive oxide materials having capability of growing at low substrate temperature, but also to develop a deposition processes in order to obtain good electrical characteristics. Thus, in this study structural, electrical and optical properties of highly transparent conductive polycrystalline Ga-doped ZnO (GZO) and In, Ga-doped ZnO (IGZO) films deposited on plastic substrates at below 100 °C by magnetron sputtering were investigated. The dependences of crystal structure, electrical and optical properties of the GZO and IGZO films on plastic substrates have been systematically studied. The surfaces of plastic substrates and optically properties were controlled by coating buffer layers (CBLs).

The aim of this study is to investigate the effect of surface roughness of plastic substrates on characteristics of GZO and IGZO films of less than 150 nm thickness, such as structural and electrical characteristics. Then optically properties of GZO and IGZO films, for example transmittance, reflectance, yellow index, haze, a* and b* value, were depend on GZO and IGZO films thickness and CBLs. The GZO and IGZO films in the thicknesses range from 20 to 120 nm were prepared by magnetron sputtering. The resistivity and average transmittance in the visible wavelength region of GZO films of 120 nm thickness on plastic substrates were 1.0 x 10^{-3} ohm·cm and more than 85 %, respectively.

TC-TuP5 Influence of Rapid Thermal Annealing Treatment on Various Properties of Texture-Etched Al- or Ga-Doped ZnO Thin Films Deposited by Magnetron Sputtering, *T. Minami, J. Nomoto,* ***T. Miyata****, T. Yamanaka*, Kanazawa Institute of Technology, Japan

This paper describes an investigation of the influence of a rapid thermal annealing (RTA) treatment on various properties of transparent conducting Al- or Ga-doped ZnO (AZO or GZO) thin films that was conducted in an effort to develop thin-film transparent electrodes suitable for thin-film solar cell applications. These doped ZnO thin films were deposited by an r.f. power superimposed d.c. magnetron sputtering deposition using AZO or GZO target : prepared with Al_2O_3 contents of 0.5-2 wt.% or Ga_2O_3 contents of 0.5-5.7 wt.%, respectively. The optical and electrical properties and texture-etched surface structures as well as the stability of electrical properties after use for long terms in moist environment in these thin films were found to be considerably influenced after heat treatment with RTA at 500ºC for 5 min in air. In particular, the obtained electrical properties in these thin films were considerably dependent on the RTA treatment conditions as well as the kind and content of impurity doped into the films. For example, the heat treatment with RTA always decreased the carrier concentration in both the AZO and GZO films, irrespective of the doped impurity content, whereas the resulting carrier concentration in as-deposited AZO and GZO thin films increased as the impurity content doped into the films was increased. In addition, the Hall mobilities in both the AZO and GZO films doped with impurity contents up to approximately 1.25 at.% always decreased after heat treatment with RTA, which is in contrast to the slight increase of the Hall mobilities exhibited in films doped with an impurity content above approximately 1.5 at.%. The etch pit size developed in AZO and GZO films that were surface textured by wet-chemical etching in 0.2 mol./l HCl at 25ºC tended to increase as the content of impurity doped in the films was increased up to approximately 2.5 at.%; however, the etch pit size obtained in GZO films decreased as this content was increased further. It should be noted that the heat treatment with RTA resulted in considerably enhanced etch pit size in these films, irrespective of the kind and content of doped impurity. As a result, in the films that were wet-chemically etched after being heat treated with RTA, the transmittance and the haze value in the near infrared range of 800-1200nm both increased as the size of the etch pits increased. It should be noted that the improvement in the transmittance and the haze value obtained in texture-etched AZO and GZO thin films heat treated with RTA is sufficient to enable the use of the surface textured these films described above for thin-film transparent electrode applications in thin-film solar cells.

Transparent Conductors and Printable Electronics Focus Topic
Room: 102 B - Session TC+EM+TF-WeM

Oxide and Flexible Electronics
Moderator: G. Exarhos, Pacific Northwest National Laboratory, L.M. Porter, Carnegie Mellon University

8:00am **TC+EM+TF-WeM1 Characterization of Thermal Plasma....**, ***M. Kinsler***, *K. Teh, R. Harrison*, San Francisco State University

A low-vacuum thermal plasma system is designed and developed to enable plasma-enhanced chemical vapor deposition and rapid plasma annealing of metal oxide thin films within the same system. Using this system, we have successfully synthesized optically transparent and electrically conductive, nanocrystalline zinc oxide (ZnO) thin films, with average grain sizes of between 75 nm and 150 nm at substrate temperatures ranging from 550C to 600C. Prior to synthesis, argon and oxygen are first introduced into the synthesis vessel, consisting of a quartz tube positioned in the center of an inductive copper coil, at 42 sccm and 0.07 sccm, respectively, with a background vacuum level of 1.15 PSIA. During synthesis, pure solid zinc precursor is melted and ionized by thermal plasma, and reacted with oxygen to form ZnO which is deposited on the substrate. Keeping the vessel pressure and substrate temperature constant, the growth rate of the ZnO films is approximately 15 nm/min. Using the same system, the ZnO-coated substrate can next be mounted on a different fixture and be annealed by thermal plasma at temperatures from 300C to 800C (0.25 to 0.38 T_m of ZnO) in a pure argon environment at 1.15 PSIA background pressure. Comparing the as-synthesized and annealed samples using techniques such as scanning electron microscopy (SEM), x-ray diffraction (XRD), UV-Vis spectroscopy, and four-point probe sheet resistance measurements, we observed improvements in the properties of the post-annealed ZnO films in the following ways: 1) ZnO grain size increased from approximately 50 nm to 100 nm, 2) the number of grains decreased and hence the number of grain boundaries decreased, 3) grain morphology became smoother possibly indicating less internal strain, and 4) sheet resistance of the film decreased. We hypothesize the improved electrical properties are attributed to the reduction in both grain boundaries and internal stress--both of which are known to reduce electron mobility. Synthesizing and annealing metal oxides, such as ZnO, in the same system would reduce overall turnaround time as moving samples between systems is avoided. Ultimately, this method could pave the way for the production of high-quality, optically transparent, and electrically conductive metal oxide semiconductor thin films in a single, rapid operation within a low-cost, small-footprint benchtop system.

8:20am **TC+EM+TF-WeM2 Effects of High Pressure on InGaZnO Thin Film**, ***S.H. Yoon***, *Y.J. Tak, D.H. Yoon, U.H. Choi, H.J. Kim*, Yonsei University, Republic of Korea

Since Hosono et al presented amorphous oxide semiconductor (AOS) thin film transistor (TFTs) in 2004, AOS TFTs have been attracting attention from many researchers for a decade [1]. AOS TFTs have high enough mobility for organic light emitting diodes, and high resolution display. One of the technologies for improving electrical characteristics is high pressure annealing [2,3]. We studied pressure effects on AOS TFTs without additional annealing process. We applied pressure on inverted staggered InGaZnO (IGZO) TFTs. IGZO layer (50nm) was deposited by sputtering. SiO_2 layer (200 nm) was deposited by plasma enhanced chemical vapor deposition (PECVD) as a gate insulator and an etch stop layer, respectively. MoW (200 nm) was deposited by sputtering as a gate metal, and Mo was deposited by sputtering as source/drain metal. Applied gas was N_2, and applied pressures varied 1MPa, 3 MPa, and 5 MPa for 2 hours, respectively. Figure 1 shows transfer curves on different pressure, and mobility and sub-threshold swing were improved. References:

[1] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, and H. Hosono, Nature **432**, 488-492 (2004).

[2] K.H. Ji, J.-I. Kim, H.Y. Jung, S.Y. Park, R. Choi, U.K. Kim, C.S. Hwang, D. Lee, H. Hwang, and J.K. Jeong, Appl. Phys. Lett. **98**, 103509 (2011).

[3] R.S. Rim, W.H. Jeong, D.L. Kim, H.S. Lim, K.M. Kim, and H.J. Kim, J. Mater. Chem. **22**, 12491-12497 (2012).

8:40am **TC+EM+TF-WeM3 Surface Chemistry of Amorphous $InGaZnO_4$ Films**, *B. Flynn*, Oregon State University, *S.A. Thevuthasan*, Pacific Northwest National Laboratory, *H. Bluhm*, Lawrence Berkeley National Laboratory, ***G.S. Herman***, Oregon State University

Thin film transistors (TFT) utilizing amorphous $InGaZnO_4$ (a-IGZO) have multiple applications in high performance electronic devices, from flat-panel displays and integrated circuits to non-volatile memories. A-IGZO enables low processing temperatures, while retaining large electron mobilities, and low operation voltages and off currents. These stable carrier transport and electrical characteristics are crucial for many applications, and can be strongly affected by backchannel surface chemistry of a-IGZO TFTs. Understanding the chemistry of absorbed species and their effect on the electronic structure of a-IGZO is critical to improve the stability of these TFTs, while reactions at the metal/a-IGZO interface strongly influences switching characteristics of resistive random access memories. In this study we have characterized sputter-deposited thin films of a-IGZO using in-situ x-ray photoelectron spectroscopy (XPS). Both standard Al Ka and synchrotron-based radiation were used to investigate chemical changes at the a-IGZO surface. We have observed surface segregation and desorption of oxygen containing impurities for anneals up to 300 °C in ultra-high vacuum (UHV). The O 1s spectra were very sensitive to the local chemistries at the surface, and we used these spectra to characterize the interaction of molecular oxygen and water with well-defined a-IGZO surfaces for a wide range of temperatures and exposures. It was found that water adsorbs both molecularly and dissociatively at temperatures below 200 K, with corresponding downward band bending of ~0.15 eV for >20 Langmuir exposures. Oxygen did not appreciably affect the XPS spectra for the temperatures and exposures studied. We have also characterized the initial growth of platinum metal films on a-IGZO. The XPS characterization of chemical state differences of the elements and band bending due to surface effects will be discussed along with the film processing conditions.

9:00am **TC+EM+TF-WeM4 UV Radiation Effect on Electrical Characteristics of Passivated IGZO TFTs**, ***Y.J. Tak***, *D.H. Yoon, S.H. Yoon, U.H. Choi, H.J. Kim*, Yonsei University, Republic of Korea

Ultraviolet (UV) radiation effects have been intensively researched in oxide thin film transistors (TFTs). In general, UV radiation induces the increase of off-current and the existence of hump effect.[1] These changes of electrical properties in non-passivated oxide TFTs are almost recovered to original states.[2] However, back surface of oxide TFTs is sensitive to oxygen and humidity, passivation is key layer for stability and reliability on device. For this reason, we investigated the effects of post UV treatment on the SiO_2 passivated indium gallium zinc oxide (IGZO) TFTs, specifically by irradiating UV spectrum of different wavelength, intensity, and treatment time. We performed light treatment of wavelength of 365 nm and 185 nm. And then varied power intensities were performed 64.66 mW/cm^2, 0.9375 mW/cm^2 respectively. These UV experiments were carried out with various treatment time of 10 min, 20 min, 30 min, and 60 min. As a result, the increment of off-current was shown which was higher in 185 nm radiated one than that of 365 nm, and increase of the intensity and treatment time led to increase in off-current and hump effect. Also, these changes were not restored to its original state after relaxation period. The result of experiment indicated that SiO_2 passivated-TFTs need to block the UV radiation because of incompletely vanished hump effect that causes degardation on the devices.

9:20am **TC+EM+TF-WeM5 Processing Water-based TFT Materials**, ***D.A. Keszler***, Oregon State University **INVITED**

High-quality semiconductor and dielectric films can readily be deposited from aqueous solutions containing polynuclear metal nonoclusters. To support the continued development of the films and their use, new techniques have been developed to remove residual mobile ions associated with hydroxide. Examples of incorporation of the resulting films into TFTs and MIM devices will be described.

10:40am **TC+EM+TF-WeM9 Printed Circuits and Sensing Systems**, ***G.L. Whiting***, *T. Ng, D.E. Schwartz, B.J. Van Tassell,* Palo Alto Research Center, *A.M. Gaikwad,* University of California, Berkeley, *D.A. Steingart,* Princeton University, *J. Veres*, Palo Alto Research Center **INVITED**

Low-temperature processable, mechanically compliant materials and the use of printing as a manufacturing technique enables fabrication of flexible electronic systems over large areas at low-cost, potentially allowing for novel applications and more widespread use of such systems. In this report recent developments made in printed systems technology will be presented, including examples of printed complementary circuits, sensors and power sources fabricated using techniques such as ink-jet, screen and gravure

printing; as well as integration of these devices into functional printed systems.

Circuits in this work are based on ink-jet printed complementary organic field-effect transistors (FETs), which benefit from simplified design in comparison with unipolar circuits. Design rules for these devices have been determined and models describing the characteristics of these FETs have been developed to aid in designing circuits that can tolerate variation in the performance of printed transistors. In addition to ink-jet, devices have also been fabricated using a gravure method, providing a potential route to large-scale production of printed electronics. Flexible, printed batteries suitable for driving these systems have also been developed and will be described.

11:40am **TC+EM+TF-WeM12 Low Temperature Integration of Metal Oxide Thin Films for Flexible Electronic Applications**, ***P. Joshi***, *M. Shao, K. Xiao, S. Killough, P. Kuruganti, C. Duty*, Oak Ridge National Laboratory

In the last few years, there has been growing interest in the development of flexible electronics to meet the manufacturing technology demands of higher functionality, reduced material usages and device dimensions, and lower consumption of products. Metal oxide thin films are attractive for multifunctional flexible system development due to their very low cost, tunable properties, and simple electronic interface. Low temperature processing of metal oxides thin films is critical to exploit their unique structural, optical, and electrical properties for a wide range of active and passive device applications, such as flat panel displays, organic electronics, RFIDs, antennas, inductors, capacitors, sensors, batteries and energy harvesting devices. In the present paper; we report on the pulse thermal processing (PTP) processing of metal oxide thin films integrated on flexible substrates. The PTP technique is being explored for the development of cost-effective, high yield, and high quality integrated thin films and devices on low temperature substrates. This technology offers the ability to expose large areas of material to an extremely high energy flux (up to 20 kW/cm^2) during a very short period of time (as low as 30 microseconds) meeting the demands of roll-to-roll manufacturing technology. The details of the PTP processing of metal oxide thin films with specific examples related to single and multilayer thin film structures incorporating ZnO and ITO thin films are presented in this paper. The influence of the low processing temperature (<100°C) on the thin film growth and properties has been investigated in terms of process-structure-property correlation study. The impact of the substrate on the thin film growth and properties has also been analyzed. The low thermal budget PTP processing significantly impacts the microstructural, optical, and electrical characteristics on low temperature flexible substrates. The combination of low temperature deposition techniques and low thermal budget PTP processing show promise for multifunctional thin film material and device integration for flexible electronics.

Transparent Conductors and Printable Electronics Focus Topic
Room: 102 B - Session TC+EM+EN+TF-WeA

Transparent Conductors and Photovoltaics
Moderator: G.S. Herman, Oregon State University, G.L. Whiting, Palo Alto Research Center

2:00pm **TC+EM+EN+TF-WeA1 Metal Nanowires-based Composite Transparent Electrodes for Photovoltaics**, ***J. Moon***, *A. Kim, Y. Won*, Yonsei University, Republic of Korea **INVITED**

To fabricate cost-effective solar cells, it is imperative to develop a low cost transparent electrode with low resistivity and high transparency. Although crystalline indium tin oxide (ITO) has been widely adopted as a transparent electrode in solar cells, it is an undesirable material for use in low cost solar cells because of the scarcity of indium and its high deposition cost. Silver nanowires (AgNWs) network films have recently attracted substantial interest as a transparent conducting material. Transparent electrodes composed of random AgNW networks can be readily achieved by simple and scalable solution processing such as spin coating and rod coating from AgNWs dispersion. However, the AgNWs film is easy to undergo local oxidation and melting on a heated substrate, which adversely affects the conductivity of the AgNWs film. In addition, the low carrier collecting efficiency of AgNW films could pose another hurdle. The limited contact area of AgNWs with *n*-type or buffer layers is incapable of effectively collecting the charge carrier generated at the *p*-*n* junction. Here, we propose a sandwich composite electrode structure of Al doped ZnO (AZO)/AgNWs/AZO fabricated by all solution processes. The AZO/AgNW/AZO composite structure is suitable for cost-effective large area fabrication, because it involves relatively low-cost materials, and it is prepared by scalable solution processes instead of high-vacuum process. The AgNWs inserted in AZO layers reduced sheet resistance dramatically of a solution processed AZO layer, and the density of AgNWs plays an important role in determining the film conductivity and optical transparency. The AZO underlayer acts as an *n*-type buffer layer as well as a surface flattener against the absorber layer, while the upper layer prevents the AgNWs from local melting-induced disconnection. As a result, the thermal stability of the AgNWs was enhanced and the adhesion of AgNWs to the substrate was improved. Such a composite electrode is also capable of effective charge carrier collection due to filling the empty space unoccupied by AgNWs with AZO materials as well as resulting in a better surface smoothness. We applied the AZO/AgNW/AZO composite electrode on the CIGS thin film solar cells and observed the power conversion efficiency of 11% comparable to reference ITO used solar cells. We also demonstrated the similar approach involving copper nanowire (CuNW) in form of AZO/CuNW/AZO. Our low temperature processed AZO/CuNW/AZO composite electrode at 70°C exhibited highly transparency (> 88%) and low sheet resistance (< 25 ohm sq^{-1}) as well as good thermal oxidation stability against the exposure to air and flexibility.

2:40pm **TC+EM+EN+TF-WeA3 Modeling and Characterization of Ag Nanowire-Based Transparent Conductors: Towards Optimization of Electrical and Optical Properties**, ***S. Narayanan***, *C. Treacy, M.R. Bockstaller, L.M. Porter*, Carnegie Mellon University

Many contemporary devices, including displays, solar cells and LEDs, employ transparent conducting films. The traditional materials for transparent conductors are transparent, conductive metal oxides, primarily tin-doped indium oxide (ITO). However, due to the increased cost of indium and other challenges with ITO, significant effort has been devoted to develop alternatives that are cheaper, flexible, and compatible with a variety of substrates. One alternative is based on random networks of solution-processed silver nanowires (Ag-NWs). While being comparable to ITO in their electrical and optical properties, the high variability in films of Ag-NWs fabricated by solution-processing is a major concern for scalability and reproducibility. The variability in NW coverage can be attributed to instability of the NWs in solution, which can be addressed by the use of polymer additives and modified solution chemistries. For example, we found that composites of Ag-NWs and poly(ethylene dioxythiphene):poly(styrene sulfonate) (PEDOT:PSS) can be deposited more uniformly and reproducibly than films comprised of Ag-NWs only. Ag-NW films that were spun-cast from solution showed bulk-like electrical resistivities (~2-50 Ω/sq) while being highly transparent (~70-90%). The films show a variability in NW coverage of ~15%, owing to aggregation. Spun-cast films of the Ag-NW/PEDOT:PSS composites show similar transmittances and resistivities but with significantly reduced variability in NW coverage of <5%. Composites with higher aspect ratios (smaller NW diameters) also show similar resistivities at transmittance values approximately 5% higher, thus showing great potential for use as transparent conductors. Additionally, by obtaining similar resistivities at lower Ag-NW coverage densities, the composites effect a lowering of the threshold for percolative conduction.

In order to understand how the processing and physical conditions affect the electrical and optical properties of these NW networks, we have also modeled NW-networks under conditions similar to those of the experimental system. Both simulation and experiment show that the percolation threshold of these networked conductors can be shifted towards lower NW densities via parameters such as the nature of the NW dispersion, the composition of the network, and the NW geometry. In this presentation, we discuss results how each of these parameters affects the electrical and optical properties of Ag-NW networks, including their reproducibility, on the way towards achieving optimized characteristics for their use in devices.

3:00pm **TC+EM+EN+TF-WeA4 Surface Modification of ZTO/Al/ZTO Stack Structure using Inductively Coupled Plasma**, ***H.S. Kim***, Chung-Ang University, Republic of Korea, *J.C. Woo*, ETRI, Republic of Korea, *Y.H. Joo, K.R. Choi, Y.S. Chun, C.I. Kim*, Chung-Ang University, Republic of Korea

Transparent conductive oxide (TCO) is material which simultaneously possesses the properties of electrical conductivity and optical transmission. TCO is a doped metal oxide thin film mainly used in optoelectronic applications such as transparent electrodes in touch panels, flat panel displays (FPDs), and other future devices. Among the new TCO, Zinc tin oxide (ZTO) is a one of very promising candidate. ZTO has the advantage of good stability at high temperature and unlike other popular TCOs such as ITO and Cd-Sn-O, ZTO films do not contain expensive or toxic elements. Another advantage of ZTO is its low sensitivity towards visible light. Moreover, Conductivity of ZTO thin films can be increased by doping of ZTO with aluminum. In many organic and hybrid devices al-doped ZTO thin films are used as the anode or hole transport layer. In order to get excellent device characteristics in OLED applications, efficiency of hole injection is important factor. In this study, the effects of various gases employed of plasma treatments of al-doped ZTO anode surfaces have been studied in an Inductively Coupled Plasma (ICP). The surface modification of al-doped ZTO was studied as a function of the process parameters, including a RF power, a process time and a process pressure. By modifying the surface properties of the al-doped ZTO, the work function of the anode can be considerably varied to alter the hole-injection energy barrier. The work function of the treated al-doped ZTO thin film was investigated by Surface Analyzer (AC-2). The analysis of X-ray Photoelectron Spectroscopy (XPS) was carried out to investigate the chemical reactions between the surface of al-doped ZTO thin films and etch species. Surface morphology of the treated al-doped ZTO was characterized using Atomic Force Microscope. As a result of XPS and AFM analysis, plasma treatment reduces the carbon contamination of al-doped ZTO surface and increases the work function of it.

4:00pm **TC+EM+EN+TF-WeA7 Printing Photovoltaics**, ***M.F.A.M. van Hest***, *S. Habas, H. Platt, R. Pasquarelli, J. Fields, D. Ginley*, National Renewable Energy Laboratory **INVITED**

Photovoltaics are becoming an increased part of the energy supply mix, however the cost is currently too high. In order to reduce the cost, moving towards non-vacuum production routes is very attractive because of the low capital equipment cost. Non-vacuum processes can be used in several steps of the photovoltaic cell and module manufacturing process, for both wafer based and thin film photovoltaics. The different components can be deposited and processed using one of many non-vacuum techniques, e.g. inkjet printing, aerosol jetting, slot coating and spray coating. Details about these techniques will be discussed. Since non-vacuum techniques use a chemical route to the end product, inks are the key to success. Inks have been developed for metallization grids, e.g. Ag, Cu, Ni, and Al, but also for absorbers, e.g. CIGS and organics. These materials can be processed under atmospheric conditions and have properties similar to their vacuum deposited counterparts. Aside from the absorber and the metallization, transparent conductors are an intrinsic part of thin film photovoltaic devices, however transparent conductive oxides have only been deposited and processed from inks with moderate success. Research to overcome this last hurdle is under way and focuses on chemical routes to oxides as well as alternatives, i.e. metal nanowires, with the latter showing potential. Several details of non-vacuum processing of the various components of photovoltaic cells will be addressed.

5:00pm **TC+EM+EN+TF-WeA10 Interfacial Layer Engineering of Transparent Conductive Oxides for Optoelectronic Device Application**, ***I.T. Martin***, *H.M. Lemire, K.A. Peterson, M.S. Breslau, K.D. Singer, R.H. French*, Case Western Reserve University

Transparent conductive oxides (TCOs) have widespread utility as electrical contacts in photovoltaic (PV) and other optoelectronic devices, such as display screens and organic light emitting diodes (OLEDs). The TCO surface chemistry can be tailored through the addition of interfacial layers (IFLs), such as polymers, covalently bonded organofunctional silanes, and chemisorbed small molecules. These IFLs can be used to optimize rates of charged carrier transfer, and increase the compatibility of the polar TCO with nonpolar materials used in OPVs and OLEDs. Understanding the interactions between these materials and the TCO interfaces is essential to controlling device performance. For example, PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)), a polymer commonly used in OLED and OPV devices, functions as an electron blocking layer for the TCO anode, improving device efficiency. However, the polymer is highly acidic and can be corrosive to the TCO layer; in the case of organic PV devices, this can limit their lifetime.

We used organofunctional silanes, including allyl triethoxy silane (ATES), octa-decyl-trichloro silane (OTS), 3-aminopropyl-triethoxy silane (APTES) and 3-aminopropyl-dimethyl-ethoxy silane (APDMES), to modify indium tin oxide (ITO), aluminum doped zinc oxide (AZO) and fluorine doped tin oxide (FTO). We characterized the electrical and optical properties and surface energies of the silanized TCOs, and compared the results to a standard OPV polymer, PEDOT:PSS. Results demonstrate that varying the functionality and deposition conditions of the silane is a simple method of tuning and customizing the surface energy of the hydrophilic TCO; water contact angles ranging from 57° (APDMES) to 94° (OTS) are achieved without affecting the TCO transparency or conductivity. Additionally, both bare and silanized ITO, AZO and FTO were exposed to damp heat (DH, 85 °C, 85% relative humidity) for up to 1000 hours. After each exposure a standard cleaning process was used and the TCOs' electrical and optical properties and surface energies were determined. Using contact angle measurements with multiple fluids, the surface energies of the TCOs were tracked, and the largest change in total surface energy was found for AZO, then ITO, with FTO remaining essentially unchanged for the conditions studied. In preliminary degradation studies of TCO/silane stacks, ATES was found to delay and reduce the resistivity increase of ITO in damp heat. Further degradation data of TCO/silane stacks, with and without encapsulation will be presented.

5:20pm **TC+EM+EN+TF-WeA11 Growth and Characterization of Epitaxial $(Al_xGa_{1-x})_2O_3$ Alloy Films**, ***B. Krueger***, University of Washington, *N. Nguyen, T. Chikyow,* National Institute for Materials Science, Japan, *F.S. Ohuchi, M.A. Olmstead*, University of Washington

Gallium oxide is a transparent semiconductor ($E_g \sim 4.8$ eV) that exhibits n-type conductivity; it has been proposed for a variety of uses ranging from "solar-blind" conductive coatings to chemical sensing. An intriguing possibility is development of transparent, high power transistors based on carrier accumulation at an epitaxial Ga_2O_3–$(Al_xGa_{1-x})_2O_3$ alloy interface. Using pulsed laser deposition, combinatorial $(Al_xGa_{1-x})_2O_3$ thin films were fabricated on a variety of substrates, including sapphire, GaN, $SrTiO_3$ and $LaAlO_3$, with x varying smoothly across the surface. Position-dependent X-ray diffraction revealed [-201]-oriented Ga_2O_3 on hexagonal GaN (0001) surfaces (5% lattice mismatch) and predominantly [-201]-oriented on c-plane sapphire (8% mismatch). Alloy $(Al_xGa_{1-x})_2O_3$ films remain in the β-Ga_2O_3 phase for $0 < x < 0.15$ on GaN and $0 < x < 0.35$ on sapphire, with negligible lattice expansion; a new alloy phase is observed for $0.15 < x < 0.35$ on GaN. Photoemission spectroscopy shows core and valence levels both shift to higher binding energy with increasing Al concentration, and the work function decreases, consistent with a widening band gap.

This work was supported by the National Science Foundation under DMR 1104628 and OISE 1209856 and by the Micron Foundation.

5:40pm **TC+EM+EN+TF-WeA12 Weakly Bounded Zn Atoms in Polycrystalline ZnO Thin Films caused by Ga Doping**, ***H. Makino***, *H. Song, T. Yamamoto*, Kochi University of Technology, Japan

Ga-doped ZnO (GZO) is promising candidate for alternative to ITO as transparent electrodes. We have reported that thermal desorption of Zn from polycrystalline GZO films starts at a little low temperature of 150 °C, which is close to the deposition temperature [1]. The amount of desorbed Zn from GZO films showed strong correlation with carrier concentration [1]. The Zn desorption also appeared in epitaxially grown GZO films deposited on sapphire substrates. In this paper, we reports thermal desorption of Zn in comparison between GZO films and ZnO films deposited on glass substrates.

The 150 nm thick GZO and ZnO films were deposited on glass at a substrate temperature of 200 °C using ion plating with DC arc discharge. The oxygen gas was introduced to the deposition chamber during the deposition process. The oxygen gas flow rate (OFR) was varied between 5 sccm and 25 sccm. Thermal desorption spectroscopy (TDS) was employed to evaluate characteristics of Zn desorption.

The TDS of Zn for the ZnO film deposited at 10 sccm showed a dominant desorption peak at 450 °C and a shoulder peak at 500 °C. The intensities decreased with increasing the OFR, and the peak at 500 °C disappeared with increasing the OFR to 20 sccm. On the other hand, the TDS of Zn for the GZO films deposited at the OFR of 10 sccm showed two peaks at 300 and 400 °C. The intensity of peak at 300 °C decreased with increasing the OFR, and the peak at 400 °C shifted to high temperature with increasing the OFR. Then, the TDS result of GZO deposited at 25 sccm showed one peak at 450 °C, which is similar to the dominant peak observed in the undoped ZnO films. The lower temperature of TDS peak of Zn suggests existence of weakly bounded Zn atoms in the GZO films. The weakly bounded Zn atoms are obvious in the GZO films deposited at low OFR conditions. It is possible to say that the weakly bounded Zn atoms were caused by high density of Ga doping to ZnO.

[1] H. Makino, Y. Sato, N. Yamamoto, T. Yamamoto, Thin Solid Films **520**, 1407 (2011).

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