

# Wednesday Morning, October 31, 2012

**Plasma Science and Technology**  
**Room: 24 - Session PS+TC-WeM**

**Atmospheric Plasma Processing for PV, Flexible Electronics (incl. R2R)**

**Moderator: S.A. Vitale, MIT Lincoln Laboratory**

**8:00am PS+TC-WeM1 Formation Dynamics and Characterization of Organosilicon Powders in Microwave-Sustained Plasmas at Atmospheric-Pressure, V. Roy-Garofano, A. Kılıcaslan, O. Levasseur, L. Stafford, M. Moisan, Université de Montréal, Canada, C. Côté, A. Sarkissian, Plasmionique, Canada**

An atmospheric-pressure plasma sustained by a propagating electromagnetic surface wave in the microwave regime combined with a bubbler/flash evaporator developed by Plasmionique for the injection of liquid precursors was used to generate organosilicon powders. Analysis of the plasma emission revealed the apparition of strong C<sub>2</sub> (Swan system) and CN emission bands along with Si emission lines following the addition of the hexamethyldisiloxane (HMDSO) precursors in the nominally pure argon plasma. Such features were not observed in atmospheric-pressure Ar/HMDSO discharges controlled dielectric barriers, indicating that microwave-sustained plasmas are characterized by much higher precursor fragmentation levels due to their much higher electron density. The emission spectra further showed a high-intensity continuum, the intensity of which decreased with time as powders started to form on the discharge tube walls. Analysis of the powder chemical composition by Fourier-Transform Infrared Spectroscopy showed very strong Si-(CH<sub>3</sub>)<sub>x</sub> and O-Si-(CH<sub>3</sub>)<sub>x</sub> bands, consistent with the formation of a silicon carbide. On the other hand, introduction of trace amount of O<sub>2</sub> in Ar/HMDSO produced white powders with strong Si-O-Si bands and no trace of carbon, consistent with the formation of SiO<sub>x</sub>.

**8:20am PS+TC-WeM2 Infrared Gas Phase Studies in High-Current Dielectric Barrier Discharges Applied in Roll-to-Roll Deposition of Silica-Like Layers at Atmospheric Pressure, S. Welzel, Eindhoven University of Technology, Netherlands, S.A. Starostin, H. de Vries, FUJIFILM Manufacturing Europe B.V., Netherlands, M.C.M. van de Sanden, R. Engeln, Eindhoven University of Technology, Netherlands**

Large-area plasma-enhanced roll-to-roll processing of polymeric substrates in diffusive dielectric barrier discharges (DBDs) have been shown to yield high-quality SiO<sub>2</sub>-like barrier layers. This has been obtained through chemical vapour deposition at atmospheric pressure using organo-silicon precursors (HMDSO or TEOS) and industrially relevant air-like gas mixtures (N<sub>2</sub>/O<sub>2</sub>/Ar). Provided an electronic stabilisation circuit is applied, high currents in different diffusive discharge modes can be achieved without admixtures of Helium. Earlier, extensive surface analysis studies of the synthesised layers revealed a competition between deposition and etching regimes throughout the active plasma zone and led to the development of a deposition model.

This contribution is concerned with complementary studies of the gas phase composition using infrared absorption techniques. Given the challenging optical access to DBDs with gap distances smaller than 1 mm in industrial-like roll-to-roll configuration a gas sampling system was implemented to collect a fraction of the effluent into a multiple pass absorption cell. Main stable products were identified under various discharge conditions such as different O<sub>2</sub> admixtures and (average) power densities. Broadly speaking, a typical H-N-O chemistry in the presence of traces of hydrocarbons is observed for such high-current DBDs. To establish a link to earlier model assumptions both dominant etching and deposition conditions were studied separately (i.e. precursor absent and added, respectively). Formic acid (HCOOH) was found to be a good marker molecule in the gas phase for strong etching of the polymeric substrate or incomplete precursor dissociation. Particularly, the appearance of precursor fragments in the infrared gas phase spectra can be correlated to the injected power and growth rate. Under conditions of complete precursor depletion the effluent zone of the reactor resembles an air-like plasma where NO<sub>2</sub>, NO, N<sub>2</sub>O and HNO<sub>2</sub> are observed whilst hydrocarbons or alcohols are absent.

**8:40am PS+TC-WeM3 Atmospheric Pressure Plasma Processes for Preparation of Si-Based Thin Films, K. Yasutake, H. Ohmi, T. Yamada, H. Kakiuchi, Osaka University, Japan**

**INVITED**

Thin-film deposition processes using atmospheric-pressure (AP) plasmas have attracted considerable attention as the low-cost deposition methods, because they can realize low-temperature and high-rate deposition without the necessity for ultrahigh vacuum. Recently, we have demonstrated that

good-quality Si films with almost no ion damage can be prepared by using a 150-MHz very high-frequency AP plasma. Based on this result, we are studying applications of AP plasmas in semiconductor processing, e. g., i) atmospheric-pressure plasma chemical vapor deposition (AP-PCVD) of semiconductor and insulator thin films, ii) AP plasma oxidation of Si and Al, and iii) atmospheric-pressure plasma enhanced chemical transport (APECT) processes for Si purification and deposition. In this work, we will report the experimental results on the formation and characterization of Si-based thin films prepared by these AP plasma processes.

Firstly, we have studied the epitaxial Si growth by AP-PCVD. The purpose of the study is to develop a totally low-temperature semiconductor device fabrication process. Epitaxial Si films have been prepared on 4-inch-(001) Si wafers by AP-PCVD using a porous-carbon electrode. Defect-free growth of epitaxial Si is confirmed in the temperature range of 470–570°C by transmission electron microscopy and a selective etching method. A high carrier generation lifetime ( $\approx 2.0$  ms) is observed in the Si film grown at 570°C with a reasonably high growth rate ( $\approx 0.4$   $\mu\text{m}/\text{min}$ ). *In situ* H<sub>2</sub> plasma cleaning of the substrate surface is effective for eliminating O and C concentration peaks at the film/substrate interface. Heavy B doping with a carrier concentration of about  $10^{20}$  cm<sup>-3</sup> is achieved using B<sub>2</sub>H<sub>6</sub> as a doping gas at 570°C. The relation between the mobility and carrier concentration in p- and n-doped Si films can be well fitted by the reported curves for bulk Si single crystals. These results demonstrate that the electrical quality of Si epitaxial films grown by AP-PCVD is sufficiently good for semiconductor device applications.

One of the other topics is on the AP plasma oxidation of Si. AP plasma oxidation is supposed to be most compatible for a chamber-less and open-air process, which is attractive as a high-throughput oxidation process for photovoltaic applications. SiO<sub>2</sub>/Si structures have been prepared by AP plasma oxidation at 400°C using gas mixtures of O<sub>2</sub> and He. Various characterization results reveal that the properties of AP plasma oxides are similar to those of high-temperature thermal oxides, and that the SiO<sub>2</sub>/Si structure has a low interface state density of the order of  $10^{10}$  cm<sup>-2</sup>eV<sup>-1</sup>.

**9:20am PS+TC-WeM5 Deposition of Organic-Inorganic Nanocomposite Coatings by Aerosol-Assisted Atmospheric Pressure DBDs, F. Fanelli, Institute of Inorganic Methodologies and Plasmas (IMIP) - CNR, Bari, Italy, A.M. Mastrangelo, F. Fracassi, University of Bari Aldo Moro - IMIP CNR, Bari, Italy**

Aerosol-assisted atmospheric pressure cold plasma processes have been recently addressed as an attractive route towards the deposition of multifunctional coatings. This approach seems to be particularly convenient, and can even offer the only possible solution, when non-volatile precursors, solutions or dispersions need to be injected directly in the atmospheric plasma. The aerosol of a dispersion of nanoparticles (NPs) in a liquid precursor can lead to the deposition of nanocomposite coatings in which the NPs are embedded in the matrix formed by the plasma polymerization of the precursor.

This contribution is focused on the study of the growth and structure of plasma-deposited polyethylene/zinc oxide (PE/ZnO) nanocomposite coatings with several potential applications due for instance to the UV-protection and photocatalytic properties of ZnO.

The coatings are deposited in a parallel plate dielectric barrier discharge (DBD) fed with He and the aerosol of a dispersion of oleate-stabilized ZnO NPs in octane or octane/1,7-octadiene mixtures. The characterization of the coatings is performed using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), water contact angle (WCA) goniometry.

A comprehensive study on the effect of different process parameters (e.g., atomization conditions, dispersion composition in terms of liquid precursor and ZnO NPs concentration, deposition time) on the chemical composition and structure of the film will be presented.

Preliminary results show that, as expected, with increasing the concentration of ZnO NPs in the starting dispersion from 0.5 to 5% p/p, the ZnO content in the coating increases. Surprisingly, the addition of a small amount of 1,7-octadiene to octane (0.5% v/v) favors the inclusion of the NPs and hence results in an increase of the ZnO concentration of the coatings.

Advancing and receding WCAs steeply increase with the NPs content in the film and reach values higher than 165° with low hysteresis indicating the formation of slippery superhydrophobic surfaces. SEM images confirm that this superhydrophobic character is due to the hierarchical micro/nano-structured surface morphology of the coatings. ZnO NPs generally aggregate in almost spherical clusters that can be incorporated to a different

extent into the polyethylene-like matrix as a function of the deposition process conditions.

10:40am **PS+TC-WeM9 Modified Dielectric Barrier Discharges for Display Materials Processing**, *G.Y. Kim*, Sungkyunkwan University, Korea, *J.B. Park*, SKKU Advanced Institute of Nano Technology (SAINT), Korea, *G.Y. Yeom*, Sungkyunkwan University & SKKU Advanced Institute of Nano Technology (SAINT), Korea

**INVITED**

Atmospheric pressure plasmas have been investigated tens of years for the application to semiconductor and display processing. Especially, due to the uniform discharge characteristics, dielectric barrier discharges (DBDs) composed of electrodes covered with dielectric material have been investigated intensively for those applications. In our study, the conventional DBDs have been modified to enhance the plasma density and also, the different types of DBDs such as remote-type DBD and hybrid-type DBDs (which is composed of direct-type DBD and remote-type DBD) have been used for the surface treatment, growth, deposition, and etching of material applied to flat panel displays and their effects on the material processing have been studied. In this presentation, I will present the plasma characteristics and materials characteristics obtained with those different types of modified DBDs and will suggest possible applications of the DBD-type atmospheric pressure plasmas for the next generation display processing such as in-line/roll-to-roll processing, flexible display substrate processing, inkjet processing, etc.

11:20am **PS+TC-WeM11 Etching of PTFE by Atmospheric Plasmas: Effect of the Gas Composition on the Reactions Processes and Hydrophobicity**, *J. Hubert\**, *T. Dufour*, *N. Vandencastele*, Université Libre de Bruxelles, Belgium, *S. Desbief*, *R. Lazzaroni*, Materia Nova Research Center, Belgium, *F. Reniers*, Université Libre de Bruxelles, Belgium

Poly(tetrafluoroethylene) (PTFE) is a hydrophobic material due to its fully fluorinated backbone (-CF<sub>2</sub>-CF<sub>2</sub>-), with properties interesting for practical applications such as self-cleaning surfaces. It has been shown that super-hydrophobic surfaces can be obtained by the treatment of PTFE in a helium-oxygen plasma at atmospheric pressure [1]. Contrary to oxygen-containing plasmas, the modification of PTFE by a pure helium plasma at atmospheric pressure usually leads to a strong decrease in water contact angle, in addition to an oxygen incorporation [2].

The treatment of PTFE by the atmospheric post-discharge of an RF plasma torch supplied in He and He-O<sub>2</sub> highlighted two totally different behaviors [3]. For this reason, the effect of the gas composition (ratio He/O<sub>2</sub>) on the polymer modifications has been investigated. The treated surfaces have been characterized by WCA, XPS and AFM. Moreover, the species responsible for the modifications have been identified by optical spectroscopies (OES/OAS).

In pure helium plasmas, no significant change of the surfaces regarding chemical composition (XPS), wettability (WCA) and morphology (AFM) has been observed and this, despite an important mass loss measured. According to these observations, we presume a layer-by-layer physical etching without any preferential orientation, where the highly energetic helium metastables should be the main species responsible for the scission of -(CF<sub>2</sub>)*n*- chains. The XPS analysis of an aluminum foil (known to be an efficient fluorine trap) placed close to the PTFE tends to confirm this assumption as fluorine atom and -CF<sub>2</sub> fragments have been detected.

In He-O<sub>2</sub> plasmas, the helium metastables species being consumed by oxygen, fewer of them are then available to etch the PTFE, reducing the mass losses and fluorine detection on aluminum for higher O<sub>2</sub> flow rates. However, as it was previously shown [2], WCA and AFM measurements indicate an increase in hydrophobicity and roughness of the PTFE surface. The alveolar structures observed by AFM are then assumed to come from the anisotropic etching where the atomic oxygen etches mainly the amorphous phase.

[1] T. Dufour, J. Hubert, P. Viville, C.Y. Duluard, S. Desbief, R. Lazzaroni, F. Reniers, PTFE surface etching in the post-discharge of a scanning RF plasma torch: evidence of ejected fluorinated species, *Plasma Process. Polym.* 2012, DOI: 10.1002/ppap.201100209.

[2] N. Zetsu, H. Itoh, K. Yamamura, *Thin Solid Films*, 2008, 516,6683.

[3] J. Hubert, T. Dufour, N. Vandencastele, S. Desbief, R. Lazzaroni, F. Reniers, Etching processes operating on a PTFE surface exposed to He and He-O<sub>2</sub> atmospheric post-discharges. (Accepted : *Langmuir*).

11:40am **PS+TC-WeM12 Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition of Hydrophobic Thin Film Coatings Using Liquid Precursors**, *J. Yim*, *V. Rodriguez-Santiago*, *A. Williams*, *J. Hirvonen*, *D. Pappas*, U.S. Army Research Laboratory

Hydrophobic coatings are known to impart self-cleaning, anti-fouling, anti-fog and wicking properties on polymeric substrates and textiles. These coatings are largely derived from either wet chemical methods or low pressure plasma-based chemical vapor deposition techniques using gaseous precursors. In an effort to eliminate the use of large quantities of chemicals and solvents associated with wet chemistries and to deter the use of costly vacuum systems, we explored the practicality of an atmospheric pressure plasma jet (APPJ) as a comparable alternative to low pressure plasma systems. To obtain coatings typically achieved through wet chemistry, and often limited by commonly used fluorocarbon gases such as C<sub>3</sub>F<sub>6</sub>, liquid fluorinated precursors such as fluoroalkyl silanes (FAS) were explored. FAS with varying fluorocarbon chain lengths were studied and deposition conditions as a function of electrode-substrate gap distance, deposition time and power were investigated. Ultra high molecular weight polyethylene (UHMWPE) films served as the model polymer system in which the coatings were deposited owing to its simple molecular structure consisting of -CH<sub>2</sub>-CH<sub>2</sub>- chains. The characteristic properties of the coatings on UHMWPE such as hydrophobicity, chemical composition, uniformity and deposition rates were studied to establish a correlation between processing parameters and the coating properties. X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) measurements confirmed the presence of CF, CF<sub>2</sub>, and CF<sub>3</sub> functionalities in the coating composition and reveal that there is a strong dependence of these groups on the chain length of fluorocarbon groups in the FAS precursors. Water contact angle (WCA) measurements confirm hydrophobicity of the coating, where angles over 90° were recorded. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) techniques were utilized to probe the morphological profiles of the coatings. Profilometry and ellipsometry show deposition rates of the coating ranging from nanometer to sub-micrometer thick coatings. Results show that the use of APPJ with liquid precursors is promising in achieving hydrophobic coatings under atmosphere without producing large volumes of hazardous waste.

# Wednesday Afternoon, October 31, 2012

## Transparent Conductors and Printable Electronics

### Focus Topic

Room: 7 - Session TC+EM+AS-WeA

## Printable and Flexible Electronics

Moderator: G.S. Herman, Oregon State University

2:00pm TC+EM+AS-WeA1 **Metal Oxides and Organic Materials for Printed Electronics**, A. Facchetti, Polyera Corp. and Northwestern U.

INVITED

Printed electronics is a new technology envisioning the fabrication of electronic devices using printing methodologies instead of conventional photolithography employed in the silicon industry. Metal oxide- and organic-based materials will be key players for this technology. In this presentation I will discuss our latest results in developing new printable organic semiconductors. Furthermore, I will describe amorphous and polycrystalline metal oxide formulations in which the corresponding films can be annealed at temperatures  $< 250$  °C. For instance, solution-processed amorphous tin-doped indium oxide (ITO) films for TFT fabrication at temperatures  $< 250$  °C can be achieved by controlling film precursor solution  $\text{In}^{+3}$  vs.  $\text{Sn}^{+4}$  molar ratio resulting in electron mobilities  $> 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $\sim 20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for TFTs using  $\text{SiO}_2$  and a self-assembled nanodielectric (SAND) as the gate dielectrics, respectively. Finally, a new general strategy for fabricating solution-processed metal oxide TFTs at dramatically lower temperatures (as low as  $200$  °C for all TFT electrical components) using self-energy generating combustion chemistry will be presented. Our results show that by tuning the gate dielectric-semiconductor interface dramatically enhances performance, yielding  $\text{In}_2\text{O}_3$ , IZO, IZTO, and IGZO /amorphous alumina gate dielectric TFTs having electron mobilities of  $40 \text{ cm}^2/\text{Vs}$  and  $13 \text{ cm}^2/\text{Vs}$  at  $T_{\text{anneal}} = 250$  °C and  $200$  °C, respectively.

2:40pm TC+EM+AS-WeA3 **Ion Dependence of Gate Dielectric Behavior of Beta-Aluminas in Transparent Oxide Field-Effect Transistors**, Y. Liu, B. Zhang, H.E. Katz, Johns Hopkins University

Sodium beta-alumina (SBA) is an excellent gate dielectric material which can be used in low-voltage (2 V), solution-processed transparent oxide field-effect transistors (FETs). Sodium ions have been experimentally proved to be the origin of the high capacitance observed in SBA gate dielectric. With this discovery, the investigation of dielectric properties of alumina with the incorporation of other alkali metal ions (for example  $\text{K}^+$ ,  $\text{Li}^+$ ) becomes compelling.

High field-effect mobility (about  $20 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ ), high saturation drain current (about 1 mA), and small subthreshold swing (about 200 mV/decade) were achieved in low-voltage (2 V), spin-coated zinc-tin-oxide (ZTO) FETs with potassium beta-alumina (PBA) and lithium beta-alumina (LBA) dielectrics. This proves that the incorporation of alkali metal ions in beta-aluminas is a general route to reduce operation voltage of transistors while achieve excellent electrical performance.

To investigate the effect of alkali metal ions on beta-alumina capacitance, beta-alumina Metal-Insulator-Metal (MIM) capacitors (PBA, LBA, and SBA) were analyzed in a frequency range from 100 Hz to 1 MHz. A tendency for beta-alumina capacitance to increase with increasing atomic number of alkali metal ions was observed. Besides, beta-alumina capacitance was found to decrease as temperature increases and LBA showed the strongest temperature dependence of capacitance. Moreover, capacitance of beta-aluminas with different thickness was measured and they were independent of thickness. With these results, electric double layer (EDL) structure was proposed as one way to explain the high capacitance of beta-alumina dielectrics. Ion exchange experiments showed significant diffusion of both lithium ion and potassium ion between PBA and  $\text{LiNO}_3$  solution; however, a high concentration difference did not seem to cause obvious diffusion of either lithium ion or potassium ion between LBA and  $\text{KNO}_3$  solution. This selective ion exchange behavior in beta-aluminas showed that the  $\text{Al}_2\text{O}_3$  matrix structure would be affected by the alkali metal ions incorporated, and/or that Li ions are much more strongly bound. Thus, varying intercalated ion types and concentrations can be a means of tuning frequency-dependent capacitance of alumina films.

3:00pm TC+EM+AS-WeA4 **Selection Rule of Preferred Doping Site for N-Type Transparent Conducting Oxides**, S.-H. Wei, National Renewable Energy Laboratory, C. Li, J.B. Li, Institute of Semiconductor Physics, CAS, China

Traditionally, it is believed that the conduction band edges of  $d^0$  or  $d^{10}$  oxides are derived mostly from cation  $s$  states, thus doping on anion sites is

expected to cause less perturbation and produce shallow donor levels in these materials. Using first-principles calculations, we show that although this paradigm is applicable for more covalent oxides such as  $\text{SnO}_2$  where  $F_O$  is a better n-type dopant than  $\text{Sb}_{\text{Sn}}$ , for more ionic oxides such as ZnO, the conduction band edge actually contains a considerable amount of O  $s$  orbitals, thus  $F_O$  in ZnO causes larger perturbation and consequently produces deeper donor levels than cation site doping such as  $\text{Al}_{\text{Zn}}$ . The rule that anion site doping is preferred for more covalent oxides and cation site doping is preferred for more ionic oxides for n-type metal oxides should be general and can be used to guide future study of and search for functional oxide materials.

4:00pm TC+EM+AS-WeA7 **Single-Walled Carbon Nanotube Aerogel Based Elastic Conductors**, K.H. Kim, Y. Oh, I. Lee, M.F. Islam, Carnegie Mellon University

INVITED

Flexible conductors of various shapes and sizes with high electrical stability under large elastic stretching and bending are of significant importance in diverse fields ranging from microelectronics to biological implants. A major roadblock in the development of flexible conductors is the disparity between elastomers and stiff conducting materials used in microelectronics. We have developed a novel scheme to create flexible conductors by completely backfilling a prefabricated conducting porous single wall carbon nanotube (SWCNT) three-dimensional network, called SWCNT aerogel, with an elastic polymer polydimethylsiloxane (PDMS). Our approach allowed us to control SWCNT dispersion quality, and tune shapes, sizes and thicknesses of the SWCNT-aerogel/PDMS composite films to make them transparent. The resistance of our stretchable conductors remains nearly unchanged under repeated stretch-release cycles up to a tensile strain of 100% and high bending strain. We believe that the simple but unique fabrication method can be combined with different types of elastic polymers for different electrical, mechanical or biological demands.

4:40pm TC+EM+AS-WeA9 **Networked Metal Nanowire-Polymer Composites for Flexible, Transparent and Conducting Devices**, S. Narayanan, S. Fu, M.R. Bockstaller, L.M. Porter, Carnegie Mellon University

Transparent conductive metal oxides (TCOs) exhibit inherent disadvantages such as limited supply, brittle mechanical properties, expensive processing that present major barriers for the more widespread economic use in applications such as flexible transparent conductors. A promising alternative route towards flexible, transparent conductive materials is based on silver nanowire network structures, which can be easily processed from solution. We report a systematic analysis of the effect of nanowire geometry and solution processing on the network characteristics of nanowire deposits, and the associated electronic and optical properties of silver nanowire-based transparent electrodes. Ag nanowire (of average diameter  $\sim 100$  nm) films drop-cast from solution were shown to exhibit bulk-like electrical conductivity ( $\sim 2\text{-}50 \text{ } \Omega/\text{sq}$ ) and high transparency ( $\sim 70\text{-}75\%$ ). The electrical properties of nanowire networks were found to be sensitive to geometric parameters of the wire assembly that can be interpreted by use of percolation theory. At concentrations below the percolation threshold the sheet resistance increases dramatically, effecting a marked deviation from bulk-like behavior [1]. The dispersion of Ag nanowires in a conducting medium, like that of a conducting polymer was found to significantly reduce nanowire aggregation and thus decrease the percolation threshold. Preliminary results of spun-cast films of composites of these nanowire networks with PEDOT:PSS show higher transmittances ( $\sim 79\text{-}82\%$ ) with similar conductivities ( $\sim 10\text{-}170 \text{ } \Omega/\text{sq}$ ) combined with better film forming properties. The use of composites was found to bring about a consistent improvement in electrical conductivity with very little change in the transmittance. Samples prepared on flexible PET substrates showed no degradation in conductivity on flexing thereby showing ample promise for incorporating flexibility in such structures. Through analysis of microstructural characteristics of these films, a quantitative correlation of the density of nanowires with conductivity and transmittance will be presented. The advantages of using such a composite structure in reducing the percolation threshold will be discussed.

[1] Sukanta De *et al.* ACS Nano 4 12 (2010) 7064-7072

# Thursday Morning, November 1, 2012

## Transparent Conductors and Printable Electronics

### Focus Topic

Room: 7 - Session TC+EM+AS+TF+EN-ThM

## Transparent Conductors and Devices

Moderator: L.M. Porter, Carnegie Mellon University

8:20am TC+EM+AS+TF+EN-ThM2 **High Conductivity in Thin ZnO:Al Deposited by Means of the Expanding Thermal Plasma Chemical Vapor Deposition**, K. Sharma, H.C.M. Knoops, M.V. Ponomarev, Eindhoven University of Technology, The Netherlands, R. Joy, M. Velden, D. Borsa, R. Bosch, Roth and Rau BV, Germany, W.M.M. Kessels, M. Creator, Eindhoven University of Technology, The Netherlands

Session: Transparent Conductors and Devices

The ever-increasing demand for transparent conducting oxides (TCO) for application in flat panel displays, light emitting diodes (LEDs), and thin film photovoltaics drives the present research in the field of TCOs. Aluminum-doped zinc oxide (ZnO:Al) is often referred to as a potential alternative to e.g. indium tin oxide. The ZnO:Al is considered appealing due to the relatively low cost, high abundance, non-toxicity, resistance to H<sub>2</sub> etching and, under specific conditions, surface texturing for light management/trapping. Thin ZnO:Al films (~ 100 nm) with low resistivity ( $2.5 \cdot 10^{-4}$  ohm\*cm) along with high transmission (> 85 %) are desirable in many devices. Furthermore, large area processing/ high throughput are essential pre-requisites for industrial applications.

ZnO:Al thin films (< 150 nm) have been deposited by using an in-line industrial expanding thermal plasma chemical vapor deposition (ETP-CVD) technique,<sup>1,2,3</sup> by means of O<sub>2</sub>/diethylzinc/trimethylaluminium mixtures. High diethyl zinc flow rate conditions<sup>2</sup> were applied, which enable the development of a conductive ( $5 \cdot 10^{-4}$  Ω·cm), 300 nm-thick ZnO:Al layer by promoting the development of a densely packed structure at early stages of growth, as very recently reported.<sup>2</sup>

In the present contribution, the effect of the dopant, i.e. trimethylaluminium, is investigated to further improve the electrical quality of even thinner ZnO:Al layers. ZnO:Al films were analyzed with spectroscopic ellipsometry, four point probe, hall measurements, X-ray photon spectroscopy (XPS), Rutherford backscattering (RBS), elastic recoil backscattering (ERD), and X-ray diffraction (XRD).

A remarkable low resistivity of  $5 \cdot 10^{-4}$  Ω·cm was measured for a ZnO:Al film with thickness of only 120 nm, characterized by a carrier concentration of  $1 \cdot 10^{21}$  cm<sup>-3</sup>, with an electron mobility in the range of 10-25 cm<sup>2</sup>/V · s.<sup>2,3</sup> The obtained mobility values are higher than previously reported value of 13 cm<sup>2</sup>/V · s for 300 nm thick ZnO:Al.<sup>2</sup> The improvement in terms of conductivity is attributed to the large hydrogen content ( $2-4 \cdot 10^{21}$  at/cm<sup>3</sup>) promoting the chemical passivation of the grain boundaries.

A broad characterization of highly conductive thin ZnO:Al films along with insights on charge transport process will be presented.

### Reference List

1. B. Hoex *et al.*, Progress in Photovoltaics **13**, 705 (2005).
2. M. V. Ponomarev *et al.* Journal of Applied Physics **112**, 043708 (2012).
3. M. V. Ponomarev, *et al.*, Journal of Applied Physics **111**, 063715 (2012).

8:40am TC+EM+AS+TF+EN-ThM3 **Recent Progress in Oxide Semiconductors and Oxide TFTs**, H. Hosono, Tokyo Institute of Technology, Japan **INVITED**

Transparent conductive oxides (TCOs) and transparent oxide semiconductors (TOSS) have a long history since 1950s. The material design concept for TCOs looks almost established, i.e., ionic oxides of block metals with an electronic configuration of (n-1)d<sup>10</sup>ns<sup>0</sup> and a spatial spread of ns orbitals which is enough to have large overlap with neighboring metal ns orbitals irrespective of intervening oxygen ion<sup>1)</sup>. Concretely, most of the TCOs have been realized in the material systems of In<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub>-CdO-Ga<sub>2</sub>O<sub>3</sub>-ZnO. Materials based on light metal oxides such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> have not been regarded as the candidates of TCOs. In 2002, we<sup>2)</sup> reported high electronic conductivity in 12CaO·7Al<sub>2</sub>O<sub>3</sub>(C12A7) which had been a typical insulator and this discovery was followed by transparent conductivity in cubic SrGeO<sub>3</sub> in 2011.<sup>3)</sup> These two materials are TCOs realized by a new material design concept.

As for TOS, the striking advances are seen in transparent amorphous oxide semiconductors (TAOS) in science and technology due to strong demand for

active layer materials in thin film transistors (TFTs). Amorphous In-Ga-Zn-O (IGZO) TFTs, which was first reported in late 2004,<sup>4)</sup> has adopted to drive high resolution displays of new iPad.<sup>5)</sup> This is a first mass production of TOS family. The major reasons for this adoption are high electron mobility (an order of larger than that of a-Si:H) and easy fabrication process. A major advance in TOS-TFTs is realization of p-channel TFTs and subsequent fabrication of C-MOS using ambipolar SnO.<sup>6)</sup>

In this talk, I review these progresses viewed from electronic state of these materials.

- 1) H. Kawazoe, H. Yanagi, K. Ueda, and H. Hosono. *MRS Bull.*, **25**, 28 (2000)
- 2) K. Hayashi, S. Mitsuishi, T. Kamiya, M. Hirano, H. Hosono, *Nature* **419**, 462 (2002).
- 3) H. Mizoguchi, T. Kamiya, S. Mitsuishi, H. Hosono: *Nat. Commun.*, **2**, 470 (2011).
- 4) K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, H. Hosono, *Nature* **432**, 488 (2004).
- 5) Sharp Press Release April 6, 2012
- 6) K. Nomura, T. Kamiya, and H. Hosono: *Adv. Mater.*, **23**, 3431 (2011)

9:20am TC+EM+AS+TF+EN-ThM5 **Surface Functionalization of Amorphous Zinc Tin Oxide Thin Film Transistors**, G.S. Herman, M.S. Rajachidambaram, Oregon State University, A. Pandey, S. Vilayrganapathy, P. Nachimuthu, S. Thevuthasan, Pacific Northwest National Laboratory

Amorphous zinc tin oxide semiconductor materials have been studied primarily as the active semiconducting material for thin film transistors (TFT) for applications including transparent and flexible electronics. Due to the amorphous nature of these materials excellent uniformity can be obtained over large areas while still having reasonably high electron mobilities (>10 cm<sup>2</sup>/Vs). Considerable control over the electrical properties of ZTO can be maintained, where insulating, semiconducting, and conductive films can be obtained by varying the processing and post-annealing conditions. We have recently characterized sputter-deposited zinc tin oxide (ZTO) as the active material for TFTs and found that the switching properties of ZTO are closely related to deposition, post-annealing, and electrical test conditions. In this presentation we will discuss bias stress induced instabilities for ZTO TFTs. We have found that devices with a backchannel exposed to the atmosphere have a positive subthreshold shift under positive bias, which can be well explained by a stretched exponential model. Using this model the shifts may be related to either electron trapping at the dielectric semiconductor interface or due to metastabilities of the active material. We have found that the adsorption of a self-assembled monolayer (SAM) on the backchannel of the TFT effectively passivates the device and significantly reduces the bias stress induced instabilities. In this study we will present contact angle measurements and x-ray photoelectron spectroscopy to better understand the interaction of the SAM with the ZTO surface, and the improved stability of the ZTO TFTs will be discussed in regards to the interfacial chemistry of the backchannel.

9:40am TC+EM+AS+TF+EN-ThM6 **Work Function and Valence Band Structure of Oxide Semiconductors and Transparent Conducting Oxides Grown by Atomic Layer Deposition**, A. Yanguas-Gil, Argonne National Laboratory, R.T. Haasch, University of Illinois at Urbana Champaign, J.A. Libera, J.W. Elam, Argonne National Laboratory

Atomic Layer Deposition offers a low-temperature, scalable route to the synthesis of a wide range of oxide semiconductors and transparent conducting oxides both in flat and high aspect ratio surfaces. We have carried out studies on the influence of concentration and spatial distribution on the electrical properties within the ZnO-SnO<sub>2</sub>-In<sub>2</sub>O<sub>3</sub> compositional map, including standard TCO materials such as Al:ZnO and ITO. We will present results on the work function and valence band structure of transparent conducting oxides grown by ALD using ex-situ UPS measurements, including the influence of the surface termination on the interfacial properties of the materials. Finally, the ability of ALD to tailor the surface and interfacial properties of TCOs based on its layer-by-layer nature will be discussed.

10:40am TC+EM+AS+TF+EN-ThM9 **Low Temperature, High Performance Solution-Processed Metal Oxide Thin Film Transistors formed by a 'Sol-Gel on Chip' Process**, H. Sirringhaus, University of Cambridge, UK **INVITED**

N-type amorphous mixed metal oxide semiconductors, such as ternary oxides, where M<sup>1</sup> and M<sup>2</sup> are metals such as In, Ga, Sn, Zn, have recently gained momentum because of high carrier mobility and stability and good optical transparency, but they are mostly deposited by sputtering. To date

only limited routes are available for forming high-performance mixed oxide materials from solution at low process temperature  $< 250^{\circ}\text{C}$ . Ionic mixed metal oxides should in principle be ideal candidates for solution processible materials because the conduction band states derived from metal s-orbitals are relatively insensitive to the presence of structural disorder and high charge carrier mobilities are achievable in amorphous structures. Here we report the formation of amorphous metal oxide semiconducting thin films via a 'sol-gel on chip' hydrolysis approach from soluble metal alkoxide precursors, which affords unprecedented high field-effect mobilities of  $10\text{ cm}^2/\text{Vs}$ , reproducible and stable turn-on voltages  $V_{\text{on}} \gg 0\text{V}$  and high operational stability at maximum process temperature as low as  $230^{\circ}\text{C}$ . We discuss the effect of film composition on device performance and stability.

11:20am **TC+EM+AS+TF+EN-ThM11 *In Situ* Measurements of Interface States and Junction Electrical Properties of Electrically Biased Metal /  $\beta\text{-Ga}_2\text{O}_3$  Structures**, *H. Pham, X. Zheng, B. Krueger, M.A. Olmstead, F.S. Ohuchi*, University of Washington

A significant issue in application of wide-band-gap transparent conducting oxides is formation of reliable ohmic and rectifying metal contacts. The metal-oxide interface properties are dominated by chemical reactions during growth and the resultant interface state distribution once the interface is formed. We have investigated interface formation between the wide band gap TCO  $\beta\text{-Ga}_2\text{O}_3$  ( $E_g = 4.8\text{ eV}$ ) and the metals Pd, Ni, Ti and Al with in-situ xray photoemission spectroscopy (XPS) both during growth and during sputter profiling. The two techniques give very similar results, demonstrating that in this case sputter profiling does not significantly alter the interface chemistry. Consistent with the relative compound heats of formation, Ni and Pd show very little interface reaction with either Ga or O, while Ti interacts strongly with both Ga and O and Al interacts primarily with oxygen. Electrically, Ni and Pd have similar Schottky barriers on the intrinsically n-type oxide (about  $0.9\text{ eV}$ ), Ti forms a symmetric, nearly ohmic contact, while Al exhibits a smaller barrier (about  $0.6\text{ eV}$ ). To probe the nanoscopic origins of the Schottky contact behavior through the interface state energy distribution, we combined *in-situ* deposition of thin metal layers and application of forward/reverse biases to the metal-oxide junction with XPS measurements of the relative positions of the  $\text{Ga}_2\text{O}_3$  bands (via the Ga 3d or O 1s core level) and the metal Fermi level. The density of interface states determines the rate at which the Fermi level can be moved through the oxide band gap, so variation of the oxide core-level shift with respect to the bias voltage yields the interface state density. We find the metal and oxide bands maintain their relative alignment under forward bias (back-plane negative with respect to metal), while they separate at a rate about half that of the applied bias under reverse bias (positive bias with respect to metal).

11:40am **TC+EM+AS+TF+EN-ThM12 Atmospheric Pressure Dielectric Barrier Discharge (DBD) Post Annealing of Aluminium Doped Zinc Oxide (AZO) Films**, *Y.L. Wu, E. Ritz, J. Hong, T.S. Cho, D.N. Ruzic*, University of Illinois at Urbana Champaign

Aluminum-doped Zinc Oxide (AZO) is a material that has high electrical conductivity while being highly transparent at the same time. It could find many useful applications in our daily lives such as displays, mobile devices, solar cells, etc. Currently AZO films are considered as attractive alternatives to materials such as Indium Tin Oxide (ITO) due to its much cheaper cost and comparable high electrical conductivity. A process of depositing AZO film by dual DC magnetron system has been developed. Film thicknesses were measured to be about  $300\text{nm}$  by stylus contact profilometer and transparency of greater than  $90\%$  in the visible range were measured with spectrophotometry methods. Film conductivities were in the order of  $10^3\text{ Ohm-cm}$  with the four-point probe method. By using a Dielectric Barrier Discharge operating at atmospheric pressure, conductivity of film can be further lowered. A  $500\text{mm} \times 30\text{mm}$  line source operating at a Nitrogen flow of  $250\text{L}/\text{min}$  was used and  $\sim 0.4\text{L}/\text{min}$  Hydrogen gas was also introduced into the discharge system to create Hydrogen radicals. A  $10\%$ - $15\%$  decrease in electrical resistance was observed with no changes in the optical properties of the AZO films. The elemental composition of the film was measured by X-ray photoelectron spectroscopy (XPS) and the change of crystal structure after DBD post annealing was measured by X-ray diffraction (XRD).

# Thursday Afternoon Poster Sessions

## Transparent Conductors and Printable Electronics

### Focus Topic

Room: Central Hall - Session TC-ThP

## Transparent Conductors and Printable Electronics

### Poster Session

#### **TC-ThP2 Ellipsometry Characterization of Thin Organic Films for Flexible Electronics, C. Eypert, M. Stehakovsky, L. Yan, Horiba Scientific**

In recent years, there has been an enormous research effort on both materials and processes for the production of electronic devices on flexible polymeric substrates. Flexible electronics encompass a broad set of technologies applicable across a range of products, from flexible solar cells, printed solid state lighting, to medical devices, etc. Precise control of film thickness and optical constants is vital for optimization of the device performance (efficiency, reliability, cost, etc.) In this work, we demonstrate the use of ellipsometry as a non-destructive, powerful and sensitive optical means of studying organic electronic devices. Examples in two specific areas of applications are included: OLED, and organic solar cell based on the blend of P3HT and PCBM.

#### **TC-ThP4 Toward Active-Matrix Lab-On-Chip: Programmable Electrofluidic Device Integrated with the Arrayed IGZO Oxide Thin Film Transistors, J.H. Noh, J. Noh, P.D. Rack, University of Tennessee Knoxville**

Agile micro- and nano-fluidic control is critical to numerous life science and chemical science synthesis as well as kinetic and thermodynamic studies. Electrical addressability of lab-on-chip devices currently requires external switching devices for each individual electrode for droplet transport, merging, and splitting. Thus for complex arrays, many switching devices and interconnections are needed and scale directly with the number of elements (increased size or resolution). Therefore fabrication processes and cost can be complicated and expensive as the number of input-output connections becomes unwieldy. The active matrix (AM) addressing method integrated with an electrofluidic platform is a significant breakthrough for complex electrofluidic arrays (increased size or resolution) with enhanced function, agility and programmability because the AM method can minimize the number of control lines necessary ( $m + n$  lines for the  $m \times n$  elements array) as is used in liquid crystal display technologies.

We have previously demonstrated arrayed amorphous indium gallium zinc oxide (a-IGZO) thin film transistors as a platform and the control of an electrofluidic array by AM addressing method. An a-IGZO semiconductor active layer is used because of its high mobility, low-temperature processing and transparency for spectroscopy and imaging. However, the a-IGZO transistors and an electrofluidic array were connected by external wires because the electrical properties of the a-IGZO thin film transistors were degraded after passivation. The degradation is likely due to reaction of hydrogen with a-IGZO active layer during PECVD  $\text{SiO}_2$  passivation and post-annealing process, and this can be mitigated by changing deposition temperature and annealing ambient. In this study, the effects of hydrogen and oxygen on the PECVD passivated a-IGZO thin film transistors is investigated as a function of deposition temperature and post annealing ambient. The change of hydrogen and oxygen concentration in both the IGZO active layer and  $\text{SiO}_2$  passivation layers are discussed. Finally, we review the process flow for fully integrated electrofluidic arrays on an a-IGZO transistor array and the programmable addressability of electrofluidic devices by AM addressing method. The requisite material and device parameters will be discussed for optimal active matrix addressing from device measurements in context with a VGA scale active matrix addressed electrofluidic platform.

# Authors Index

**Bold page numbers indicate the presenter**

## — B —

Bockstaller, M.R.: TC+EM+AS-WeA9, **3**  
Borsa, D.: TC+EM+AS+TF+EN-ThM2, **4**  
Bosch, R.: TC+EM+AS+TF+EN-ThM2, **4**

## — C —

Cho, T.S.: TC+EM+AS+TF+EN-ThM12, **5**  
Côté, C.: PS+TC-WeM1, **1**  
Creatore, M.: TC+EM+AS+TF+EN-ThM2, **4**

## — D —

de Vries, H.: PS+TC-WeM2, **1**  
Desbief, S.: PS+TC-WeM11, **2**  
Dufour, T.: PS+TC-WeM11, **2**

## — E —

Elam, J.W.: TC+EM+AS+TF+EN-ThM6, **4**  
Engeln, R.: PS+TC-WeM2, **1**  
Eypert, C.: TC-ThP2, **6**

## — F —

Facchetti, A.: TC+EM+AS-WeA1, **3**  
Fanelli, F.: PS+TC-WeM5, **1**  
Fracassi, F.: PS+TC-WeM5, **1**  
Fu, S.: TC+EM+AS-WeA9, **3**

## — H —

Haasch, R.T.: TC+EM+AS+TF+EN-ThM6, **4**  
Herman, G.S.: TC+EM+AS+TF+EN-ThM5, **4**  
Hirvonen, J.: PS+TC-WeM12, **2**  
Hong, J.: TC+EM+AS+TF+EN-ThM12, **5**  
Hosono, H.: TC+EM+AS+TF+EN-ThM3, **4**  
Hubert, J.: PS+TC-WeM11, **2**

## — I —

Islam, M.F.: TC+EM+AS-WeA7, **3**

## — J —

Joy, R.: TC+EM+AS+TF+EN-ThM2, **4**

## — K —

Kakiuchi, H.: PS+TC-WeM3, **1**  
Katz, H.E.: TC+EM+AS-WeA3, **3**  
Kessels, W.M.M.: TC+EM+AS+TF+EN-ThM2, **4**

Kilicaslan, A.: PS+TC-WeM1, **1**

Kim, G.Y.: PS+TC-WeM9, **2**

Kim, K.H.: TC+EM+AS-WeA7, **3**

Knoops, H.C.M.: TC+EM+AS+TF+EN-ThM2, **4**

Krueger, B.: TC+EM+AS+TF+EN-ThM11, **5**

## — L —

Lazzaroni, R.: PS+TC-WeM11, **2**

Lee, I.: TC+EM+AS-WeA7, **3**

Levasseur, O.: PS+TC-WeM1, **1**

Li, C.: TC+EM+AS-WeA4, **3**

Li, J.B.: TC+EM+AS-WeA4, **3**

Libera, J.A.: TC+EM+AS+TF+EN-ThM6, **4**

Liu, Y.: TC+EM+AS-WeA3, **3**

## — M —

Mastrangelo, A.M.: PS+TC-WeM5, **1**

Moisan, M.: PS+TC-WeM1, **1**

## — N —

Nachimuthu, P.: TC+EM+AS+TF+EN-ThM5, **4**

Narayanan, S.: TC+EM+AS-WeA9, **3**

Noh, J.: TC-ThP4, **6**

Noh, J.H.: TC-ThP4, **6**

## — O —

Oh, Y.: TC+EM+AS-WeA7, **3**

Ohmi, H.: PS+TC-WeM3, **1**

Ohuchi, F.S.: TC+EM+AS+TF+EN-ThM11, **5**

Olmstead, M.A.: TC+EM+AS+TF+EN-ThM11, **5**

## — P —

Pandey, A.: TC+EM+AS+TF+EN-ThM5, **4**

Pappas, D.: PS+TC-WeM12, **2**

Park, J.B.: PS+TC-WeM9, **2**

Pham, H.: TC+EM+AS+TF+EN-ThM11, **5**

Ponomarev, M.V.: TC+EM+AS+TF+EN-ThM2, **4**

Porter, L.M.: TC+EM+AS-WeA9, **3**

## — R —

Rack, P.D.: TC-ThP4, **6**

Rajachidambaram, M.S.: TC+EM+AS+TF+EN-ThM5, **4**

Reniers, F.: PS+TC-WeM11, **2**

Ritz, E.: TC+EM+AS+TF+EN-ThM12, **5**

Rodriguez-Santiago, V.: PS+TC-WeM12, **2**

Roy-Garofano, V.: PS+TC-WeM1, **1**

Ruzic, D.N.: TC+EM+AS+TF+EN-ThM12, **5**

## — S —

Sarkissian, A.: PS+TC-WeM1, **1**

Sharma, K.: TC+EM+AS+TF+EN-ThM2, **4**

Sirringhaus, H.: TC+EM+AS+TF+EN-ThM9, **4**

Stafford, L.: PS+TC-WeM1, **1**

Starostin, S.A.: PS+TC-WeM2, **1**

Stchakovsky, M.: TC-ThP2, **6**

## — T —

Thevuthasan, S.: TC+EM+AS+TF+EN-ThM5, **4**

## — V —

van de Sanden, M.C.M.: PS+TC-WeM2, **1**

Vandencastele, N.: PS+TC-WeM11, **2**

Velden, M.: TC+EM+AS+TF+EN-ThM2, **4**

Vilayurganapathy, S.: TC+EM+AS+TF+EN-ThM5, **4**

## — W —

Wei, S.-H.: TC+EM+AS-WeA4, **3**

Welzel, S.: PS+TC-WeM2, **1**

Williams, A.: PS+TC-WeM12, **2**

Wu, Y.L.: TC+EM+AS+TF+EN-ThM12, **5**

## — Y —

Yamada, T.: PS+TC-WeM3, **1**

Yan, L.: TC-ThP2, **6**

Yanguas-Gil, A.: TC+EM+AS+TF+EN-ThM6, **4**

Yasutake, K.: PS+TC-WeM3, **1**

Yeom, G.Y.: PS+TC-WeM9, **2**

Yim, J.: PS+TC-WeM12, **2**

## — Z —

Zhang, B.: TC+EM+AS-WeA3, **3**

Zheng, X.: TC+EM+AS+TF+EN-ThM11, **5**