

Wednesday Afternoon, October 30, 2013

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 dioxythiophene):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, SrTiO₃ and LaAlO₃, 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).

Authors Index

Bold page numbers indicate the presenter

— B —

Bockstaller, M.R.: TC+EM+EN+TF-WeA3, 1
Breslau, M.S.: TC+EM+EN+TF-WeA10, 2

— C —

Chikyow, T.: TC+EM+EN+TF-WeA11, 2
Choi, K.R.: TC+EM+EN+TF-WeA4, 1
Chun, Y.S.: TC+EM+EN+TF-WeA4, 1

— F —

Fields, J.: TC+EM+EN+TF-WeA7, 1
French, R.H.: TC+EM+EN+TF-WeA10, 2

— G —

Ginley, D.: TC+EM+EN+TF-WeA7, 1

— H —

Habas, S.: TC+EM+EN+TF-WeA7, 1

— J —

Joo, Y.H.: TC+EM+EN+TF-WeA4, 1

— K —

Kim, A.: TC+EM+EN+TF-WeA1, 1
Kim, C.I.: TC+EM+EN+TF-WeA4, 1
Kim, H.S.: TC+EM+EN+TF-WeA4, **1**
Krueger, B.: TC+EM+EN+TF-WeA11, 2

— L —

Lemire, H.M.: TC+EM+EN+TF-WeA10, 2

— M —

Makino, H.: TC+EM+EN+TF-WeA12, **2**
Martin, I.T.: TC+EM+EN+TF-WeA10, **2**
Moon, J.: TC+EM+EN+TF-WeA1, **1**

— N —

Narayanan, S.: TC+EM+EN+TF-WeA3, **1**
Nguyen, N.: TC+EM+EN+TF-WeA11, 2

— O —

Ohuchi, F.S.: TC+EM+EN+TF-WeA11, 2
Olmstead, M.A.: TC+EM+EN+TF-WeA11, 2

— P —

Pasquarelli, R.: TC+EM+EN+TF-WeA7, 1
Peterson, K.A.: TC+EM+EN+TF-WeA10, 2
Platt, H.: TC+EM+EN+TF-WeA7, 1
Porter, L.M.: TC+EM+EN+TF-WeA3, 1

— S —

Singer, K.D.: TC+EM+EN+TF-WeA10, 2
Song, H.: TC+EM+EN+TF-WeA12, 2

— T —

Treacy, C.: TC+EM+EN+TF-WeA3, 1

— V —

van Hest, M.F.A.M.: TC+EM+EN+TF-WeA7, **1**

— W —

Won, Y.: TC+EM+EN+TF-WeA1, 1
Woo, J.C.: TC+EM+EN+TF-WeA4, 1

— Y —

Yamamoto, T.: TC+EM+EN+TF-WeA12, 2