Thursday Morning, November 12, 2009

Electronic Materials and Processing
Room: B1 - Session EM-ThM

Oxide Semiconductors

Moderator: S.M. Durbin, University of Canterbury, New Zealand

8:20am EM-ThM2 Defect States in the Wide Gap Semiconducting Oxide Ga₂O₃, *T.C. Lovejoy, S. Zheng,* University of Washington*, E.G. Villora, K. Shimamura,* National Institute for Materials Science, Japan*, F.S. Ohuchi, M.A. Olmstead,* University of Washington

Ga_2O_3 is a transparent wide gap semiconducting oxide with potential applications as a transparent conductive oxide (TCO) or phase change memory (PCM) materials system. The mechanism for conductivity in this material is still under debate. The long established picture involves conduction by oxygen vacancy defect states, but unintentional silicon doping may also contribute. A recent paper [Appl. Phys. Lett. 92 202120 (2008)] shows the conductivity can be intentionally controlled over three orders of magnitude by silicon doping on the order of typical Si impurity levels in Ga_2O_3 source materials. In light of this, the actual role of oxygen vacancies is unclear. We illuminate this issue by studying separately the contribution to the electronic density of states of single crystal β-Ga_2O_3 by intentional silicon doping and oxygen deficiency with X-ray photoemission spectroscopy (XPS). Ar^+ ion sputtering is an effective means of reduction that causes states to appear above the valence band maximum, which disappear on subsequent annealing. We demonstrate qualitative agreement with previously published density functional theory results [Nature Materials 7 391 (2008)] on the effect of oxygen deficiency in Ga_2O_3. Forthcoming hard x-ray photoemission and transport measurements will further elucidate this issue.

8:40am EM-ThM3 Trends in Surface Electronic Properties of Oxide Semiconductors, *T.D. Veal, P.D.C. King, C.F. McConville,* University of Warwick, UK **INVITED**

Oxide semiconductors have enormous potential for new and innovative uses and may also improve existing device applications. However, the fundamental properties of some of the oxide semiconductors (such as In_2O_3, Ga_2O_3 and CdO) remain either controversial or largely unknown. The semiconducting oxides have traditionally been grown using low cost, low quality techniques, such as sputtering, resulting in poor microstructure material with high levels of impurities and defects. The fact that some of these materials in their low quality form have seen significant industrial use as transparent conductors has perhaps contributed to the belated recognition of their possibilities as semiconductors in their purer form. Relatively recently, with the advent of high-purity oxide semiconductor films by high-quality growth methods, such as molecular-beam epitaxy and metal-organic vapor phase epitaxy, the fundamental properties have begun to emerge and the material characteristics have been vastly improved. Here the surface and bulk electronic properties of several such high-quality oxide semiconductors (In_2O_3, CdO, $SrTiO_3$, ZnO and SnO_2) will be reported. Optical, electrical and structural properties of the semiconducting oxide films will be presented, including data on the revision of the band gap of In_2O_3 from 3.7 eV to less than 3.0 eV [1]. Both the valence band density of states and the surface electronic properties of the oxide semiconductors have been studied using high-resoultion photoemission spectroscopy [1,2]. A common property of the materials with a high size and electronegativity mismatch between the cation and oxygen atoms is found to be the presence of a surface electron accumulation layer [3,4] which is in marked contrast to the electron depletion generally observed at the surface of conventional compound semiconductors. The origin of this phenomenon will be discussed in terms of the band structure of the semiconducting oxides. The five groups where the samples were grown are gratefully acknowledged.

[1] P. D. C. King, T. D. Veal, F. Fuchs, Ch. Y. Wang, D. J. Payne, A. Bourlange, H. Zhang,

G. R. Bell, V. Cimalla, O. Ambacher, R. G. Egdell, F. Bechstedt, and C. F. McConville,

Phys. Rev. B 79 (2009) in press.

[2] P. D. C. King, T. D. Veal, A. Schleife, J. Zúñiga-Pérez, B. Martel, P. H. Jefferson, F. Fuchs,

V. Muñoz-Sanjosé, F. Bechstedt, and C. F. McConville, Phys. Rev. B 79 (2009) 205205.

[3] P. D. C. King, T. D. Veal, D. J. Payne, A. Bourlange, R. G. Egdell, C. F. McConville,

Phys. Rev. Lett, 101 (2008) 116808.

[4] P. D. C. King, T. D. Veal, P. H. Jefferson, J. Zúñiga-Pérez, V. Muñoz-Sanjosé, and

C. F. McConville, Phys. Rev. B 79 (2009) 035203.

9:20am EM-ThM5 STM and XPS studies of ITO (001) Surfaces, *H. Morales, U. Diebold,* Tulane University

Tin-doped Indium Oxide (ITO) is a transparent conducting oxide and extensively used in flat panel displays, solar cells, and organic-light-emitting-diodes. Despite the industrial significance and versatility of this material, little is known about its surface structure.

Epitaxial In_2O_3 (001) thin films with a Sn content between 0 and 30 at% were grown on Yttria stabilized Zirconia YSZ (001) using oxygen-plasma-assisted molecular beam epitaxy (MBE). The growth was monitored with Reflection-high-energy-electron-diffraction (RHEED). Low-energy-electron-diffraction (LEED) showed well ordered surfaces.

Angle-resolved X-ray photoemission (ARXPS) performed *in situ* shows that Sn^{4+} substitutes In^{3+} in the In_2O_3 bixbyite lattice and Sn enrichment in the near-surface region. A shoulder at the *Sn $3d_{5/2}$* peak at off-normal-emission angles indicates a Sn^{2+} oxidation state. The *O 1s* peak shows significant asymmetry in In_2O_3 and a more symmetric peak shape with increasing Sn content. This indicates that the charge imbalance, produced by substituting Sn^{4+} for In^{3+} in the In_2O_3 lattice, is compensated by introducing extra oxygen in the bixbyite structure.

Preparing a flat ITO (001) surface is challenging due to its polar character. A Sn concentration of more than 15 at% is necessary to stabilize ITO (001). Empty-states Scanning Tunneling Microscopy (STM) shows terraces 100 to $400nm^2$ in size and an overall surface roughness of 0.5nm. In agreement with previous theoretical work we find that the ITO (001) surface is oxygen terminated. Features in atomically-resolved STM images are interpreted with a model involving dimerization of surface oxygen.

9:40am EM-ThM6 Cyclic In-Situ Deposition and Etching for Growth of High-Quality Zinc Oxide by Metalorganic Chemical Vapor Deposition, *E.J. Adles, D.E. Aspnes,* NC State University

Zinc oxide (ZnO) is a transparent conducting oxide with a room-temperature band gap of 3.37 eV. It is currently under investigation for magneto-optic applications and as a cheap alternative for optic and optoelectronic devices currently depending on gallium and indium. While epitaxial ZnO can be grown by a number of laboratory-scale methods, growth by industrial-scale processes such as metalorganic chemical vapor deposition (MOCVD) is hampered by particulate ZnO formed in the gas phase and by the natural tendency of ZnO to deposit in multiple orientations. Both prevent deposition of high-quality epitaxial material. After careful consideration of gas-phase chemistry and our real-time polarimetric data, we have developed a cyclic MOCVD growth process based entirely on diethylzinc where conditions are alternated between brief periods of deposition and etching. The gas-phase particles are used as the source of ZnO. The etching part of the cycle preferentially removes unwanted orientations, since these typically have higher free energies. The result is dense two-dimensional epitaxial ZnO. Because etching is driven chemically instead of thermally, infilling and smoothing occur at much lower temperatures and shorter time scales than previously discussed in the literature.

10:40am EM-ThM9 Formation of Zn Nanoparticles on Single Crystal ZnO Surfaces with Ultraviolet Laser Irradiation, *E. Kahn, S. Langford, T. Dickinson,* Washington State University

Many dielectric crystals color in the visible region of the spectrum under intense ultraviolet light such as excimer laser irradiation. We have shown previously that in many cases these are due to electron hole pair production via two photon absorption. Examples are coloration of alkali halides and alkaline earth halides where self=trapped excitons lead to formation of strongly absorbing defects. Recently we were surprised to see dramatic coloration of single crystal ZnO, a wide bandgap (3.37 eV) semiconductor of significant technological interest, under exposure to 193 nm ArF excimer laser radiation. The increase in absorption is very broadband, extending from the bandgap into the infrared, appearing as near black to grey. We present careful measurements of the properties of this coloration and determine its origin. We present convincing evidence that it is due to the formation of zinc metal nanoparticles residing on the surface of the irradiated region. This evidence involves AES, TEM, XRD, UV-VIS reflection and absorption spectroscopy as well as Positron Annihilation Spectroscopy. As expected, laser fluence has considerable impact on the size, number, and spatial distribution of these nanoparticles. We present a

model for the production of this Zn metal rich surface and discuss applications including plasmonics. Related optical property measurement will be presented. Furthermore, we show that with suitable choices of laser exposure we are able to convert the originally n-type ZnO to p-type. We are carrying out additional experiments to confirm that this transformation is dependent on the formation of O-vacancies. Supportive UHV mass spectroscopy measurements of the emitted particles during laser exposure show copious release of atomic and molecular oxygen suggesting O depletion is occurring.

11:00am EM-ThM10 Preparation of N-doped p-type ZnO Film by Metal-Organic Chemical Vapor Deposition, *W. Chen*, *Y. Chen*, *J. Liang*, *C. Lu*, National Dong Hwa University, Taiwan

ZnO is a promising material used in short-wave optoelectronic devices such as light emitting diodes. However, one important issue that should be resolved beforehand is the fabrication of p-type ZnO film, which is difficult due to various intrinsic donor defects inside ZnO crystals such as zinc interstitials or oxygen vacancies. Nitrogen (N) has been considered to be an effective acceptor dopant to realize p-type ZnO. In this work, we prepared N-doped p-type zinc oxide thin films deposited on sapphire by metal organic chemical vapor deposition. We have successfully prepared high quality p-type ZnO film by changing VI/II ratio (O_2 / DMZn flow ratio), and the p-type ZnO film can be fabricated reproducibility using this method. Dimethylzinc (DMZn) and N_2O were used as zinc precursor and N dopant source. The growth temperature was in the range of $300\text{-}400^{\circ}C$ and the chamber pressure was 100 Torr. The O_2 flow rate is in the range 900-1100 sccm and DMZn carrier gas flow rate is in the range 2-10 sccm. We found ZnO film prepared using N_2O only as O source show n-type. After $800^{\circ}C$ under O_2 ambient annealing for 1 hr, a few sample originally n-type became p-type. The p-type concentration is $1.4\text{x}10^{18}$ cm^{-3}. XRD shows higher ZnO (002) peak intensity of the film after annealing than that before annealing. On the other hand, if we use O_2 and N_2O together as O source during ZnO growth, most films show p-type even before annealing. XRD spectrum and PL analysis suggest that appropriate oxygen flows can improve the quality of ZnO film to eliminate those excessive donor defects. Hall measurement shows that the resistance is 0.24 Ωcm and its corresponding hole concentration is $7.16\text{x}10^{18}$ cm^{-3}. The N $1s$ peak in XPS spectra is located at 398.5 eV, which represent N–Zn bonds. The N–Zn bonds imply that N is located at O position in ZnO crystal and forms bond with Zn. N_O is known as an acceptor defect in the ZnO film, so the presence of N-Zn bonds suggest the acceptor formation in the ZnO film. Since N_2O is the only source for N, the formation of N–Zn bond suggests that using N_2O in the process is helpful in p-type formation of ZnO films.

11:20am EM-ThM11 Growth of Ga-doped ZnO Thin Film Prepared by MOCVD for TCO Application, *K. Chou*, *J. Liang*, *Y. Chen*, *C. Yang*, National Dong Hwa University, Taiwan

The group-III elements, such as Al, Ga and In, are possible dopants for ZnO to improve the electric conductivity of ZnO thin film. Since Ga has lower cost than In and has higher oxidation resistance than Al, it becomes the preferred dopants for ZnO thin film for transparent conducting oxide (TCO) application. In the research, we used MOCVD method with Ga doping to prepare the Ga-doped ZnO thin film (GZO) on the corning-1737 glass substrate. We changed the amount of Ga doping into ZnO thin films to increase the carrier concentration and decrease the electric resistivity of ZnO thin film. We used dimethylzinc (DMZn) and oxygen as Zn and O sources, respectively, and kept both of them constant. The trimethylgallium (TMGa) was used as Ga source, and the Ga/Zn was controlled in the range of 0.8% to 2.8% by adjusting TMGa flow rate. From the top views of GZO thin films, we observed that there are small grains arranged loosely on the surface of the undoped ZnO thin film. After doping Ga into ZnO thin films the grains become bigger, and the arrangement of grains becomes compact. However, when the Ga/Zn flow ratio is over 1.6%, the grains of the GZO thin film become small again. The variation trend of grain size observed by SEM is similar with the results of FWHM in XRD spectra. The FWHM decreases as Ga/Zn flow ratio increases to 1.6%, but then the FWHM increases as Ga/Zn flow ratio increases from 1.6% to 2.8%. It implies the crystallinity of GZO thin films was improved with the Ga/Zn flow ratio and has the best crystallinity at 1.6% of the Ga/Zn flow ratio. Afterwards the crystallinity of GZO thin film worsens when the Ga/Zn ratio increases from 1.6% to 2.8%. The Hall measurement shows the electrical resistivity decreases with increasing Ga/Zn flow ratio, and the carrier concentration increases with Ga/Zn flow ratio. In addition, we found the mobility is still about 29 cm^2/Vs even as the carrier concentration has the highest value around 7.1×10^{19} cm^{-3}. It reveals that the Ga doping can significant improve the conductivity and increase the carrier concentration. Since the site which the Ga occupies in ZnO thin films can influence the electric behavior and the structure, we will use XPS to determine the Ga bond for determining the site of Ga occupied. Because the transparency is an important factor for TCO application, we will also show the transparency of GZO by the transmission spectra.

11:40am EM-ThM12 Preparation of p-type ZnO by Codoping Method using Gallium and Arsenic, *H. Jen*, *Y. Chen*, *M.S. Wong*, *H. Kuo*, National Dong Hwa University, Taiwan

In this research, we successfully prepared p-type ZnO films by rapid thermal annealing (RTA) of Ga and As codoped ZnO films deposited by magnetron DC sputtering using target made of ZnO mixed with Ga_2O_3 and Zn_3As_2 powders. These codoped p-type ZnO films were deposited on undoped silicon substrates at $300^{\circ}C$ and have hole concentrations of $10^{18}\sim 10^{19}$ cm^{-3} and resistivities of $10^{-1}\sim 10^{-2}$ ohm-cm. We changed the oxygen flow rate from 0 to 50 sccm and the RTA time for 30 seconds, 2 minutes, and 5 minutes. From the Hall measurement, the electrical conduction type of codoped ZnO film converted from n-type to p-type after RTA of the films at $1000^{\circ}C$ for 30 seconds. But it converted to n-type conduction again for longer annealing time of 2 minutes and 5 minutes. The X-ray diffraction (XRD) data indicates the crystallinity of the codoped films is improved by increased RTA time. From the field emission scanning electronic microscopy (FESEM) observation, we found the grain size of ZnO increases with annealing time, but there is less significant change of grain size after 30 seconds of RTA. The result indicates the grain boundary may not affect the electrical conduction type. According to the room temperature photoluminescence (PL) spectra, we found that the sample prepared with oxygen flow rate of 30 sccm followed by RTA at $1000^{\circ}C$ for 30 seconds in O_2 ambient had the highest near band edge (NBE) emission intensity. It indicates this RTA condition is the optimum RTA condition among other conditions. We found that the p-type ZnO films can be obtained with the same RTA parameter even though the ZnO films are prepared with different oxygen flow rate during deposition, i.e., the p-type conduction is independent of the oxygen flow rate in the deposition process and the ZnO films need an RTA process to activate the p-type conduction. From the X-ray photoelectron spectroscopy (XPS), we can not find the Ga-As bonding either in Ga 3d peak or As 3d peak. It indicates the Ga and As do not bond together in the ZnO film. This fact agrees with the codoping theory proposed by Yamamoto and Katayama-Yoshida. According to others researches and calculations, doped p-type ZnO films are produced in the oxygen-rich growth condition. We think the codoping method, which can lower the Madelung energy and activate the deep acceptor state may enhance p-type formation. Thus even in the zinc-rich condition, we can still obtain p-type ZnO thin films at appropriate RTA condition by codoping method.

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