

# SYMPOSIUM DD

## Materials for Transparent Electronics

November 28 - 30, 2005

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\* Invited paper

**8:45 AM \*DD1.1**

**Thermophysical Properties of ITO and IZO Thin Films.**  
Yuzo Shigesato, Graduate School of Science and Engineering, Aoyama Gakuin University, Kanagawa, Japan.

Reliable thermophysical properties of thin films are of importance to develop advanced industrial technologies such as highly-integrated electric devices, optical storage media and thermo electric devices. Since thermophysical properties of thin films often do not agree with those of bulk materials, it is necessary to measure thin films specimens which are synthesized to the same thickness by the same deposition method as the films in the real productions. Recently, NMIJ(AIST) and Aoyama Gakuin University have developed nanosecond laser pulse system in order to measure thermal diffusivity of multi-layered thin films including ITO and IZO [1,2]. In order to derive the thermal diffusivity of the ITO thin films, the thermoreflectance signals were analyzed based upon an analytical solution of one dimensional heat flow across the three-layered film/substrate system. The mechanism of heat conduction in ITO will be discussed in terms of electron and phonon contributions. [1]T. Baba, Y. Shigesato, et al., Proc. 25th Jpn. Symp. Thermophys. Prop., (2004, Nagano) pp.240-242. [2]T. Yagi, Y. Shigesato, et al., J. Vac. Sci. Technol. A 23(4), Jul/Aug (2005).

**9:15 AM DD1.2**

**High Electron Mobility W-doped In<sub>2</sub>O<sub>3</sub> Thin Films by Pulsed Laser Deposition.** Paul F. Newhouse<sup>2</sup>, Janet Tate<sup>1</sup>, Cheol-Hee Park<sup>2</sup>, Douglas A. Keszler<sup>2</sup> and Peter S. Nyholm<sup>3</sup>; <sup>1</sup>Physics, Oregon State University, Corvallis, Oregon; <sup>2</sup>Chemistry, Oregon State University, Corvallis, Oregon; <sup>3</sup>Hewlett-Packard Company, Corvallis, Oregon.

High electron mobility thin films of In<sub>2-x</sub>W<sub>x</sub>O<sub>3+d</sub> (0 < x < 0.075) were prepared on amorphous SiO<sub>2</sub> and single crystal yttria-stabilized zirconia substrates by pulsed laser deposition. The highest mobility polycrystalline and textured films show mobility >100 cm<sup>2</sup>/Vs and low carrier density of 2-2.5 x 10<sup>20</sup> cm<sup>-3</sup> at room temperature. The W dopant concentration for films with optimized electrical properties was measured to be x ~ 0.03 by electron probe microanalysis. A slight widening of the band gap was detected from films with increasing electron density, and the electron effective mass calculated from shifted band gap data using Moss-Burstein theory was 0.3m<sub>e</sub>. In<sub>2-x</sub>W<sub>x</sub>O<sub>3+d</sub> films have high transmittance > 80% from 0.35-2 μm.

**9:30 AM DD1.3**

**Titanium Doped Indium Oxide: A High Mobility n-Type Transparent Conductive Oxide.** M. F. A. M. van Hest, M. S. Dabney, J. D. Perkins and D. S. Ginley; National Renewable Energy Laboratory, Golden, Colorado.

Recently, transition metal doped In<sub>2</sub>O<sub>3</sub> has shown improved properties in terms of both transparency and mobility. In this study, we use combinatorial/high throughput research tools to study Ti doped indium oxide materials. Combinatorial co-sputtering from two different targets was used to produce compositionally graded transparent conducting oxides (TCO) films on 2" x 2" glass substrates. This approach allows for a large or small composition gradient across the deposited film. The Ti doped indium oxide material is grown using an indium oxide target and a Ti doped indium oxide target. The targets have been sputtered using RF power in a pure argon or argon/oxygen atmosphere. Deposition temperatures range from room temperature to 550 °C. Ti doping of indium oxide results in films with very good conductivity (>6000 Ω<sup>-1</sup>cm<sup>-1</sup>) and high mobility (>80 cm<sup>2</sup>/Vs). The best conductivity is obtained when the doping is in the range from 1.5 to 6% for films deposited at high temperature (550 °C) in a pure argon atmosphere. Ti doping results in the generation of one carrier per Ti doping atom. Films were analyzed by four-point probe, Hall probe, XRD and optical transmission and reflection spectroscopy. The best films are highly crystalline and high optical transmission across the visible portion of the spectrum (>85%).

**9:45 AM DD1.4**

**PLD Growth of Indium Tin Oxide at Room Temperature on Polymer Substrates.** Guus Rijnders, Matthijn Dekkers and Dave H. A. Blank; Faculty of Science and Technology and MESA+ Institute for nanotechnology, University of Twente, Enschede, Netherlands.

In opto-electronic devices, such as switches and solar cell applications, there exists a strong need to replace the current substrate material (silicon or glass) by cheaper and flexible synthetic materials. Polycarbonate (PC) and polyethylene terephthalate (PET) are plastics that fulfill these conditions and moreover, they are highly

transparent for visible light. However, since the low heat-sustainability of these substrates, process temperature should be limited to approximately 370K. Indium-tin-oxide (ITO) is used for decades as a transparent conductor, and known for its excellent properties if grown at high temperatures (T>500K). Here we studied the growth of ITO at room temperature on plastic substrates, using pulsed laser deposition (PLD). By carefully controlling the process parameters during growth, films were obtained with properties comparable to ITO grown at high temperature. Moreover, the doping of tin shows a negative effect on the electrical properties of this material. In contrast to films grown at high temperatures, the conductivity decreases if more tin is added. The tin-atoms act as nucleation sites during PLD growth at room temperature, resulting in smaller grain sizes in the polycrystalline film. This affects the mobility of the charge carriers, i.e. increases the resistivity.

**10:30 AM \*DD1.5**

**II-VI Based Transparent Hybrid Semiconductors by Design.** Xiaoying Huang<sup>1</sup>, Wooseok Ki<sup>1</sup>, Jing Li<sup>1</sup>, Yong Zhang<sup>2</sup> and Angelo Mascarenhas<sup>2</sup>; <sup>1</sup>Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey; <sup>2</sup>National Renewable Energy Laboratory, Golden, Colorado.

There has been a tremendous interest in the areas of transparent electronics in the recent years. Materials that are transparent and have high electronic conductivity may lead to many important applications. We have designed, developed and studied a unique class of wide band-gap hybrid materials based on II-VI semiconductors [1-3]. These hybrid structures are assembled as single-atomic chains or slabs of II-VI or MQ (M = Zn, Cd; Q = S, Se, Te) that are interconnected by mono- or bi-functional organic molecules via chemical bonds. They exhibit extremely strong quantum confinement effect (QCE) that results in very large blue shifts in their optical absorption edges (1.0-2.0 eV), and thus, very large band gaps. These transparent hybrid semiconductors can be synthesized cost effectively under mild conditions, and their structures and properties can be tuned systematically. They show numerous improved properties over their parent II-VI bulk, including broader band-gap tunability and higher absorption coefficients [4-7]. More significantly, they have the potential to become good p-type transparent conductors that are difficult to achieve for conventional transparent oxides. References: [1] X.-Y. Huang, J. Li and H.-X. Fu, J. Am. Chem. Soc. 122 (2000) 8789. [2] X.-Y. Huang, H. R. Heulings IV, V. Le and J. Li, Chem. Mater. 13 (2001) 3754. [3] X.-Y. Huang, J. Li, Y. Zhang and A. Mascarenhas, J. Am. Chem. Soc. 125 (2003) 7049. [4] H. R. Heulings IV, X.-Y. Huang, J. Li, T. Yuen and C.L. Lin, Nano Lett. 1 (2001) 521. [5] H.-X. Fu, J. Li, J. Chem. Phys., 120 (2004) 6721. [6] B. Fluegel, Y. Zhang, A. Mascarenhas, X.-Y. Huang and J. Li, Phys. Rev. B70 (2004)205308. [7] Y. Zhang, G. M. Dalpian, B. Fluegel, Su-Huai Wei, A. Mascarenhas, X.-Y. Huang, J. Li, and W.-L. Wang Submitted.

**11:00 AM DD1.6**

**Surface electronic structures of treated indium tin oxide (ITO) thin films using Scanning Probe Microscopy.** Chanhyung Kim, Lee Bongki, Yang Hee Jung, Lee Jae Gab and Shin Hyunjung; School of Advanced Materials Engineering, Kookmin University, Seoul, South Korea.

Influence of CF<sub>4</sub> plasma, UV-ozone and chemical treatments with acids and bases on the surface electronic structures of Indium-Tin-Oxide (ITO) thin films has been studied by x-ray photoelectron spectroscopy (XPS) and scanning probe microscopy (SPM). Conducting atomic force microscopy (C-AFM) and spectroscopic technique using Kelvin Probe Force Microscopy (KPFM), in this study, were used to measure surface conductivity and local work function of ITO surfaces. In order to measure work function, spectroscopic technique using Kelvin Probe Force Microscopy (KPFM) was used. The technique is a method to measure the CPD at one point under the AFM probe tip. Prior to measure the work function of ITO, all tips were calibrated their work functions using HOPG (highly oriented pyrolytic graphite), Pt (111) and Au films. Local current maps of ITO surfaces using C-AFM showed two distinct conducting and non-conducting regions at applied bias of 0.1V. Local I-V measurements in conducting regions of as-received ITO showed Ohmic behavior. Most of ITO surfaces became to be non-conducting showing Schottky behavior after surface treatment with CF<sub>4</sub> plasma, but other treatments showed no change at all. Work function of ITO increased just after surface treatments using CF<sub>4</sub> plasma, UV-ozone, and acidic solutions. However, treatments by basic solutions are decreased by ~ -0.1 eV. When ITO films exposed in ambient, work function of ITO decreased gradually because water molecules and any other adventitious are absorbed onto the surfaces. The CF<sub>4</sub> plasma, UV-ozone and acid treatments allowed making more negative surfaces with more dangling bonds of fluorine ions (F<sup>-</sup>), oxygen ions (O<sup>-</sup>) and chlorine ions (Cl<sup>-</sup>). The surfaces with electronegative ions induced to deplete electrons from the surfaces. In subsequent, it caused the band bent upward. As a result, mechanism

for the increase and decrease gradually with function of time for work function by the surface treatment and in ambient are proposed. Our conclusion helps to understand the injection of holes into the active light-emitting layer from ITO electrodes in the application of organic light emitting diodes (OLEDs), thus to enhance devices' performance as well as reliability.

#### 11:15 AM DD1.7

**Deposition Conditions and Electrical and Optical Properties of ZITO Thin Films.** Clewa W. Ow-Yang<sup>1</sup>, Hyo-Young Yeom<sup>2</sup>, Burag Yagliglu<sup>2</sup> and David C. Paine<sup>2</sup>; <sup>1</sup>Faculty of Engineering & Natural Sciences, Sabanci University, Istanbul, Turkey; <sup>2</sup>Division of Engineering, Brown University, Providence, RI, Rhode Island.

Currently ITO films are the preferred TCO for flat panel display applications, typically grown by dc magnetron sputtering due to the large area uniformity that can be obtained. However, due to the more limited supply and thus higher cost of In, much activity has been devoted to decreasing the amount of indium in In<sub>2</sub>O<sub>3</sub>-based thin films, such as by varying the composition of ITO. Individually, Zn and Sn dopants have very limited solubility in In<sub>2</sub>O<sub>3</sub>, but when co-substituted as metal oxides into bulk In<sub>2</sub>O<sub>3</sub>, their solubility limit dramatically increases from < 6 cation% to ~20 cation% each. We will present a study on Zn-In-Sn-O (ZITO) thin films grown by dc magnetron sputtering from sintered ceramic targets of two Zn:In:Sn compositions, (i) 1:2:1 and (ii) 1:2:1.5, under a range of oxygen partial pressures at both room temperature and at 300°C. The thin film microstructure was characterized by the glancing-incidence angle diffraction of x-rays. The optical spectra were measured using a UV-visible-near IR spectrophotometer, and electronic properties were measured by Van der Pauw and Hall effect techniques. The absorption edge was extrapolated from the optical spectra using the Tauc equation to enable determination of the electronic bandgap. Interestingly, the bandgap narrowed with increasing film thickness, which is consistent with reported observations in ZnO thin films, but opposite of what has been observed in ITO thin films.

#### 11:30 AM DD1.8

**Pulsed Energy Deposition of Functional Oxides on Low-Thermal Budget Plastic Substrates.** Solomon H. Kolagani, Mikhail Strikovski and Jeongoo Kim; Thin Films, Neocera, Inc, Beltsville, Maryland.

Pulsed Laser Deposition (PLD), where an excimer laser (248 nm, 20 ns pulse width) is used as an energy source to ablate a target material forming a thin film, is the preferred method for the deposition of a variety of multi-component metal-oxide films. Stoichiometric preservation of film composition and ability to deposit films over a wide range of deposition parameter space lend PLD a unique advantage as a rapid prototyping technique relative to other vapor deposition methods. The wide range of kinetic energies available to the ablated species (0.1 eV to 100 eV) also makes PLD, an attractive candidate for processing a variety of functional ceramic oxides on temperature sensitive substrates such as plastics which can not withstand high temperatures in excess of 350C. In this presentation, we will discuss our recent experimental results obtained on ceramic oxide films such as transparent conducting Indium Tin Oxide, ferromagnetic Fe<sub>3</sub>O<sub>4</sub> and paraelectric Ba-SrTiO<sub>3</sub> films, all deposited on low thermal budget plastic substrates such as Kapton. We will also discuss the applicability of a relatively less known Pulsed Electron Deposition Technology for cost effective large area, high volume scale-up.

SESSION DD2: Transparent Conducting Oxides II  
Chairs: Clewa W. Ow-Yang and John D. Perkins  
Monday Afternoon, November 28, 2005  
Room 309 (Hynes)

#### 1:30 PM \*DD2.1

**A new transparent conductor anatase Ti<sub>1-x</sub>Nb<sub>x</sub>O<sub>2</sub> : transport and optical properties.** Yutaka Furubayashi<sup>1</sup>, Taro Hitosugi<sup>1,2</sup>, Yukio Yamamoto<sup>1</sup>, Yasushi Hirose<sup>1</sup>, Makoto Otani<sup>1</sup>, Kazuhisa Inaba<sup>1,3</sup>, Toshihiro Shimada<sup>1,2</sup> and Tetsuya Hasegawa<sup>1,2</sup>; <sup>1</sup>"Nano-structured Magneto-optical devices" project, Kanagawa Academy of Science and Technology, Kawasaki, Japan; <sup>2</sup>Department of Chemistry, University of Tokyo, Tokyo, Japan; <sup>3</sup>Materials and Structures Laboratory, Tokyo institute of Technology, Yokohama, Japan.

We have discovered a new transparent conducting oxide (TCO), anatase Ti<sub>1-x</sub>Nb<sub>x</sub>O<sub>2</sub>, in thin film form. The 0.03 ≤ x ≤ 0.06 films with a thickness of 40 nm showed resistivity of 2-3 × 10<sup>-4</sup> Ωcm and internal transmittance of ~97 % in the visible light region, at room temperature. These values are comparable to those of typical TCOs,

such as In<sub>2-x</sub>Sn<sub>x</sub>O<sub>3</sub>. We have also investigated effective mass and scattering time of electron carriers in Ti<sub>1-x</sub>Nb<sub>x</sub>O<sub>2</sub> films with 0 < x ≤ 0.1. From the plasma-frequency and frequency dependence of optical conductivity, it was revealed that Nb-doping slightly enhances the effective mass. On the other hand, the scattering time strongly depends on Nb-concentration, reflecting strong x dependence of Hall mobility. These results indicate that the transport properties of Ti<sub>1-x</sub>Nb<sub>x</sub>O<sub>2</sub> are mainly governed by scattering factors, such as impurities, phonons and grain boundaries, but are insensitive to the structure of conduction band.

#### 2:00 PM DD2.2

**Band structures, defect levels and compensation in n-type and p-type conducting oxides In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub> and CuAlO<sub>2</sub>.** John Robertson and Barbara Falabretti; Engineering, University of Cambridge, Cambridge, United Kingdom.

In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub> and CuAlO<sub>2</sub> are important n- and p-type transparent conducting oxides (TCOs). Their doping and conduction depends on the properties of their dopant levels and on any self-compensation mechanism via intrinsic defects such as vacancies. We study the compensation mechanism via calculations of the defect levels using ab-initio local density formalism based (LDA) methods. LDA and generalised gradient approximation (GGA) generally give a good description of the ground state properties of compounds but tend to under-estimate the band gap of semiconductors and insulators. For example, the GGA band structures of SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> have band gaps on only ~1.2 eV [1,2] compared to their experimental values of ~3.6 eV. This is much greater than the usual 30% error, and means that defect level calculations must be particularly careful. Here we use more advanced methods, the screened exchange (sX) method and the weighted density approximation (WDA) which give the correct band gap [3]. We use them to calculate the band structures and defect levels. Full lattice relaxation was carried out at defects. We calculate the levels of substitutional Sn in In<sub>2</sub>O<sub>3</sub>, substitutional Sb in SnO<sub>2</sub>, interstitial Sn in SnO<sub>2</sub>, O vacancies in all the oxides, and Cu interstitials in CuAlO<sub>2</sub>. This allows us to understand the doping mechanism in the n-type TCOs and the compensation mechanism in the p-type TCOs [4]. 1. C Kilic, A Zunger, Phys Rev Lett 88 095501 (2002) 2. H Okada, Y Shigesato, Jpn J App Phys 40 3231 (2001) 3. J Robertson, K Xiong, B Falabretti, IEEE Trans Device Mats Reliability 5 84 (2005) 4. J Robertson, P W Peacock, M D Towler, R Needs, Thin Solid films 411 96 (2002)

#### 2:15 PM DD2.3

**Electronic Surface Properties of Transparent Conducting Oxides.** Brian J. Ingram<sup>1</sup>, Mariana I. Bertoni<sup>1</sup>, Steven P. Harvey<sup>1,2</sup>, Stephen J. Sollenberger<sup>1</sup>, Thomas O. Mason<sup>1</sup>, Yvonne Gassenbauer<sup>2</sup>, Jochen Fritsche<sup>2</sup> and Andreas Klein<sup>2</sup>; <sup>1</sup>Materials Science & Engineering, Northwestern University, Evanston, Illinois; <sup>2</sup>Institute of Materials Science, Darmstadt University of Technology, Darmstadt, Germany.

Matching band offsets with active organics is crucial for transparent electrode applications, e.g., in organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs). Indium-tin oxide or ITO is routinely used, owing to its ready availability, in spite of the mismatch-both electronic and chemical-with p-type organics. This study reports electronic surface properties for a range of transparent conducting oxides or TCOs, including the basis oxides (e.g. pure and doped In<sub>2</sub>O<sub>3</sub>, CdO, etc.) and a variety of compound and solid solution TCOs (e.g., co-doped bixbyite and spinel systems). We have been able to demonstrate good agreement between XPS/UPS results on thin films vs. those on properly prepared and cleaned bulk specimens. Our survey of TCO materials suggests that so-called "self-doped" TCOs remain degenerately doped to the surface, in contrast to ITO, which is susceptible to surface oxidation and depletion of carriers. We also present work functions for TCOs, many of which have not been previously reported. Ramifications for transparent electrode applications (e.g., OLEDs, OPVs) will also be discussed.

#### 3:30 PM \*DD2.4

**Metal-Insulator Transition in Room Temperature Stable Inorganic Electride [Ca<sub>24</sub>Al<sub>28</sub>O<sub>64</sub>]<sup>4+</sup>(O<sup>2-</sup>)<sub>2-x</sub>(e<sup>-</sup>)<sub>2x</sub> (0 < x < 2).** Satoru Matsuishi<sup>1</sup>, SungWng Kim<sup>1</sup>, Yoshitake Toda<sup>1</sup>, Masashi Miyakawa<sup>1</sup>, Katsuro Hayashi<sup>1</sup>, Toshio Kamiya<sup>2</sup>, Masahiro Hirano<sup>1</sup> and Hideo Hosono<sup>1,2</sup>; <sup>1</sup>Frontier Collaborative Research Center, Tokyo Institute of Technology, Tokyo, Japan; <sup>2</sup>Materials and Structure Laboratory, Tokyo Institute of Technology, Tokyo, Japan.

Transparent insulating oxide crystal 12CaO·7Al<sub>2</sub>O<sub>3</sub> (C12A7) is converted into electrical conductor by replacing oxygen ions (O<sup>2-</sup>) captured in the crystallographic cages ([Ca<sub>24</sub>Al<sub>28</sub>O<sub>64</sub>]<sup>4+</sup>) with electrons as anions (e<sup>-</sup>) via reduction treatments using calcium or titanium metals. [1] As electron concentration increases, the DC electrical conductivity (—\*mu\*<sub>DC</sub>) increases up to 1500 S·cm<sup>-1</sup> at

room temperature and the temperature dependence of conductivity changes from semiconductive ( $d\mu_{DC}/dT > 0$ ) to metallic ( $d\mu_{DC}/dT < 0$ ). To investigate the modification of electronic structure with increase in electron concentration, the optical reflectance spectra of C12A7 single crystals having various electron concentrations were measured at room temperature in the photon energy region from 0.05 to 5 eV and the optical conductivity was obtained by spectral fitting using Drude-Lorentz model. When the electron concentration is below  $\sim 10^{19} \text{ cm}^{-3}$ , electrons are trapped in cages distorted by Coulombic interaction between electrons and ions forming the cages and occupy the deep energy levels below the narrow "cage conduction band" consisting of unoccupied orbitals confined in empty cages. Then, the optical conductivity spectrum in infrared region is dominated by Lorentz type response centered at  $\sim 0.4$  eV due to charge transfer (CT) transition between the occupied and unoccupied cages and electron conduction is controlled by hopping mechanism. When the concentration goes up to  $\sim 10^{20} \text{ cm}^{-3}$ , the level of trapped electron is close to the bottom of cage conduction band. Therefore, some electron is thermally excited to the cage conduction band and yield Drude-type optical response in addition to CT band. Further increase in electron concentration close to maximum,  $2 \times 10^{21} \text{ cm}^{-3}$  (1 electron per 3 cages), the distortion of cage is removed and the cage conduction band is partially occupied by electrons delocalized in neighboring cages. Then, the optical conductivity spectrum of infrared region is dominated by Drude type response with plasma frequency of 1.7 eV. The present study demonstrates that microporous crystal composed of typical insulating oxides, CaO and  $\text{Al}_2\text{O}_3$ , may convert to metal by appropriate electron-doping processes. [1] S.Matusishi, Y.Toda, M.Miyakawa, K.Hayashi, T.Kamiya, M.Hirano, I.Tanaka, and H.Hosono, Science 301, 626(2003).

#### 4:00 PM \*DD2.5

**Influence of Physical Structure on the Transparency of Novel Conducting Materials.** Arthur F. Hebard, Sinan Selcuk, Partha Mitra, Andrew G. Rinzler, Zhuangchun Wu, David B. Tanner, Kwangje Woo and Nacira Tache; Physics, University of Florida, Gainesville, Florida.

Transparent conductors have traditionally been prepared from a variety of materials including metals such as Ag, Au, and TiN and doped oxides of Zn, Cd, In, and Sn. Optimized materials usually have uniform composition and density down to near atomic length scales. In this talk, we present examples of novel thin-film materials where physical structure at specific length scales plays an important role in determining transparency and/or conductivity. Specifically, we discuss the following three rather disparate systems: (1) carbon nanotube films prepared by filtration, (2) indium oxide films prepared by reactive ion beam sputter deposition and (3) patterned thin silver films prepared by thermal deposition. The nanotube films are homogeneous on optical length scales but inhomogeneous on shorter length scales. This network porosity lends itself to facile charge transfer doping and de-doping thereby modifying the sheet resistance. In contrast, the transparency of indium oxide films, and to a lesser extent the conductivity, is sensitive to the relative proportions of amorphous and crystalline phases on optical length scales. This sensitivity to structure on optical length scales is further illustrated in lithographically patterned apertureless Ag films, which show enhanced transmission at wavelengths related to the structural periodicity. Electrical, optical and structural characterization will be presented to illustrate the common aspects of these phenomena and assess the feasibility of using structure in a controlled way to modify the transparency and conductivity of novel materials.

SESSION DD3: Transparent Thin Film Transistors  
Chairs: Kenji Nomura and Janet Tate  
Tuesday Morning, November 29, 2005  
Room 309 (Hynes)

#### 8:00 AM DD3.1

**Incorporation of Perovskite Oxides Into Gate Insulator of Zinc Oxide TFTs.** Jeffrey J. Siddiqui, Emine Cagin, Patrick B. Shea, Jerzy Kanicki and Jamie D. Phillips; Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan.

Zinc Oxide (ZnO) is a wide-bandgap compound semiconductor that is one of the few oxides that can be grown as a crystalline material at relatively low deposition temperatures. These properties make ZnO an attractive material for thin film transistors (TFT). ZnO TFTs have shown promise, but key performance issues continue to be low mobility, off current, and small on/off ratio. Many of these properties are associated with the material interface of the ZnO with the gate insulator material. In this work, the characteristics of ZnO TFTs with varying gate insulators are studied. TFT performance characteristics are presented with gate insulators of  $\text{SiO}_2$ ,  $\text{SiN}_x$ , and perovskite oxides. Perovskite oxides are studied to examine the possibility of

incorporating high-k dielectric materials, such as barium strontium titanate (BST), for improved transistor performance, and the possibility of incorporating polarization effects, as seen in lead zirconate titanate (PZT), to control the conduction properties of the ZnO material. ZnO bottom-gate TFT devices were fabricated using pulsed laser deposition and standard metallization and photolithography techniques. The devices were fabricated on silicon substrates and platinum coated silicon substrates, with the substrate acting as the gate electrode. ZnO thin films deposited by pulsed laser deposition on these gate insulators show a (0001) preferred orientation, with electron mobility on the order of  $1\text{-}10 \text{ cm}^2/\text{Vs}$ . Initial current-voltage results show an on/off ratio of  $\sim 10^4$  and a transconductance of  $7 \times 10^{-6}$  mhos. ZnO TFT performance will be compared for varying gate insulators, and the outlook for the incorporation of perovskite oxides as gate insulators will be discussed.

#### 8:15 AM \*DD3.2

**Amorphous Multi-component Heavy Metal Cation Oxides for Thin-Film Transistor Applications.** John Wager, School of Electrical Engineering and Computer Science, Oregon State University, Corvallis, Oregon.

Amorphous multi-component heavy metal cation (a-MHMC) oxides constitute an interesting new class of electronic materials. Zinc tin oxide (ZTO) and zinc indium oxide (ZIO) are two a-MHMC oxide examples which have recently been employed as channel layers for high performance transparent thin-film transistors (TTFTs). The purpose of this presentation is to introduce this new class of materials and to assess their potential for transparent and non-transparent thin film transistor (TFT) applications.

#### 8:45 AM \*DD3.3

**Transparent Flexible Transistor using Amorphous Oxide Semiconductors.** Kenji Nomura<sup>1</sup>, Hiromichi Ohta<sup>2</sup>, Akihiro

Takagi<sup>2</sup>, Toshio Kamiya<sup>1,2</sup>, Masahiro Hirano<sup>1</sup> and Hideo Hosono<sup>1,2,3</sup>; <sup>1</sup>ERATO-SORST, JST, Yokohama, Japan; <sup>2</sup>Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; <sup>3</sup>Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan.

Flexible electronics will be indispensable for feature information technology as they can develop advanced opto-electronic applications such as wearable computers and displays attachable to winding windows and walls, and they may have advantages such as flexibility, light weight, and low cost. Fabrication of thin film transistors (TFTs) on flexible plastic sheets is a key technique to realize them. Hydrogenated amorphous silicon (a-Si:H) and organics have been examined as active layer materials in such flexible devices. However, the device performances and applications are limited by the properties inherent to these materials (e.g. mobilities are  $< 2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for a-Si:H TFTs). Therefore, it is vital to develop larger mobility amorphous materials that can be formed at low temperatures for developing high performance flexible TFT. Recently we have demonstrated that amorphous oxide semiconductors (AOSs) have much favorable properties for developing high performance flexible TFTs than the conventional amorphous semiconductors do. AOS based TFTs fabricated using In-Ga-Zn-O system (a-IGZO) on plastics at room temperature (RT) exhibited field effect mobilities of  $6\text{-}9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which values are almost one order of magnitude larger than those reported for a-Si:H and organic TFTs[1]. The a-IGZO channel layers were deposited at room temperature (RT) by a pulsed laser deposition (PLD) with a KrF excimer laser. Top gate TFT structures were fabricated on plastic sheets (polyethylene terephthalate (PET)) by a standard photolithography and lift-off technique. Also ITO source / drain / gate electrodes and  $\text{Y}_2\text{O}_3$  gate insulator were deposited by PLD at RT. The flexible TFTs fabricated at room temperature exhibited good performances with on / off current ratios  $\sim 10^6$  and field effect mobilities  $\sim 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which were almost the same values as those obtained from the linear region of transfer characteristics ( $\mu_{lin} \sim 9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  at  $V_{DS} = 2 \text{ V}$ ). The transfer characteristic showed low off-currents less than the order of  $10^{-10} \text{ A}$  and the IDS was modulated by approximately six orders of magnitude by the applied gate bias. The threshold voltage ( $V_{th}$ ) obtained by extrapolating the  $I_{DS}\text{-}V_{GS}$  curve in the linear region was positive, approximately  $+ 1.3 \text{ V}$ . The materials exploration of AOSs for high-performance flexible & transparent TFTs and the detailed carrier transport properties in AOSs will also be presented. [1] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, H. Hosono, Nature 488, 432(2004).

#### 9:15 AM DD3.4

**High mobility amorphous indium zinc oxide transparent thin film transistors.** Pedro Barquinha, Rodrigo Martins and Elvira Maria Fortunato; Materials Science, FCT-UNL, Caparica, Portugal.

The recent application of semiconducting oxides to fully transparent thin film transistors (TFTs) is making a (r)evolution on the contemporary solid-state electronics. Nevertheless, the ability to have simultaneously TFTs with a high mobility and fabricated at low temperature, to meet the requirements of the new emergent low cost technologies (like wearable computers, heads-up displays, electronic paper and rollable memories, among others) has not yet been demonstrated. The known published results of TFTs grown at or near room temperature are far to respond to the above demands due to their poor carrier mobility (not exceeding in general  $9 \text{ cm}^2/\text{Vs}$ ), including the emergent organic based TFTs. In this paper we demonstrate the use of an amorphous oxide semiconductor based on the  $\text{In}_2\text{O}_3$  -  $\text{ZnO}$  system used simultaneously at the active channel layer as well as at the source/drain TFT regions. The obtained TFTs operate in the enhancement mode with threshold voltages of the order of 2 V, a saturation mobility higher than  $30 \text{ cm}^2/\text{Vs}$ , a gate voltage swing of 0.2 V/dec and an ON/OFF current ratio of 109. The high performances presented by these TFTs and their high channel electron mobility comparable to or even better than other polycrystalline semiconductors, opens new doors for applications in flexible, wearable and disposable electronics.

#### 9:30 AM DD3.5

**Amorphous zinc indium oxide for transparent thin-film transistors.** Hai Chiang<sup>1</sup>, Nicole L. Dehuff<sup>1</sup>, David Hong<sup>1</sup>, Emma S. Kettenring<sup>1</sup>, John Wager<sup>1</sup>, Randy Hoffman<sup>3</sup>, Cheol-hee Park<sup>2</sup> and Douglas Keszler<sup>2</sup>; <sup>1</sup>Electrical Engineering and Computer Science, Oregon State University, Corvallis, Oregon; <sup>2</sup>Chemistry, Oregon State University, Corvallis, Oregon; <sup>3</sup>Hewlett Packard, Corvallis, Oregon.

Amorphous, multicomponent heavy-metal cation oxides have recently emerged as an interesting class of materials for transparent thin-film transistor (TFT) applications. One example is zinc indium oxide; the wide band gap of  $\sim 2.9 \text{ eV}$  renders zinc indium oxide visibly transparent. Zinc indium oxide-based TFTs exhibit field-effect mobilities in excess of  $30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  at processing temperatures of  $\sim 200^\circ\text{C}$ . The objective of this presentation is to provide an overview of electrical device characteristics of zinc indium oxide transistors.

#### 9:45 AM DD3.6

**Structural and Electrical Characterization of  $\text{In}_2\text{O}_3$ -10wt% $\text{ZnO}$  Thin Films for Device Applications.** Burag Yaglioglu, Hyo-Young Yeom and David Paine; Engineering, Brown University, Providence, Rhode Island.

Materials for oxide-based transparent electronics have been recently reported in the literature. These materials include  $\text{ZnO}$  and various amorphous and crystalline compounds based on multi-component oxides with Zn as the primary cationic component and many of them offer useful combinations of transparency, controllable carrier concentrations, and reasonable n-carrier mobility. In this study we report on amorphous and crystalline  $\text{In}_2\text{O}_3$ -10wt% $\text{ZnO}$ , IZO, for potential use in oxide electronics. The material was deposited using dc magnetron sputtering and has, in the as-deposited state, an amorphous structure with a carrier concentration of  $\sim 1\text{E}+20 / \text{cm}^3$  and a Hall mobility of  $\sim 50 \text{ cm}^2/\text{Vs}$ . Annealing amorphous IZO films at  $500^\circ\text{C}$  produces a previously unknown crystalline product compound. We report that the crystal structure of this compound is based on the high-pressure corundum phase of  $\text{In}_2\text{O}_3$  and that this compound has a controllable carrier concentration ( $< 1\text{E}+18 / \text{cm}^3$ ) and reasonable mobility ( $\sim 18 \text{ cm}^2/\text{Vs}$  at  $1\text{E}+18 / \text{cm}^3$ ). We report on the use of reducing and oxidizing annealing ambients to modify carrier concentration and on our preliminary efforts to fabricate thin film transistors using crystalline IZO.

#### 10:30 AM \*DD3.7

**On the Road to Transparent Flexible Electronics.** Peter F. Carcia and Robert S McLean; Central Research Department, DuPont, Wilmington, Delaware.

The realization of transparent, flexible, active electronics will require the confluence of new or improved technologies for substrates, transparent conductors, semiconductors, dielectrics, chemical and gas diffusion barriers, and circuit patterning. Critical for nearly all of these functional layers is a transparent plastic substrate with high operating temperature ( $> 250^\circ\text{C}$ ), good chemical stability, and low coefficient of thermal expansion. In this talk, we will present preliminary properties for experimental, high performance substrates, currently in development at DuPont, that meet most of these criteria. Active electronics will also need a semiconductor, compatible with processing on a plastic substrate. A leading semiconductor candidate for transparent electronics is  $\text{ZnO}$  and its related oxides. While transparent thin film transistors (TFTs) based on these oxides have higher mobility than amorphous Si or organic semiconductors, with equally low processing temperature, the polycrystalline and defect structure of oxide TFTs can limit their performance. In this regard we show that control of the oxygen partial pressure during  $\text{ZnO}$

preparation can significantly alter the density of interface trap states, consequently affecting transistor mobility, on/off ratio, and turn-on voltage. Inherently important for reducing interface trap density and thereby optimizing TFT properties is development of a high quality, compatible gate dielectric. In the IC industry, where there is a need to replace the thermally grown  $\text{SiO}_2$  gate dielectric in the highest performance transistors, atomic layer deposition (ALD) is emerging as the preferred method for growing dense, pinhole-free, high performance gate dielectric films. In this talk we compare  $\text{ZnO}$  thin film transistor (TFT) properties on gate dielectrics of  $\text{Al}_2\text{O}_3$ ,  $\text{HfO}_2$ , and  $\text{HfSiO}_2$  grown by ALD with corresponding properties on thermally grown  $\text{SiO}_2$ . Specifically for  $\text{HfO}_2$ ,  $\text{ZnO}$  TFTs had a mobility  $> 10 \text{ cm}^2/\text{V-s}$ ,  $V_{\text{th}} = 2.5 \text{ V}$ , and a subthreshold slope  $\sim 0.5 \text{ V/decade}$ . Finally we propose that large-area electronics can be patterned on flexible plastic substrates by imaging a laminated, photopolymer dry film resist through a phototool, as exemplified by DuPont printed circuit materials.

#### 11:00 AM DD3.8

**Zinc Tin Oxide Based Transparent Thin-film Transistors.** David Hong<sup>1</sup>, Hai Q. Chiang<sup>1</sup>, John F. Wager<sup>1</sup>, Randy L. Hoffman<sup>3</sup>, Cheol Hee Park<sup>2</sup> and Douglas A. Keszler<sup>2</sup>; <sup>1</sup>School of Electrical Engineering and Computer Science, Oregon State University, Corvallis, Oregon; <sup>2</sup>Chemistry, Oregon State University, Corvallis, Oregon; <sup>3</sup>Hewlett-Packard, Corvallis, Oregon.

Zinc tin oxide is a high-performance channel material for transparent thin-film transistor (TFT) applications. Zinc tin oxide exhibits relatively high carrier mobility in spite of its amorphous nature. Zinc tin oxide TFTs exhibit field-effect mobilities in excess of  $20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  at processing temperatures of  $600^\circ\text{C}$ . Additionally, zinc tin oxide has a sufficiently large bandgap to render it transparent. The objective of this presentation is to provide an overview of the fabrication of zinc tin oxide TFTs, including the passivation of zinc tin oxide TFTs and the deposition of zinc tin oxide via a sequential sputtering and annealing methodology.

#### 11:15 AM DD3.9

**Zinc Tin Oxide Thin Film Transistors.** Gregory S. Herman<sup>1</sup>, Randy L. Hoffman<sup>1</sup>, Lorraine C. Wang<sup>1</sup>, Warren B. Jackson<sup>2</sup>, John A. Rogers<sup>3</sup>, Seung-Hyun Hur<sup>3</sup> and Anshu Gaur<sup>3</sup>; <sup>1</sup>Hewlett-Packard Company, Corvallis, Oregon; <sup>2</sup>Hewlett-Packard Laboratories, Palo Alto, California; <sup>3</sup>Materials Science & Engineering, Univ. of Illinois Urbana/Champaign, Urbana, Illinois.

Zinc oxide transistors have received considerable interest due to their high performance at relatively low process temperatures. Recent results have demonstrated that completely transparent thin-film transistors (TFTs) using zinc oxide and related materials can be fabricated on both rigid and flexible substrates which may enable unique applications. Recently we have shown that TFTs fabricated with zinc tin oxide (ZTO) channels can have relatively high mobilities ( $\sim 30 \text{ cm}^2/\text{Vs}$ ), for amorphous ZTO films, after annealing up to  $600^\circ\text{C}$ . In this talk, we present data on high performance ZTO transistors produced on rigid and flexible substrates. We have evaluated the effect of channel composition, processing temperature, and source/drain electrode and gate dielectric materials on ZTO TFT performance. Two methods have been utilized to determine the effect of channel composition and processing temperature for sputter deposited ZTO in TFT test structures. The first method is to fabricate TFTs using ZTO from one of several individual oxide targets with various zinc to tin ratios. The second approach is to perform co-deposition experiments in which pure  $\text{ZnO}$  and  $\text{SnO}_2$  targets are used simultaneously to form a compositional gradient with respect to location between the two targets. In both cases, considerable variation can be observed for both the mobility and turn-on voltage depending on the channel composition and process temperature. To assess contact resistance for ZTO on rigid substrates, we have performed experiments in which channel length has been varied using liftoff patterning methods for source and drain electrodes. We have found that both chromium/gold and indium tin oxide/gold contacts have low contact resistance for channel lengths down to  $1.5 \mu\text{m}$ . Care must be taken when operating ZTO TFTs with such short channel lengths since currents greater than 10 mA can result in damage to these devices. A number of gate dielectrics were evaluated on both rigid and flexible substrates. Flexible transistors utilizing gate dielectrics deposited by PECVD on Al-coated polyimide sheets indicate that the choice of gate dielectric material exerts a strong influence on the turn-on voltage, for which we have obtained values of -1 V and -15 V for silicon nitride and silicon oxide gate dielectrics, respectively. Capacitance-voltage (C-V) measurements have been employed to further characterize these devices; these measurements indicate the existence of a relatively high-quality channel / gate dielectric interface. In addition, based on capacitance measurements and on observation of current crowding in the TFT output characteristics, it was found that the use of aluminum source/drain electrodes results in significant contact resistance, whereas indium tin oxide provides efficient, low-resistance

carrier injection and extraction from the ZTO channel.

### 11:30 AM DD3.10

**Low-voltage ZnO thin film transistors with high-K gate insulators for transparent and flexible electronics.** Il-Doo Kim<sup>1</sup>, YongWoo Choi<sup>2</sup>, KyongTae Kang<sup>3</sup>, Mi-Hwa Lim<sup>3</sup> and Harr L. Tuller<sup>2</sup>; <sup>1</sup>Optoelectronic Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea; <sup>2</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>3</sup>Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Seoul, South Korea.

Transparent electronic circuits offer the opportunity to create new optoelectronic devices and applications. Especially, ZnO based transparent thin film transistors (TFTs) have been studied intensively as transparent FETs due to their potential of replacing hydrogenated amorphous or polycrystalline silicon (a-Si:H or poly-Si) TFTs that now serve as the backplane for active matrix (AM) displays such as liquid crystal displays (AMLCD) and organic light emitting diodes (AMOLED). Zinc oxide (ZnO) is a transparent compound semiconductor with a wide band gap (3.37 eV) which can be grown as a polycrystalline film at low or even room temperature. ZnO is, therefore, considered to be an ideal material for serving as the channel layer in transparent and flexible FETs. Recently, ZnO films were formed at low temperature, without need for vacuum environment, by spin-coating or printing ZnO nanoparticles, which could lead to considerable reductions in fabrication costs. However, the operating voltages of the ZnO TFTs fabricated at reduced temperature were high. High operating voltage results in high power consumption, a potential critical barrier for portable, battery-powered applications. We report on the fabrication of field-effect transistors with transparent oxide semiconductor ZnO serving as the electron channel and high-K BZN ( $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$ ) as the gate insulator. The devices exhibited very low operation voltages (< 4 V) due to high capacitance of the BZN dielectric. The threshold voltage and subthreshold swing were 2 V and 0.25 V/dec, respectively. The high optical transparency (> 80% for wavelength > 400 nm), low temperature processing, and low operation voltage of ZnO based thin film transistors with integrated BZN dielectric offer a promising route for the development of transparent and flexible electronics.

### SESSION DD4: Zinc Oxide: Film Growth & Device Application

Chairs: Peter Garcia and Hiromichi Ohta  
Tuesday Afternoon, November 29, 2005  
Room 309 (Hynes)

### 1:30 PM \*DD4.1

**Transparent and conductive ZnO:Al films: From thin film photovoltaics towards flat panel display technology.** Bernd Szyszka, Sittinger Volker, Florian Ruske and Andreas Pflug; Fraunhofer IST, Braunschweig, Germany.

Transparent and conductive Al doped ZnO films have shown excellent performance as a transparent front electrode for amorphous or microcrystalline silicon based thin film solar cells. However, the use of this material for flat panel display applications is limited due to several drawbacks which are related to the difficult micro patterning of that material and to the dependence of properties on film thickness. We report on our material research on ZnO:Al films and on our investigations for wet chemical patterning and dry etching using a variety of etching techniques.

### 2:00 PM \*DD4.2

**Advances in ZnO thin film growth by laser molecular-beam epitaxy.** Atsushi Tsukazaki<sup>1</sup>, Akira Ohtomo<sup>1</sup>, Masashi Kawasaki<sup>1,6</sup>, Masashi Kubota<sup>2</sup>, Takeyoshi Onuma<sup>2</sup>, Shigefusa F Chichibu<sup>2</sup>, Masatomo Sumiya<sup>3</sup>, Sunro Fuke<sup>3</sup>, Tomohiro Kita<sup>4</sup>, Keita Ohtani<sup>4</sup>, Yuzo Ohno<sup>4</sup>, Hideo Ohno<sup>4</sup>, Takayuki Makino<sup>5</sup>, Yusaburo Segawa<sup>5</sup> and Hideomi Koiuma<sup>6</sup>; <sup>1</sup>Institute for Materials Research, Tohoku University, Sendai, Japan; <sup>2</sup>Tsukuba University, Tsukuba, Japan; <sup>3</sup>Shizuoka University, Hamamatsu, Japan; <sup>4</sup>Laboratory for Nanoelectronics and Spintronics, Tohoku University, Sendai, Japan; <sup>5</sup>Photodynamics Research Center, RIKEN, Sendai, Japan; <sup>6</sup>National Institute for Materials Science, Tsukuba, Japan.

ZnO has been attracting much attention not only for short-wavelength light-emitting diodes and lasers but also for transparent thin film transistors. Extensive activities of ours were triggered in 1996 by the observation of excitonic laser action with a low threshold under optical pumping [1]. It has been a key for realizing high performance devices based on ZnO to reduce both the donor-like and the acceptor-like defects. We have been paying efforts to reduce the defects by developing original techniques such as lattice-matched

ScAlMgO<sub>4</sub> substrate and high-temperature-annealed self-buffer layer (HITAB) [2]. Here we show that the crystalline quality of ZnO thin film can be so excellent that we can convert ZnO into p-type and we can observe quantum transport phenomena. We have found that the electron transport properties of ZnO thin films strongly depends on the growth condition, especially growth temperature, because the point defects such as Zn vacancy and interstitial Zn are incorporated through kinetic reasons at the growing surface. By optimizing the growth temperature, ZnO thin films grown on HITAB exhibited a photoluminescence lifetime at room temperature as long as 3.8 ns (bulk single crystal : 0.97 ns) and an electron mobility as large as 5000 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> at 100 K [3]. These record-breaking results manifest themselves the reduction of crystalline defects. Such films can be turned into p-type by applying repeated temperature modulation method to facilitate acceptor (nitrogen) incorporation [3]. Blue light-emission has been readily observed from current driven ZnO pn homojunction diodes [4]. By optimizing the heterostructures, we start to observe quantum transport phenomena such as Shubnikov-de Haas oscillation. [1] P. Yu, et al, 23rd International Conference on the Physics of Semiconductors, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), p. 1453. [2] A. Tsukazaki et al. Appl. Phys. Lett. 83, 2784 (2003). [3] A. Tsukazaki et al. Nature Mater. 4, 42 (2005). [4] A. Tsukazaki et al. Jpn. J. Appl. Phys. 44, L643 (2005).

### 3:30 PM DD4.3

**Metal-insulator transition in Ga:ZnO thin film - an ideal candidate for TCO.** Vikram Bhosle, Ashutosh Tiwari and Jagdish Narayan; Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

Recent discovery of transparent metals has generated considerable interest in the field of TCO. We report similar observations in Ga:ZnO system. The films were deposited by PLD on sapphire substrates using ZnO targets with different concentrations of Ga (2-7 at%). Experiments were also performed under different oxygen pressure to study the effect of oxygen on the film quality and properties. The best films obtained were deposited in the pressure range of ~10-2 Torr of oxygen, which were crystalline with the electrical resistivity < 2 x 10<sup>-4</sup> Ω-cm, while transmittance > 80% in the visible region. The structure of the films was characterized by XRD, electron diffraction and HR-TEM and the chemical analysis was performed using EELS and XPS. Electrical properties were measured using a four-probe measurement and the optical properties using photoluminescence and absorption spectroscopy. The films with 5% Ga grown under above-mentioned conditions also showed a metal-insulator transition at ~ 157 K when resistivity was measured as a function of temperature. Above 157 K these films show a positive temperature coefficient of resistivity, characteristic of metallic behavior and also a sharp edge in the transmission spectrum characteristic of ZnO bandgap (~3.4 eV). Mechanisms responsible for these observations will be discussed in the terms of combined effect of oxygen vacancies and dopant concentration. The properties of Ga doped ZnO truly rival those of commercially available ITO films and is, therefore, a promising candidate for TCO applications.

### 3:45 PM DD4.4

**ZnO MOCVD Growth: Effects of Processing Parameters on the Oxide Nanostructures.** Graziella Malandrino, Manuela Blandino and Ignazio L. Fragala<sup>1</sup>; Dipartimento di Scienze Chimiche, Università di Catania, Catania, Italy.

Zinc oxide (ZnO) is a unique material that exhibits semiconducting, piezoelectric, and pyroelectric multiple properties. Due to its various properties, ZnO is an exceptionally important material for applications in gas sensors, varistors, optical devices, solar cells, and light emitting diodes. Most of the research has been focused on the growth of ZnO thin films. Many groups have reported on optically transparent ZnO thin films deposited by techniques such as sputtering, spray pyrolysis, sol-gel, electron-deposition and metal organic chemical vapour deposition (MOCVD). Among them, MOCVD offers several advantages, including the amenable production of high-quality films through a fine tuning of various processing parameters. In addition, one dimensional (1-D) nanometer-sized semiconductor materials have recently attracted considerable research activities because of their great potential for fundamental studies of the roles of dimensionality and size in their physical properties as well as for applications in optoelectronic nanodevices and functional materials. Quite recently the room temperature lasing action of highly oriented ZnO nanorod array has been reported. Nevertheless, their large scale manufacturing at low cost remains a crucial challenge for the development of novel devices. Also for this kind of applications MOCVD represents a strategic approach due to large deposition areas, lower deposition temperatures, and adaptability to large scale processing. In this communication, we report the synthesis of ZnO films and highly oriented 3-D nanorod arrays through a simple catalyst-free MOCVD route. The films and nanorods have been

deposited on quartz and silicon (100) substrates from the novel Zn(tta)<sub>2</sub>med precursor (Htta=2-thenoyl-trifluoroacetone, tmed = N,N,N',N'-tetramethylethylen-diammine). Optimization of MOCVD deposition parameters (deposition temperature, oxygen partial pressure and deposition time) yielded high quality ZnO films in terms of phase purity, morphology and transparency. The structural nature has been assessed through X-ray diffraction (XRD), while the morphology has been investigated through scanning electron microscopy (SEM) and atomic force microscopy (AFM). The transmission spectra of ZnO films grown on quartz at suited temperatures show that films are highly transparent in the visible region with an almost 90% transmission between 450 and 800 nm. The growth of the nanorod arrays has been obtained under particular conditions of substrate temperature, oxygen partial pressure, concentration of doping agent, precursor evaporation temperature. The nanorod arrays growth mechanism will be discussed considering morphological and structural results obtained at various deposition times. Finally, note that the nanorod tips are free of catalytic species and therefore this approach represents a low cost easy route to 3-D nanostructures potentially suited for lasing applications.

#### 4:00 PM DD4.5

**P-Type Doping of Zinc Oxide Obtained by Arsenic Ion Implantation.** Gabriel Braunstein<sup>1</sup>, Andrey Muraviev<sup>1</sup>, Himanshu Saxena<sup>1</sup>, Neelkanth Dhere<sup>2</sup>, Vladimir Richter<sup>3</sup> and Rafi Kalish<sup>3</sup>; <sup>1</sup>Department of Physics, University of Central Florida, Orlando, Florida; <sup>2</sup>Florida Solar Energy Center, University of Central Florida, Cocoa, Florida; <sup>3</sup>Department of Physics, Technion, Israel Institute of Technology, Haifa, Israel.

P-type doping of polycrystalline zinc oxide thin films, has been obtained by implantation with arsenic ions. Implantation doses of  $5 \times 10^{14}$  -  $1 \times 10^{15}$  As/cm<sup>2</sup>, at energies of 100 - 150 keV, were utilized. Conventional room temperature ion implantation of arsenic into zinc oxide did not produce p-type doping, and therefore a somewhat different implantation procedure was utilized. This procedure consisted in carrying out the implantations at liquid nitrogen temperature ( $\sim -196$  °C) to freeze the interstitials created by the irradiation, and thus avoid the creation of a defect imbalance that precludes the proper annealing of the implantation-induced lattice damage in zinc oxide. The low temperature implantation was followed by a rapid heating of the sample, at 560 °C, for 10 minutes, to induce short range, interstitial-vacancy recombination, and substitutional lattice location of the dopants. Subsequent heat treatment was carried out in a tube furnace, at 900 °C, for 45 minutes, in flowing oxygen, to further anneal any residual lattice defects, and enhance the electrical activation of the dopants. Hall effect and conductivity measurements of samples implanted using this procedure revealed unambiguous Hall voltages indicative of successful p-type doping, with sheet carrier concentrations of the order of  $10^{13}$  cm<sup>-2</sup>. A comparison between the conventional and non-conventional implantations approaches is presented, and the reasons for the different outcomes are discussed.

#### 4:15 PM \*DD4.6

**Charge Carrier and Spin Doping in ZnO Thin Films for Device Applications.** David P. Norton<sup>1</sup>, Mat Iivil<sup>1</sup>, Yuanjie Li<sup>1</sup>, Jean Marie Erie<sup>1</sup>, Hyun-Sik Kim<sup>1</sup>, Kelly Ip<sup>1</sup>, Stephen Pearton<sup>1</sup>, Fan Ren<sup>2</sup>, Arthur Hebard<sup>3</sup> and Josh Kelly<sup>3</sup>; <sup>1</sup>Department of Materials Science and Engineering, University of Florida, Gainesville, Florida; <sup>2</sup>Department of Chemical Engineering, University of Florida, Gainesville, Florida; <sup>3</sup>Department of Physics, University of Florida, Gainesville, Florida.

ZnO thin films are potentially useful for transparent electronics, UV light emission, and spin-based electronics. For each of these device applications, there are critical issues related to doping, whether for carrier type or magnetism. In this talk, recent progress in acceptor and spin doping of (Zn,Mg)O films will be described. In particular, the behavior of As, P, or N doping in doping for p-type (Zn,Mg)O films using pulsed laser deposition will be discussed. In addition, the present understanding of the magnetic properties in transition metal doped ZnO will be described within the context of potential for spintronic device applications.

SESSION DD5: Poster Session: Film Growth and Characterization of Materials for Transparent Electronics

Chair: John D. Perkins  
Tuesday Evening, November 29, 2005  
8:00 PM  
Exhibition Hall D (Hynes)

DD5.1  
Abstract Withdrawn

#### DD5.2

**The Electrical and Optical Properties of In<sub>0.70</sub>Zn<sub>0.30</sub>O<sub>y</sub> Thin Films Deposited at Room Temperature.** Matthew P. Taylor<sup>1,2</sup>, Dennis Readey<sup>1</sup>, Maikel F. A. M. van Hest<sup>2</sup>, Charles Teplin<sup>2</sup>, Jeff Alleman<sup>2</sup>, Matthew Dabney<sup>2</sup>, Lynn Gedvilas<sup>2</sup>, Brian Keyes<sup>2</sup>, Bobby To<sup>2</sup>, John Perkins<sup>2</sup> and David Ginley<sup>2</sup>; <sup>1</sup>Colorado School of Mines, Golden, Colorado; <sup>2</sup>National Renewable Energy Laboratory, Golden, Colorado.

Indium-zinc-oxide (IZO) compounds show very desirable properties as transparent conducting oxides (TCOs) for photovoltaic and display devices. These films can be deposited at room temperature, retain the high conductivity and optical transparency necessary for such applications and are very smooth with an rms roughness of  $\sim 0.5$  nm. In order to optimize the In:Zn ratio, high-throughput combinatorial techniques were employed to analyze the electrical, optical and structural properties of these films. The optimal composition was determined to be 70% In and 30% Zn, In<sub>0.70</sub>Zn<sub>0.30</sub>O<sub>y</sub>. This film showed a conductivity of  $\sim 3000$  ( $\Omega \cdot \text{cm}$ )<sup>-1</sup>, optical transmission  $> 85\%$  and was amorphous. A target of this composition was then produced using ZnO and In<sub>2</sub>O<sub>3</sub> powders. Films from this target were deposited on glass substrates by sputtering at room temperature using argon, argon with oxygen and argon with hydrogen (forming gas). The highest conductivity for any film deposited from this target was  $\sim 2000$  ( $\Omega \cdot \text{cm}$ )<sup>-1</sup> and was obtained when sputtering in Ar. The introduction of O<sub>2</sub> to the system resulted in a monotonic decrease in the carrier concentration (N) from  $N > 3 \times 10^{20} / \text{cm}^3$  for pure Ar to  $N < 4 \times 10^{16} / \text{cm}^3$  for Ar+6% O<sub>2</sub>. The mobility varied from a maximum of  $48 \text{ cm}^2 / \text{V} \cdot \text{s}$  at 2% O<sub>2</sub> to a minimum of  $15 \text{ cm}^2 / \text{V} \cdot \text{s}$  at 6% O<sub>2</sub>. All of the films deposited in Ar or Ar+O<sub>2</sub> showed an optical transmission  $> 85\%$  and the optical band gap of these films varied linearly with  $N^{2/3}$ . The effective mass and intrinsic band gap were calculated from this relationship to be 0.3 and 3.20 eV, respectively. The film deposited with forming gas (Ar+4%H<sub>2</sub>) showed a conductivity of  $\sim 1400$  ( $\Omega \cdot \text{cm}$ )<sup>-1</sup> with  $N = 4.64 \times 10^{20} / \text{cm}^3$  and  $\mu = 18.8 \text{ cm}^2 / \text{V} \cdot \text{s}$ . However, this film was visibly gray with an optical transmission of  $\sim 55\%$ . All films were amorphous as determined by x-ray diffraction.

#### DD5.3

**Low Temperature Patterned ZnO Thin Films Processed by Laser Assisted Maskless Aerosol Deposition.** Uma Choppali, Michael J. Kaufman and Brian P. Gorman; Department of Materials Science and Engineering, University of North Texas, Denton, Texas.

Zinc oxide (ZnO), a wide band gap semiconductor, is a promising transparent conducting oxide material. Many methods of synthesizing ZnO thin films are currently being studied. In this work, a new method of preparing dense, nanocrystalline ZnO thin film structures at low temperatures using a modified M3D (Optomec, Inc.) is presented. This novel technique of preparing directly patterned thin films of ZnO from polymeric precursors allows for mesoscale pattern depositions at low temperatures. The prepared precursor is converted into an aerosol, which is then directed by a focused carrier gas stream onto prepared substrates. ZnO lines less than 10microns in diameter are deposited in predetermined patterns defined by CAD drawings. Subsequent laser annealing (either post-deposition or during deposition) converts the precursor into the oxide form at temperatures which do not damage polymeric substrates. The effect of precursor aerosol density and laser fluence on film morphology was analyzed using X-ray diffraction, electron backscattered diffraction in a dual-beam FESEM / FIB, as well as HRTEM.

#### DD5.4

Abstract Withdrawn

#### DD5.5

**Solution-processed ZnO nanowire-network thin film transistors for transparent electronics.** Teymur Bakhishev, Steven K Volkman and Vivek Subramanian; Electrical Engineering and Computer Sciences, University of California Berkeley, Berkeley, California.

We report on the first demonstration of ZnO nanowire network thin film transistors. ZnO has garnered substantial attention in recent years as a candidate material for use in transparent electronics since it may be used as both a transparent semiconductor in NMOS TFTs, and also as a transparent conductor when heavily doped. The transparency of ZnO makes it extremely attractive for display backplane applications. Due to their transparency, ZnO-based TFTs may be sized to cover substantial fractions of the display pixel without reducing aperture ratio. This allows the use of wide devices, realizing higher drive current with correspondingly reduced transistor mobility requirements. Sputtered and laser-deposited ZnO TFTs have been demonstrated with performance more than adequate for display applications. Solution-processing techniques are substantially more attractive for low-cost displays, since they may be used to deposit



films on a wide variety of low-cost, large area substrates using such low-cost methods as printing, casting and spray coating. Here, we demonstrate solution-deposited ZnO nanowires to realize the first ZnO nanowire network TFTs, offered transparency, air stability, and NMOS operation, all of which are desirable for active matrix displays. We describe a process to grow ZnO nanowires in water in the presence of Hexamine and Zinc Nitrate to obtain a network of nanowires 0.5-1.5 $\mu$ m long. The growth was initiated on ZnO nanoparticles spun-cast onto thermal SiO<sub>2</sub>. We demonstrate bottom-gate FET structures formed using these nanowire networks as channel layers. Resulting transistors are well-behaved with on-off ratios >10<sup>4</sup> and mobility >10<sup>2</sup> cm<sup>2</sup>/V-s, calculated without accounting for actual surface coverage of nanowires. Actually nanowire mobility is therefore substantially higher, attesting to the potential for this technique as a method for realizing low-cost, high-brightness displays.

#### **DD5.6**

**Non-linear Optic Investigations of ZnO Films Deposited on MgO and other Substrates.** Kazimierz J. Plucinski<sup>1</sup>, Ivan V. Kityk<sup>2</sup> and K. Nouneh<sup>4,3</sup>; <sup>1</sup>Electronics, Military University of Technology, Warsaw, Poland; <sup>2</sup>Institute of Physics, J. Dlugosz University, Czestochowa, Poland; <sup>3</sup>Semiconductor Group, University of Montpellier, Montpellier, France; <sup>4</sup>Laboratory of Applied Physics, University of Perpignan, Perpignan, France.

Using a bicolor coherent treatment with a Nd-YaG laser with wavelength 1.32  $\mu$ m and its second harmonic generation, we have achieved a very large effective second harmonic generation of about 56 pm/V in a 3  $\mu$ m thick film deposited on MgO. The written grating was stable for 24 days and optical susceptibility decreased not more than 26 % after the interruption of the optical treatment. The process was tried for different substrates and it was shown that the maximum values of the second order susceptibilities are achieved for the MgO substrates. The films were investigated for dependence on temperature and it was shown that there is a maximum near the temperature of 261 K in the corresponding dependences of the second order susceptibility. The best results were received for films obtained through rf-sputtering and substantially less by the spray pyrolysis method. Varying the film thickness, we achieved an optimum thickness of about 2.75  $\mu$ m.

#### **DD5.7**

**Transparent Thin Film Transistor using GaN Particles.** Huaqiang Wu<sup>1</sup>, Jie Lu<sup>1</sup>, Dan Bernards<sup>2</sup>, George G. Malliaras<sup>2</sup> and Michael G. Spencer<sup>1</sup>; <sup>1</sup>School of Electrical and Computer Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Materials Science and Engineering, Cornell University, Ithaca, New York.

The recent development of transparent thin film transistors (TTFTs) represents a major advance in the emerging field of transparent electronics. These transistors have been fabricated on the basis of crystalline oxide channels that are typically produced at relatively high processing temperatures. However, here are few reports on using GaN as the channel materials for TTFT. GaN is a direct wide band gap semiconductor material. The band gap is 3.4 eV which is very similar to ZnO. GaN epi-layer is widely used on HEMT, MESFET and other electrical devices. GaN has high mobility and saturation velocity. In this report, we will focus on TTFT fabricated from micro- or nano- GaN particles. High purity and high quality GaN powder is made in our lab by reaction between molten Ga and ammonia. The purity of this lab-made GaN powder is higher than 99.9% based on glow discharge mass spectrometry analysis. The particles size distributes from less than 1  $\mu$ m to more than 10  $\mu$ m. Two different methods are developed to put GaN layer on transparent substrates. One is spin coating technique and the other is rf magnetron sputtering process. Using the methyl cellulose as a dispersant, GaN particle can be successfully disaggregated and dispersed into water. Then the colloidal dispersion is spun on glass or Si substrates. The dispersant can be removed by annealing process at 450°C. After these processes, a uniform GaN layer is deposited on the substrate. XRD data shows the particles to be highly orientated. Typical back gate structure is used in GaN TTFT. The rf magnetron sputtering process is under development. TTFTs fabricated from these two different processes will be compared. Detail electrical performances (IV characteristics, mobility, etc.) will be presented during the meeting.

#### **DD5.8**

**The Interfacial Reaction between Silicon Nitride and IZON Underlayer Deposited by Reactive DC Sputtering in Fringe Field Switching Device.** Je-Hun Lee, Young-Wook Lee and Chang-Oh Jeong; Samsung Electronics Co., Young-in, Gyeonggi-Do, South Korea.

The interaction of the reactively DC sputtered indium zinc oxy-nitride (IZON) layer with PECVD silicon nitride (SiN<sub>x</sub>) film was investigated in the fringe field switching (FFS) device, which exhibits wider-viewing angle than the conventional twisted nematic (TN)

device and high transmittance in comparison with the in-plane switching (IPS) device in thin film transistor liquid crystal display (TFT-LCD). For a FFS cell, two electrodes as a common and a pixel electrode, which are separated by the SiN<sub>x</sub> layer, are needed and in order to enhance transmittance, transparent conducting oxides such as indium-tin oxide (ITO) or indium-zinc oxide (IZO) should be used. However, during the silicon nitride layer deposition onto the transparent oxide films by plasma enhanced vapor deposition, SiH<sub>4</sub> or NH<sub>3</sub> gas having hydrogen radical caused the reduction of indium oxide to metallic indium and reduced the transmittance of the device. IZON interlayer prevented the interface reaction with increasing nitrogen content but decreased optical transmittance in the device. To optimize the overall property, we employed IZO/IZON structure as a common electrode. We analyzed the interface structures of IZO/IZON/SiN<sub>x</sub> layers by x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) and explained the reduction prevention mechanism.

#### **DD5.9**

**Structural and optical properties of transparent conducting CuAlO<sub>2</sub> thin films prepared by RF reactive sputtering.** Bruno Meyer, Bin Yang, Angelika Polity, Thorsten Kraemer and Baker Farangis; 1. Physikalisches Institut, Giessen, Germany.

In recent years, transparent conducting oxide compounds based on the delafossite structure have attracted much attention because of their potential in preparing novel transparent p-n junction for device applications. In this work, transparent conducting CuAlO<sub>2</sub> thin films have been deposited by RF reactive sputtering technique on sapphire and silica substrates using a CuAlO<sub>2</sub> ceramic target. A study of structural and optical properties was performed on the films, varying deposition parameters such as the substrate temperature, the oxygen partial pressure and the post growth annealing temperature. The crystalline phase in the films was identified to be the delafossite structure by x-ray diffraction. The optical properties, such as the wavelength dependence of the transmittance and the band gap, were determined.

#### **DD5.10**

**Molybdenum doped Indium Oxide thin films prepared by rf sputtering.** Elamurugu Elangovan, Antonio Marques, Ana Pimentel, Rodrigo Martins and Elvira Maria Fortunato; Materials Science, FCT-UNL, Caparica, Portugal.

Transparent Conductive Oxides (TCO) has been study for more than a half of century and is still under investigation in several laboratories around the world. One of the major issues related to these materials are the increase on the electrical conductivity and also the increase on the optical transmittance, especially in the visible part of the spectra. Nevertheless the obtained values for optical transmittance around 90% are difficult to increase, because we are close to the theoretical optical limits of these oxides. The other possibility is by reducing the electrical conductivity. Concerning this point the only way to achieve such goal is by increasing the carrier concentration (N) or the electron mobility. The carrier concentration is limited to the maximum solid solubility of the dopant, while the electron mobility depends more on the structural defects, grain size and also on the dopant concentration. So a special interest deals with the use of other dopants in order to reach such goals. In this paper we present results of molybdenum doped indium oxide (IMO) deposited at room temperature by rf magnetron sputtering. The as-deposited films were studied as a function of oxygen volume percentage (O<sub>2</sub> vol. %), calculated from the partial pressures of oxygen (O<sub>2</sub>) and argon (Ar). The O<sub>2</sub> vol. % varied between 0 and 17.5. X-ray diffraction analysis revealed that the as-deposited films were amorphous in nature irrespective of the O<sub>2</sub> vol. % in the sputtering chamber. Optical studies indicate that the films deposited without oxygen had very poor transmittance in the visible part of the spectrum. The transmittance of films increased with increasing O<sub>2</sub> vol. %, which eventually reached a maximum of 90 % for 4 O<sub>2</sub> vol. %. The optical band gap value was lower for films deposited without oxygen (3.82 eV) than with 3.9 O<sub>2</sub> vol. % (3.97 eV). Hall measurements showed that the films were highly resistive; however, the hall coefficients were not detectable except for the films deposited without oxygen. Owing to the poor electrical conductivity of these films, annealing treatments were carried out in a wide range of temperatures ranging from 300 to 500 C, in open-air and N<sub>2</sub> atmospheres for 1 hour, which resulted in films that were polycrystalline in nature with enhanced electrical and optical properties. The effect of the annealing temperature as well as the type of atmosphere used will be discussed in detail.

#### **DD5.11**

**Electrical and Optical Properties of Segregated ITO Networks in PMMA.** Charles Capozzi and Rosario Gerhardt; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.



Indium tin oxide (ITO) has been the premier electrode material for electro-optic applications due to its high electrical conductivity and its ability to transmit light in the visible range. The majority of the papers in literature focus on the development ITO as a thin film. However, there have been fewer reports that discuss ITO as a filler in nanocomposites. This paper investigates the electrical and optical properties of hot pressed poly(methyl) methacrylate (PMMA) containing segregated networks of ITO powder. Our data shows that these nanocomposites have the potential to be optically selective transparent materials, which only permit the transmittance of light at higher wavelengths. Specimens of 600-700  $\mu\text{m}$  thickness containing varying concentrations of ITO particles (31 nm) were fabricated and characterized. AC impedance was used to determine the concentration of ITO necessary to form a continuous path through the cross-section of the nanocomposites, while transmittance measurements were used to determine their interaction with wavelengths in the 200 nm-1100 nm range. A continuous network through the PMMA was observed to form with only 0.66 % vol. ITO and an increase in the electrical conductivity of the PMMA from  $3.3 \times 10^{-16} (\Omega\text{-cm})^{-1}$  to  $1.5 \times 10^{-7} (\Omega\text{-cm})^{-1}$  occurred with only 1.64 % vol. ITO. Specimens that possessed an ITO concentration below 0.66 % vol. transmitted over 59% of wavelengths of 1100 nm, which was nearly twice the transmittance observed in the visible light wavelength range. For materials that possessed above 0.66 % vol. ITO, the transmittance dramatically decreased. This likely corresponds to the agglomeration of ITO powder at the PMMA grain boundaries, which is typical for nanocomposites that have a segregated network microstructure. It is speculated that reducing agglomeration of the ITO and decreasing the thickness of the composite specimens may improve the transmittance at higher wavelengths.

#### **DD5.12**

**Photoinduced Solid Phase Transformation in Vanadium Dioxide Films.** Sergiy Lysenko, Valentin Vikhnin, Armando Rua, Felix Fernandez and Liu Huijin; Department of Physics, University of Puerto Rico, Mayaguez, Puerto Rico.

Vanadium dioxide is the object of increasing interest in modern optoelectronics due to its promising applications in ultrafast electronic and optical switching, memory, and bistable electrooptical devices, optically controlled laser cavity infrared mirrors. The  $\text{VO}_2$  thin films exhibit thermochromic effect of insulator-to-metal (I-M) phase transition (PT) with a characteristic hysteresis at the temperature near 340 K. The ultrafast I-M PT was also realized by light without thermally heating on the films.  $\text{VO}_2$  thin films were grown by reactive pulse laser deposition (PLD) on  $\text{SiO}_2$  and  $\text{MgO}$  substrates. A metallic vanadium target was used, which was rotated during laser ablation to avoid crater formation. The KrF excimer laser was used for ablation. By selections of  $\text{O}_2/\text{Ar}$  gas flow rate in the chamber, target-substrate distances and pressure in PLD chamber, the optimal parameters to form the uniform  $\text{VO}_2$  thin film on  $\text{SiO}_2$  and  $\text{MgO}$  substrates has been found. Otherwise the multicomponent  $\text{VO}_2$  and VO system can be formed. The X-Ray diffraction (XRD) spectra of  $\text{VO}_2$  films evidence the presence of  $\text{VO}_2$  crystallites with preferred orientations along (011) direction (monoclinic symmetry). Examination of the samples with an optical microscope, atomic force microscope (AFM) and XRD showed nano- and micron-sized particles. Surface images obtained by AFM show statistical homogeneity of the surface geometry with different roughness parameters. Different surface free energies and surface forces of  $\text{SiO}_2$  and  $\text{MgO}$  substrates make for the formation of different structures of  $\text{VO}_2$  film during PLD. The features of  $\text{VO}_2$  relief correlate with the results of  $\text{VO}_2$  temperature hysteresis loop (narrow loop width  $\Delta T \approx 4$  K for  $\text{VO}_2/\text{MgO}$ , and broad one for  $\text{VO}_2/\text{SiO}_2$  with  $\Delta T \approx 20$  K). This difference is associated with different numbers of oxygen vacancies in the films. Femtosecond optical pump-probe spectroscopy was employed for investigation of phase transformations in the  $\text{VO}_2$  films. Transient optical reflection was measured using 130 fs laser pulses operated at 400nm serving as pump light, and 800 nm serving as probe. They were measured as a function of pump pulse energy and time delay between pump and probe pulses. The dynamic of photoexcited electrons and phonon relaxation process were studied using an optical delay line which can precisely change the timing between pump and probe pulses. Analysis of relaxation times of  $\text{VO}_2$  system during phase transition allows suggesting the formation of an intermediate state by pure electronic mechanism without complete lattice relaxation from monoclinic to tetragonal structure. The excitonic model is suggested for light-induced insulator-metal phase transformation. The tunnel transition is caused by photoinduced Frenkel and clusterized Wannier-Mott vibronic excitons. It is expected that the specific intermediate states are related to vibronic Wannier-Mott excitons cooperated in clusters.

#### **DD5.13**

**Laser MBE growth and characterization of Ge-doped  $\text{SnO}_2$  epitaxial thin films.** Takashi Okada<sup>1</sup>, Takahiro Watanabe<sup>1</sup>, Masayasu Kasahara<sup>1</sup>, Akifumi Matsuda<sup>1</sup>, Wakana Hara<sup>1</sup>, Shusaku Akiba<sup>1</sup>, Takao Hiraide<sup>2</sup>, Kazuhiko Saeki<sup>2</sup>, Satoshi Kaneko<sup>3</sup>, Masahiko

Mitsuhashi<sup>3</sup> and Mamoru Yoshimoto<sup>1</sup>; <sup>1</sup>Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; <sup>2</sup>Industrial Research Institute of Tochigi Prefecture, Utsunomiya, Tochigi, Japan; <sup>3</sup>Industrial Research Institute of Kanagawa Prefecture, Ebina, Kanagawa, Japan.

Transparent conducting oxide (TCO) material of  $\text{SnO}_2$  has chemical stability and high permeability. Generally, by carrier-doping  $\text{M}^{+5}$  ( $\text{M}=\text{Sb}, \text{Nb}$ ) ions into  $\text{SnO}_2$  matrix as "Aliovalent substitution",  $\text{SnO}_2$  thin films are known to have much lower resistivity. By the way it is important from the view point of new TCO explorations to examine the electronic and photonic effects of "Homovalent cation substitution" in  $\text{SnO}_2$  thin films, which is related to matrix modification. In this study,  $\text{Ge}^{+4}$  ions were used as homovalent substituting dopant. As the result, we found that the resistivity of Ge-doped epitaxial  $\text{SnO}_2$  thin film is lower than that of non-doped  $\text{SnO}_2$  thin films prepared under the same condition. Ge-doped  $\text{SnO}_2$  thin films were fabricated on sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ) (0001) substrate by pulsed laser deposition method. The sapphire substrates had the ultrasmooth surface with atomic steps [1]. KrF excimer laser beam (wavelength of 248 nm, duration time of 20ns) was irradiated onto the sintered ceramics targets. Sintered ceramics targets of  $\text{SnO}_2$  and  $\text{SnO}_2/\text{GeO}_2 = 50/50$  mol% were used. At the substrate temperature of 500 °C and  $1.0 \times 10^{-5}$  Torr  $\text{O}_2$  atmosphere, the obtained thin films for the  $\text{SnO}_2/\text{GeO}_2$  target were found to grow epitaxially by x-ray diffraction (XRD), reflection high-energy electron diffraction (RHEED) and X-ray photoelectron spectroscopy (XPS) measurements. The decreased resistivity via Ge-doping into  $\text{SnO}_2$  might be due to an increase in oxygen deficiency of  $\text{SnO}_2$  thin films. We also present the electronic and photonic results on Sb or Nb doped  $(\text{Sn}_{1-x}\text{Ge}_x)\text{O}_2$  thin film as well as homovalent substituted  $(\text{Sn}_{1-x}\text{Ge}_x)\text{O}_2$  thin films. [1]Yoshimoto et al. Appl.phys.lett.67 (1995) 2615

#### **DD5.14**

**Electrical and Optical Properties of Epitaxial Molybdenum Oxide Films.** Vikram Bhosle, Ashutosh Tiwari and Jaddish Narayan; Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

Study of multi-valent oxides such as molybdenum oxides in thin film form is of particular importance since they have found use in wide variety of applications such as optically switchable coatings, flexible displays (hole injecting layers), lithium batteries, sensors, and catalysis. However, very few reports are available on electrical and optical characterization of MoOx films which can exhibit interesting properties as a function of multiple valence states of molybdenum and oxygen vacancies. Here, we report the growth of epitaxial MoOx ( $2 < x < 3$ ) films on c-plane of sapphire substrate using pulsed laser deposition and discuss the effect of chemical composition and oxygen non-stoichiometry on the structure and properties of the film. The chemistry and stoichiometry were changed by varying the various deposition parameters, such as target composition, oxygen partial pressure, substrate temperature and also the annealing conditions. The structure was characterized using XRD, HR-TEM, EELS, XPS, and the physical properties such as electrical resistivity and optical properties were investigated using four-point-probe resistivity measurements and spectroscopy techniques, respectively. It was found that the films showed exciting electrical and optical properties in the as-deposited and annealed condition depending on the composition. One of the interesting features was that over a wide range of oxygen concentration the crystal structure of the films was retained even if the physical properties changed. For a small oxygen partial pressure range, the films were also found to be transparent as well as conducting and similar results were observed after annealing some of the films. A combination of high conductivity and high transmittance in the visible region was realized by systematically controlling the relative fraction of different oxidation states of Molybdenum, namely  $\text{Mo}^{4+}$ ,  $\text{Mo}^{5+}$  and  $\text{Mo}^{6+}$  in the film. For a film 60nm thick and annealed at 250°C for 1h, the ratio of  $\text{Mo}^{6+}/(\text{Mo}^{4+}, \text{Mo}^{5+})$  was determined to be  $\sim 2.9/1$  using XPS, and a typical value of transmittance was  $\sim 65\%$  and resistivity close to  $1 \times 10^{-3} \Omega\text{-cm}$ . These results demonstrate growth of epitaxial MoOx films with tunable electrical and optical properties<sup>1</sup>. Further optimization of these properties is expected to result in applications related to display panels, solar cells, chromogenic (photochromic, electrochromic, gasochromic) devices, and transparent conducting oxides (TCOs). The study will also be helpful in understanding the role of molybdenum in next generation TCOs such as Indium molybdenum oxide and thus controlling and improving their properties. Finally, the ability to grow epitaxial MoOx films can further aid their integration with optoelectronic and photonic devices. 1. V. Bhosle, A. Tiwari, J. Narayan, JAP, 8, 97 (2005).

#### **DD5.15**

**Reliable semi-transparent pentacene thin-film transistors with polymer gate dielectric layers cured at an optimum**

**temperature.** Do Kyung Hwang<sup>1</sup>, Ji Hoon Park<sup>2</sup>, Jeong Min Choi<sup>1</sup>, Jae Hoon Kim<sup>1</sup>, Eugene Kim<sup>2</sup>, Seongil Im<sup>1</sup> and Seong Hun Jeong<sup>1</sup>;

<sup>1</sup>Institute of Physics and Applied Physics, Yonsei University, Seoul, Sudaemoon-ku, South Korea; <sup>2</sup>Hongik University, Department of Information and Display, Seoul, Mapo-gu, South Korea.

To make use of the full advantages of organic thin-film transistors (OTFTs), namely, large area coverage, mechanical flexibility, and low-cost processing, it is necessary to employ polymer gate dielectric materials rather using solution processes. Poly-4-vinylphenol (PVP) is one of the popular polymer gate materials. OTFTs with PVP gate dielectric and opaque noble-metal source-drain (S/D) contacts displayed a good performance with a field effect mobility of  $\sim 0.1 \text{ cm}^2/\text{Vs}$  and an on/off ratio over  $10^5$ . However, the charging capacitances (or dielectric capacities) of the polymer gate dielectric are still inferior to those of inorganic dielectric materials. Moreover, unreliable gating in OTFTs with the polymer dielectric, such as threshold voltage change depending on the direction of gate voltage sweeping has been often found and reported. Few studies were reported on the reasons of the threshold voltage shift or of the unreliable behavior. Hence no report has been found on optimum PVP curing conditions for cross-linking of polymer chains, which may substantially influence the electrical properties of polymer gate dielectrics films and further influence the reliability of the OTFTs with polymer gate. We have fabricated a semi-transparent pentacene TFT with a PVP dielectric and NiOx S/D electrode, systematically varying PVP-curing temperatures to achieve a reliable pentacene-based TFT with polymer dielectric layers. Semi-transparent NiOx electrodes showed effective transmittance of  $\sim 40\%$  in the visible range along with good sheet resistance of  $\sim 60 \Omega/\square$ . PVP films were prepared by spin coating and subsequent curing at various temperatures (155, 175, 200 °C). According to the dielectric constant and strength results from Au/PVP/p+-Si structures, the PVP film cured at 175 °C appeared the most optimum and reliable, showing about 3.9 and more than 1.5 MV/cm, respectively. Although saturation current and field mobility ( $\sim 0.13 \text{ cm}^2/\text{Vs}$ ) obtained from a TFT with PVP film cured at 200 °C appeared higher than those ( $\sim 0.07 \text{ cm}^2/\text{Vs}$ ) from the device with 175 °C-cured polymer film, the TFT prepared at 200 °C revealed a low on/off current ratio of less than  $10^4$  due to its high off-state current and also unreliable saturation behavior under repetitive gate voltage sweep. We thus conclude that the 175 °C is an optimum curing temperature for our PVP gate dielectric in regards of its dielectric properties which lead to the good reliability of pentacene-TFTs. More details on some interesting device behavior such as anomalous threshold voltage change with voltage sweep are to be presented in the coming conference.

#### **DD5.16**

**Holographic Memory Materials Based on Stepwise Two-photon Absorption of Oligothiophenes.** Masaki Shimizu<sup>1</sup>, Michael Schelper<sup>1</sup>, Tamejiro Hiyama<sup>1</sup>, Masafumi Adachi<sup>2</sup>, Yutaka Sasaki<sup>2</sup>, Seiji Akiyama<sup>2</sup>, Shuichi Maeda<sup>2</sup>, Hirohisa Kanbara<sup>3</sup>, Yuhei Mori<sup>3</sup> and Takashi Kurihara<sup>3</sup>; <sup>1</sup>Material Chemistry, Kyoto University, Kyoto, Japan; <sup>2</sup>Mitsubishi Chemical Group, Science and Technology Research Center, Inc., Japan, Yokohama, Japan; <sup>3</sup>NTT Photonics Laboratories, Nippon Telegraph and Telephone Corporation, Japan, Atsugi, Japan.

Three-dimensional optical data storage has attracted much attention to increase the memory density of optical devices. To explore organic materials that allow us to realize writing information to and readout from multilayered organic media without erasing the information, we focused on a stepwise two-photon absorption approach. We envisioned that multilayered optical data storage should be possible if a pi-conjugated molecule is efficiently excited from a ground-state to a higher triplet state via S0-S1 absorption by a gate beam, through intersystem crossing and then T1-Tn absorption by a holographic light. Subsequent energy transfer from the higher state should induce change of refractive index of an organic media and allow us to write information into the media. Although diacetyl and carbazole are known to exhibit such a two-step absorption so far, diffraction efficiencies of these are not sufficient for realization of multilayered organic media. Therefore, new pi-conjugated molecules exhibiting high diffraction efficiency in the stepwise two-photon absorption are highly desired. To this end, we chose oligothiophenes substituted by triorganosilyl groups at the terminal positions as the target molecules, on the basis of the prediction done by theoretical calculation. Accordingly, we prepared a thin layer film containing an aryl azide and one of the oligothiophenes by a blade-coating method and found that the resulting organic media exhibited much higher diffraction efficiency than that of the corresponding diacetyl-based media. Reported herein are preparation, optical properties, and theoretical studies of the oligothiophenes. Also will be presented are device preparation using the oligothiophenes and results on holographic recording experiments.

#### **DD5.17**

**A New Method of Synthesizing Diamond Carbon: A Polymer Precursor to Hexagonal Diamond and to Fully-sp<sup>3</sup> Tetrahedral Amorphous Carbon Films.** Patricia A. Bianconi, Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts.

The processing of a novel polymer, poly(hydridocarbyne), whose microstructure is tailored to include only sp<sup>3</sup> carbon, is reported. The network backbone of this polymer is composed of tetrahedrally-hybridized carbon atoms, each bearing one hydride substituent and linked via three carbon-carbon single bonds into a three-dimensional random network of fused rings. The polymer exists as nano-sized clusters in organic solvents. The sp<sup>3</sup>-carbon network backbone confers unusual properties on the polymer, including facile thermal decomposition under inert atmosphere between 100 and 400 °C to form fully sp<sup>3</sup> tetrahedral amorphous carbon (ta-C) high quality films at atmospheric pressure, without the use of hydrogen or any activated atoms or reactive atmospheres. No sp<sup>2</sup> carbon can be detected in these films by multi-wavelength Raman spectroscopy. The films have also been characterized by XPS, energy-dispersive spectroscopy, microcombustion chemical analysis, AFM, and FE-SEM. If attempts are made to provide nucleation sites within the polymer film during thermolysis, hexagonal diamond is formed, which was characterized by Raman spectroscopy and xray and electron beam diffraction. Poly(hydridocarbyne) is also a precursor to the chemical vapor deposition of hexagonal diamond, again via thermal processing at low temperatures and atmospheric pressure, without the use of hydrogen or any activated atoms or reactive atmospheres. Polymer molecules vaporize upon heating, and nucleate on surfaces downstream from the polymer source. Because poly(hydridocarbyne) is a polymeric species that is readily soluble in organic solvents, it can be easily spun or coated onto large surfaces, dip-coated onto complex shapes, pulled or drawn into fibers, molded into parts, and formed into composites with other materials. The easy thermal processing of this polymer to diamond carbon, and the lack of need for processing by any CVD reactor or activated atmosphere, provides wholly new opportunities and possible uses for diamond-carbon engineered materials.

#### **DD5.18**

**Optical Monitoring of the Surface Modification of Polymeric Materials for Flexible Electronics Applications.** Argiris Laskarakis, Christoforos Gravalidis, Spiros Kassavetis and Stergios Logothetidis; Physics Department, Aristotle University of Thessaloniki, Thessaloniki, Greece.

The implementation of polymeric substrates towards the large-scale production of Flexible Electronic Devices (FEDs) has radically expanded during the last years. The desirable properties of polymer substrates, coupled with intelligent production techniques that include surface modification, deposition of functional layers, such as active matrix thin-film transistor arrays, open up the possibility of cost-effective, roll-to-roll production of FEDs. However, the performance, efficiency and lifetime of FEDs are substantially affected by the properties of the polymer substrates in which the functional films will be encapsulated. Therefore, the flexible substrate materials should meet specific and advanced demands, such as high optical transparency and high barrier properties (low permeability values) in atmospheric gases and water vapour. These properties are determined and controlled by the bonding structure of the polymer substrates, the surface nanostructure and chemistry, and also on the functional films that are developed onto the polymer substrates and the film-substrate adhesion. In order to enhance the physical and chemical properties of the polymer surface, ion beam and plasma techniques are employed, which induce bond breaking, cross-linking, formation of new chemical groups and emission of small molecular groups leading to the reduction of gas permeability and to the enhanced adhesion of subsequent functional layers. In this work, we investigate in detail the effect of the Ar<sup>+</sup> ion bombardment on the optical and nanomechanical properties of biaxially stretched Polyethylene Terephthalate (PET) polymer films, which are excellent candidates for implementation for the large-scale production of FEDs, such as flexible displays and flexible photovoltaic cells. Fourier Transform IR Spectroscopic Ellipsometry FTIRSE and Vis-fUV Phase Modulated Ellipsometry (1.5-6.5eV) have been employed for the in situ and real time monitoring of the structural changes on the polymer surface obtained by Ar<sup>+</sup> ion bombardment. This has been found to modify the macromolecular bonding structure of PET and especially the C=O, C-C and C=C groups, whereas the detailed analysis of the real-time FTIRSE spectra reveals important information about the effect of the Ar<sup>+</sup> ion bombardment on the mechanisms that affect the modification of each of the above bonding groups. The latter are correlated with the surface properties investigated by Atomic Force Microscopy in non contact mode, which has revealed the topography variations induced by the Ar<sup>+</sup> ion bombardment procedure.

**9:00 AM DD6.1**

**Chemical Vapor Deposition of Thin Films of Electrically Conducting PEDOT.** John Patrick Lock<sup>1,2</sup> and Karen K Gleason<sup>1</sup>;  
<sup>1</sup>Chemical Engineering, MIT, Cambridge, Massachusetts; <sup>2</sup>Advanced Conductors, Inc, Cambridge, Massachusetts.

Chemical vapor deposition (CVD) technology, vital to the fabrication of traditional semiconductor devices, is also desirable for next-generation organic devices, particularly for creating layers which are difficult to process by solution methods or for coating substrates which can not tolerate exposure to solvents. In this work, a CVD process has been demonstrated for the deposition of conducting poly-3,4-ethylenedioxythiophene (PEDOT). This CVD process eliminates the need for polystyrene sulfonate (PSS), which is used to disperse PEDOT in water, but has been identified as a possible source of corrosion in OLEDs leading to shortened device lifetimes. The CVD PEDOT films range from 50 nm to several microns in thickness. Fourier transform infrared spectroscopy confirms the similarity in chemical structure of PEDOT synthesized by CVD and solution techniques. An electrical conductivity of 4.37 S/cm has been achieved. The CVD process utilizes a modest stage temperature and results in conformal coatings of high surface area features like fibers and pores. This combination of characteristics has allowed PEDOT deposition onto paper and fabric to be demonstrated. Conformal coating of microporous or fibrous materials by CVD PEDOT has the potential to lead to better efficiencies in organic devices with high effective surface areas including photovoltaics. Reversible electrochromic responses of CVD PEDOT have been observed as well. The light blue films in their as-deposited state turn darker blue upon electrochemical reduction. The maximum contrast to date is 16.5% with a switching speed of 27 msec for a film having a thickness of 50 nm.

**9:15 AM DD6.2**

**Variable Temperature Capacitance-Voltage Measurements to Investigate the Density of Localized Trapping Levels in Organic Semiconductors.** Naser Sedghi<sup>1</sup>, David Donaghy<sup>1</sup>, Munira Raja<sup>1</sup>, Samer Badriya<sup>2</sup>, Simon J. Higgins<sup>2</sup> and Bill Eccleston<sup>1</sup>;  
<sup>1</sup>Department of Electrical Engineering and Electronics, The University of Liverpool, Liverpool, United Kingdom; <sup>2</sup>Department of Chemistry, The University of Liverpool, Liverpool, United Kingdom.

Charge transport in organic disordered semiconductors occurs via variable range hopping (VRH). The density of states (DOS) in these materials is commonly believed to be described by a Gaussian distribution of energy sites. Study of the Gaussian distribution is crucial to the understanding of conduction mechanism in disordered organic semiconductors. The width of Gaussian function is related to a characteristic temperature,  $T_C$ , which is an important parameter in modeling organic thin-film transistors (OTFT) and other organic devices. The exponent parameter in the universal power law also depends on  $T_C$ . The tail of the Gaussian function, for any particular energy range, can be approximated to an exponential function. This approximation applies to most situations, since the majority of carrier hopping occurs in the band tail, except at very high temperatures. In this work we have used this approach to calculate the carrier concentration in organic materials, and subsequently the charge distribution in the accumulation region of a field effect device, the effective width of an accumulation layer (Debye Length), and the space-charge capacitance in both accumulation and depletion modes. Small signal high frequency capacitance-ramp voltage (CV) measurements performed at various temperatures show good agreement with this model and the characteristic temperature  $T_C$  has been estimated. Using the exponential approximation, the accumulation capacitance is found to be inversely proportional to the square root of temperature. The CV measurements were performed on regioregular poly(3-hexylthiophene) (P3HT) field effect device at different temperatures using a liquid nitrogen cryostat. The dielectric was alumina pre-prepared by aqueous anodization. The capacitance in the accumulation region is the series combination of oxide, space-charge, and bulk capacitance. In conventional CV measurements, the value of space-charge capacitance is much higher than the oxide capacitance; hence the oxide capacitance dominates and equals to the total capacitor. However, in this experiment a very thin layer (20 nm) of high dielectric constant alumina was used. The space-charge capacitance is in the same range as the oxide capacitance and hence its value can be accurately calculated from the total measured capacitance. The variation of  $1/C_s^2$  versus temperature for different values of gate applied voltage fit on fairly straight lines that meet the temperature axis at about 450 K. This value corresponds to the value of  $T_C$ . The authors would like to thank EPSRC for the provision of funds via Carbon Base Electronics (CBE): a national

consortium, and the European Commission, via the Framework 6 Integrated Project "PolyApply."

**9:30 AM DD6.3**

**Nanoscale measurements and conduction mechanisms in organic memory devices from C<sub>60</sub> in insulating polymer.** Alokik Kanwal and Manish Chhowalla; Materials Science and Engineering, Rutgers University, Piscataway, New Jersey.

We recently demonstrated all-organic memory devices based on a nanocomposite material consisting of C<sub>60</sub> molecules dispersed in an insulating polymer [1,2]. In this presentation, we will report on conducting atomic force microscopy (c-AFM) measurements from nanosized regions on memory devices using C<sub>60</sub> molecules dispersed in an insulating polymer (polyvinyl phenol). The c-AFM nanoscale measurements show a similar hysteresis of high and low conductance states, in agreement with our previous reports on macroscopic memory devices [2]. However, there is a lack of scaling in the current with electrode area in macroscopic and nanodevices. Specifically, the current is ~ 200 nA in 1mm<sup>2</sup> devices while it is ~ 100pA in 50nm<sup>2</sup> device. In order to verify the c-AFM measurements, we fabricated 30nm gap cell devices via e-beam lithography which also showed similar current values. We attribute the lack of scaling to local field enhancement from C<sub>60</sub> conducting regions in the insulating polymer matrix. In addition to nanoscale measurements, we will also report on the variation of the hysteresis characteristics as a function of the C<sub>60</sub> concentration. At high concentrations (> ~ 20%), conduction percolation between C<sub>60</sub> molecules is dominant. At low concentrations, the conduction mechanism is found to be independent of temperature, indicating that transport occurs via tunneling. I. A. Kanwal, S. Paul, M. Chhowalla, "Organic Memory Devices Using C<sub>60</sub> and Insulating Polymer" Mater. Res. Soc. Symp. Proc. Vol. 830 D7.2.1  
2. S. Paul, A. Kanwal, M. Chhowalla, Advanced Materials, accepted

**9:45 AM DD6.4**

**2,7-Carbazole Unit as Building Block for the Development of Well-Defined Materials for Electronic Applications.** Nicolas Drolet<sup>1,2</sup>, Jean-Francois Morin<sup>1</sup>, Salem Wakim<sup>1,2</sup>, Nicolas Leclerc<sup>1</sup>, Ye Tao<sup>2</sup> and Mario Leclerc<sup>1</sup>; <sup>1</sup>Laval University, Quebec, Quebec, Canada; <sup>2</sup>National Research Council of Canada, Ottawa, Ontario, Canada.

Carbazole unit linked at the 2,7-positions is a new building block for the development of well-defined organic semi-conductor materials having different optical and electrical properties. Indeed, polymeric and oligomeric 2,7-carbazole materials have recently shown interesting properties in polymer light-emitting diodes (PLEDs) and field-effect transistors (OFETs). Especially, the introduction of vinylene at the 2,7-positions of the carbazole unit have led to well-defined oligomers which show hole mobility up to 0.3 cm<sup>2</sup>/V.s with an excellent  $I_{on}/I_{off}$  ratio of 10<sup>6</sup> in OFETs. This high mobility is reached through molecular ordering and preferred morphology that can be related to favorable molecular interactions. The first results obtained on flexible substrates shows that these materials can also be used in the development of flexible field-effect transistors. Low-band-gap polymers derived from 2,7-carbazolevinylene unit is also currently under investigation as new absorbing and hole transporting materials in photovoltaic devices.

**10:30 AM \*DD6.5**

**Carbon nanotube networks for transparent/flexible electronics.** George Gruner, Physics & Astronomy, University of California Los Angeles, Los Angeles, CA, California.

This talk will focus on the electronic properties of carbon nanotube networks, and their application potential as passive and active electronic components in the area of electronics, photovoltaics, optoelectronics and sensors. Percolation issues, together with the frequency, temperature and voltage dependent conductivity will be discussed. I will also review of the transistor characteristics of devices that incorporate a network conducting channels. Room temperature fabrication routes that allow integration into an all-plastic architecture will be discussed, and a comparison will be made with characteristics of other conducting/transparent films and devices. References N.P.Armitage, J-C P Gabriel and G. Gruner, "Quasi-Langmuir Blodgett Thin Film Deposition of Carbon Nanotubes", J. App. Phys. 95,3228 (2004) L. Hu, D.S. Hecht and G. Gruner, "Percolation in Transparent and Conducting Carbon Nanotube Networks", Nano Letters 4, 2513-2517 (2004) E. Artukovic, M. Kaempgen, D.S. Hecht, S. Roth, G. Gruner. "Transparent and Flexible Carbon Nanotube Transistors", Nano Letters 5, 757 (2005)

**11:00 AM DD6.6**

**Carbon Nanotube Based Thin Film Conductors /Semiconductors and Elastomeric Dielectrics for Transparent Thin Film Transistors With Excellent Bendability.** Qing Cao<sup>1,3</sup>, Seung-Hyun Hur<sup>2,3</sup> and John A Rogers<sup>1,2,3</sup>;

<sup>1</sup>Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>2</sup>Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>3</sup>Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, Illinois.

This paper demonstrates how a single class of material – networks of single walled carbon nanotube (SWNT) deposited by chemical vapor deposition (CVD) – can provide high performance conducting and semiconducting layers for all of the current carrying elements of an unusual type of transparent thin film transistor (TFT). The approach uses control of the coverage (i.e. number of tubes per unit area) of a SWNT network to define its electrical properties, as measured on length scales that are large compared to the average tube length. At relatively high coverages, the metallic tubes (present at a ratio of 1:2 with semiconducting tubes, when typical growth procedures are used) form a percolating network and the system behaves like a conducting 'film'. At moderate SWNT coverages, only the semiconducting tubes form such a percolating network. In this regime the network shows semiconducting properties. The small diameters of the tubes, their high current carrying capacities and their high intrinsic mobilities (semiconducting tubes) or conductivities (metallic tubes) yield transparent SWNT network based conducting and semiconducting layers that have good electrical properties. We show here that the remarkable mechanical properties of SWNTs lead to excellent bending characteristics in the conducting and semiconducting networks and device built with them. Printing techniques provide a means to transfer the CVD networks from their high temperature growth substrates to a wide range of other types of substrates, including large area plastic sheets. These features can be collectively exploited to yield transparent, mechanically robust, printed TFTs. When transparent silicone elastomers are used as the dielectric layers, these devices exhibit degrees of bendability (as measured by the peak strains that they can accommodate) that would be difficult or impossible to achieve with known materials. Structural, optical, electrical and mechanical studies reveal the many of the properties of these unusual devices. The results could be valuable for applications that benefit from electrical, optical and/or mechanical device characteristics that would be difficult, or impossible, to achieve with other approaches.

#### 11:15 AM DD6.7

**Transparent and flexible single-walled carbon nanotube network transistors by vacuum filtering.** Husnu Emrah Unalan, Alokik Kanwal, Aurelien Du Pasquier, Giovanni Fanchini and Manish Chhowalla; Materials Science and Engineering, Rutgers University, Piscataway, New Jersey.

Individual single-walled carbon nanotube (SWNT) devices have been subject of intense interest. However, several inherent SWNT properties make it challenging to fabricate devices. SWNT thin films provide a less lithographically intensive alternative to individual SWNT devices. Several methods have been used for the fabrication of transparent and conducting SWNT thin films, including the vacuum filtration method [1]. In this report, we will present our transparent and flexible field effect transistors (TFTs) fabricated on flexible substrates (such as PET) which utilizes the nanotube films as a channel in between source and drain electrodes. Sheet resistance of the SWNT thin films was found to be a critical factor in device performance. Optimum SWNT concentration in the filtrated solution was found to be 0.2 mg/L with a filtrated volume of 30 mL. We will present the variation of device characteristics as a function of the film thickness as well as SWNT concentration in the filtrated solution, contact material and the channel length. We will present our results with both bottom and top-gate transistors in which we obtain an on-to-off ratio of around  $10^2$  to  $10^3$  and field effect mobility of  $\sim 1$  cm<sup>2</sup>/V-s. [1] Z.Wu, Z.Chen, X.Du, J.M.Logan, J.Sippel, M.Nikolou, K.Kamaras, J.R.Reynolds, D.B.Tanner, A.F.Hebard, A.G.Rinzler, Science 305 (2004) 1273.

#### 11:30 AM DD6.8

**EPR Study of Hydrogen- and Nitrogen-Incorporated Ultrananocrystalline Diamond Thin Films.** Chao Liu<sup>1</sup>, Xingcheng Xiao<sup>1</sup>, Hsien-Hau Wang<sup>1</sup>, Orlando Auciello<sup>1,2</sup> and John A. Carlisle<sup>1,2</sup>; <sup>1</sup>Material Science Division, Argonne National Laboratory, Argonne, Illinois; <sup>2</sup>Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois.

Ultrananocrystalline diamond (UNCD) thin films are deposited on silicon substrates in argon-rich microwave plasmas with the additions of hydrogen or nitrogen gases. The nanostructures, as well as properties such as electrical conductivity, of UNCD thin films have been demonstrated to be closely related with the hydrogen and nitrogen concentration in the plasma, thus incorporation in the films. Most studies on the effect of hydrogen and nitrogen incorporation into UNCD films have been performed via computer simulations at Argonne National Laboratory. However, the bonding characteristics of incorporated hydrogen and nitrogen into UNCD are less studied

experimentally. In this study, electron paramagnetic resonance (EPR) technique is employed to investigate the bonding structure between carbon and hydrogen or nitrogen atoms, as well as the details of electron density distributions of the hydrogen- or nitrogen-incorporated UNCD thin films. Free standing UNCD thin films are prepared by stripping the silicon substrate in a silicon etching bath. EPR measurements are carried out at room and low temperatures using X-band CW mode. The spin concentrations of UNCD films are calculated using the signals of a series of DPPH samples as calibration reference. The dependence of EPR signal variation, for instance, changing of line width, line shape, and spin density upon the UNCD deposition condition is studied. Several possible mechanisms are considered as the reasons for EPR line width broadening. The relative concentrations of hydrogen and nitrogen impurities acting as paramagnetic atomic species are correlated with the property variation of the UNCD thin films. Combining the results of other measurements, including FTIR, Raman and NEXAFS which have been reported elsewhere, the mechanism of hydrogen and nitrogen incorporation into UNCD is further discussed. This work is supported by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38.

#### 11:45 AM DD6.9

**Free-standing Diamond Single Crystal Film for Electronics Applications.** Jie Yang<sup>1,2</sup>, Weixiao Huang<sup>3</sup>, T. P. Chow<sup>3</sup> and James E. Butler<sup>2</sup>; <sup>1</sup>NOVA Research Inc., Alexandria, Virginia; <sup>2</sup>Gas/Surface Dynamics Section, Naval Research Laboratory, Washington DC 20375, District of Columbia; <sup>3</sup>Rensselaer Polytechnic Institute, Troy, New York.

Diamond-based semiconductor devices offer the potential of operation at very high voltages (>10 kV), power levels, and temperatures (>400 oC) and under extreme radiation conditions in an optically transparent and chemically stable material [1-3]. Single crystal homo-epitaxial diamond films were grown on (100)-single crystal diamond by microwave plasma chemical vapor deposition (MPCVD). The growth rate can be varied from 0.01 to 100 micrometers per hour, depending on doping, impurity incorporation and desired structural quality. Free-standing homo-epi films with thicknesses between 5 and 50 microns, remarkably low p-type doping (from  $1 \times 10^{14}$  to  $1 \times 10^{17}$  cm<sup>-3</sup>), and exceptionally low compensation  $\sim 1 \times 10^{13}$  cm<sup>-3</sup> [4,5] had been made using a lift-off process (US patent: 5,587,210) where the epitaxial layers were removed from the substrate by a pre-growth ion implant, followed by a post-growth electrochemical etch. Schottky barrier diodes were built and tested in Rensselaer Polytechnic Institute. In this paper, we exploited the optical transparent property of MPCVD single crystal diamond films to correlate the quality of the epilayers with the performance of Schottky barrier diodes fabricated on the layer. We used optical microscopy to observe stress induced birefringence caused by defects/dislocations in the material and micro-Raman/photoluminescence to detect relative amounts of non-diamond carbon and color centers (nitrogen and silicon atom complexes with lattice vacancies) in the material. High structural quality (low stress) is correlated with the properties of Schottky barrier diodes fabricated in the material. Devices made from a 20 microns homo-epilayer have been shown high breakdown fields of 1.85 MVcm<sup>-1</sup> and conduction of 0.6 A/cm<sup>2</sup> at 20V forward drop at 290 oC. Through device failure analysis, we can conclude that the 1.85 MVcm<sup>-1</sup> breakdown field is only a lower limit for the material. Local stresses (dislocations) and point defects appear to be the main reasons for the high voltage failure of our single crystal diamond rectifiers. Acknowledgement This work was supported by ONR / DARPA program (contract # N00014-01-1-0784). [1] J. E. Butler, M. W. Geis, K. E. Krohn, J. Lawless Jr, S. Deneault, T. M. Lyszczarz, D. Flechtner and R. Wright, Semicond. Sci. Technol. 17, 1, 2002. [2] A. Vescan, I. Daumiller, P. Gluche, W. Ebert, and E. Kohn, Diamond Relat. Mater 7, 581, 1998. [3] D. J. Twitchen, A. J. Whitehead, S. E. Coe, J. Isberg, J. Hammersberg, T. Wikstrom, and E. Johansson. IEEE Transactions on electron devices, vol. 51, 826, 2004. [4] W. Huang, T.P. Chow, J. Yang and J. E. Butler, Proceedings Lester Eastman Conference, 2004. [5] J. Yang, W. Huang, T.P. Chow, and, J. E. Butler, High Quality MPCVD Epitaxial Diamond Film for Power Device Application, MRS 04 Falls meeting, (Oral presentation, Boston, MA, Nov. 28, 2004 and accepted paper of proceedings).