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. Creatore*, 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_2 etching and, under specific conditions, surface texturing for light management/trapping. Thin ZnO:Al films (~ 100 nm) with low resistivity (2-5 * 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,[1,2,3] by means of O_2/diethylzinc/trimethylaluminium mixtures. High diethyl zinc flow rate conditions[2] 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.[2]

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^{-3}, with an electron mobility in the range of 10-25 $cm^2/V \cdot s$.[2,3] The obtained mobility values are higher than previously reported value of 13 $cm^2/V \cdot s$ for 300 nm thick ZnO:Al.[2] The improvement in terms of conductivity is attributed to the large hydrogen content (2-4 $\cdot 10^{21}$ at/cm^3) 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) andtransparent oxide semiconductors (TOSs) have a long history since 1950s. Thematerial design concept for TCOs looks almost established, i.e., ionic oxidesp-block metals with an electronic configuration of $(n-1)d^{10}ns^0$and a spatial spread of ns orbitals which is enough to have large overlap withneighboring metal ns orbitals irrespective of intervening oxygen ion[1)].Concretely, most of the TCOs have been realized in the material systems of In_2O_3-SnO_2-CdO-Ga_2O_3-ZnO. Materials based on light metal oxides such asAl_2O_3 and SiO_2 have not been regarded as thecandidates of TCOs. In 2002, we[2)] reported high electronicconductivity in $12CaO \cdot 7Al_2O_3$(C12A7) which had been a typicalinsulator and this discovery was followed by transparent conductivity in cubic$SrGeO_3$ in 2011.3) These two materials are TCOs realized by a newmaterial design concept.

Asfor TOS, the striking advances are seen in transparent amorphous oxide semiconductors(TAOS) in science and technology due to strong demand for active layermaterials in thin film transistors (TFTs). Amorphous In-Ga-Zn-O (IGZO) TFTs,which was first reported in late 2004,[4)] has adopted to drive highresolution displays of new iPad.[5)] This is a first mass productionof TOS family. The major reasons forthis adoption are high electron mobility (an order of larger than that ofa-Si:H) and easy fabrication process. Amajor advance in TOS-TFTs is realization of p-channel TFTs and subsequentfabrication of C-MOS using ambipolar SnO. [6)]

Inthis talk, I review these progresses viewed from electronic state of thesematerials.

1) H.Kawazoe,H.Yanagi,K.Ueda, and H.Hosono. *MRS Bull*,25,28(2000)

2) K.Hayashi, S.Msuishi, T.Kamiya,M.Hirano, H.Hosono, *Nature* 419, 462 (2002).

3) H.Mizoguchi,T.Kamiya, S.Matsuishi, 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. Vilayurganapathy, 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^2/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 the 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_2-In_2O_3 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^1 and M^2 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° 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 cm^2/Vs, reproducible and stable turn-on voltages V_{on} » 0V and high operational stability at maximum process temperature as low as 230°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 / β-Ga_2O_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 β-Ga_2O_3 (Eg = 4.8 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 eV), Ti forms a symmetric, nearly ohmic contact, while Al exhibits a smaller barrier (about 0.6 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 Ga_2O_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 300nm 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}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 500mm x 30mm line source operating at a Nitrogen flow of 250L/min was used and ~0.4L/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).

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