

# Thursday Evening Poster Sessions, November 16, 2006

## Thin Film

### Room 3rd Floor Lobby - Session TF-ThP

#### Thin Film Poster Session

**TF-ThP1 Electrochromic Smart Windows Based On Titanium Doped WO<sub>3</sub> Thin Films, A. Karuppasamy, A. Subrahmanyam,** Indian Institute of Technology Madras, India

Smart windows are electrochromic glass window panes that can change their transparency value in response to an applied voltage pulse. In the present study, we have developed the proton based and lithium based monolithic electrochromic structures consisting of five thin film layers; Glass/ITO/Ti:WO<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub>/NiO/ITO and Glass/ITO/Ti:WO<sub>3</sub>/LiAlF<sub>4</sub>/NiO/ITO respectively. The ionic conductor (Ta<sub>2</sub>O<sub>5</sub>) and ion storage layer (NiO) were deposited by electron beam evaporation and the active electrochromic (EC) layer (Ti:WO<sub>3</sub>) was deposited by reactive pulsed dc magnetron sputtering. Pure Titanium and Tungsten metal targets were co-sputtered in argon and oxygen atmospheres keeping the sputtering power constant. The smart window performance of the EC film was systematically studied in three steps. First, the material properties of the EC film were investigated by XRD, AFM, UV-Vis spectrophotometer and Kelvin probe. The thickness and the optical constants were estimated from the reflectance measurements. Secondly, the electrochromic behaviour of the EC film was characterized by cyclic voltammetry (CV). The CV measurements were performed using a potentiostat with a standard three-electrode configuration consisting of the sample as the working electrode. 1.0 M LiClO<sub>4</sub> in PC and 1.0 M HCl were used as electrolytes. Finally, the smart window comprising of five layers were developed and tested. The optical modulation ( $\Delta OD$ ), coloration efficiency (CE) and switching time ( $\tau_{s\%}$ ) for the proton based device was found to be better with typical values;  $\Delta OD = 60\%$ , CE = 80 cm<sup>2</sup>/C (at  $\lambda = 550$  nm) and  $\tau_{s\%} \sim 1$  s (for 1 cm x 1 cm device).

**TF-ThP2 Effect of Substrate Temperature on PMMA Nanocomposite Thin Films Grown by Laser Assisted Deposition, A.T. Sellinger, E.M. Leveugle, K. Gogick, L. Zhigilei, J.M. Fitz-Gerald,** University of Virginia

Nanocomposite thin films of poly (methyl methacrylate) (PMMA) infused with carbon nanotubes (CNT) were grown using matrix assisted pulsed laser evaporation (MAPLE) and pulsed laser deposition (PLD). MAPLE targets were formed from frozen solutions of PMMA dissolved in toluene with CNTs in suspension. Significant surface morphology was observed in films deposited at room temperature. The origin of surface feature formation was probed using scanning electron microscopy (SEM), time-gated imaging and molecular dynamics simulations. Both experimental and computational findings suggest that micron sized matrix-polymer clusters are ejected from the irradiated target and are subsequently deposited onto the substrate. In flight, a polymer rich membrane is formed around the exterior of the cluster, encapsulating the solvent within. The remaining toluene vapor eventually escapes from the cluster, leaving only a polymer "sack". In an effort to decrease the observed morphology, substrate temperature was varied between 10 and 152 °C during subsequent depositions. Significant improvements in film morphology were observed as the substrate temperature was increased. Polymer degradation in films grown at several substrate temperatures was characterized using Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC).

**TF-ThP3 Characterization of ZnO-In<sub>2</sub>O<sub>3</sub>/ZnO Laminated Thin Films Prepared by Pulsed Laser Deposition, T. Moriga, K. Ishida, A. Taki, H. Ohno, Y. Sakakibara, K. Murai,** The University of Tokushima, Japan; **M. Mikawa,** Takuma National College of Technology, Japan; **K. Tominaga,** The University of Tokushima, Japan

It is well-known that zinc oxide thin film is easy to be deposited as a crystalline wurtzite-type structure. However, heavy doping of indium in zinc oxide (~10%) led the films to be poor crystallized. When single-crystalline sapphire substrates were used instead of glass substrates, the significant reduction of resistivity and improvement of crystallinity were observed in the zinc-rich ZnO-In<sub>2</sub>O<sub>3</sub> films. In this study, we deposited the zinc-rich ZnO-In<sub>2</sub>O<sub>3</sub> film over crystalline ZnO film on a glass substrate, that is, ZnO-In<sub>2</sub>O<sub>3</sub>/ZnO laminated thin film on a glass substrate, to improve the electrical properties. Thin films were deposited on a Corning 1737 glass substrate by pulsed laser deposition using a KrF excimer laser beam with a laser fluence

of 2 J/cm<sup>2</sup>. The targets were pellets of a mixture composed of ZnO and In<sub>2</sub>O<sub>3</sub> powder, which were sintered at 1000 °C for 1 hour. The base pressure in the chamber was of the order of 10<sup>-6</sup> Torr, and pure oxygen gas was introduced into the chamber with a flow rate of 30 ccm during the deposition. The shot numbers for depositions were 10000 for a buffer film and 30000 for a major film on the buffer. At the substrate temperature of 380 °C, we could deposit the ZnO-In<sub>2</sub>O<sub>3</sub> layer over ZnO layer as a buffer layer on the glass substrate. When the composition reached  $x=0.90$  in  $x\text{ZnO}-(1-x)\text{In}_2\text{O}_3$ , the overall resistivity of the 0.90ZnO-0.10 In<sub>2</sub>O<sub>3</sub>/ZnO bilayer film was remarkably improved by one order magnitude, compared with that of the single 0.90ZnO-0.10 In<sub>2</sub>O<sub>3</sub> film on the glass substrate. Simultaneously, the diffraction intensity assigned to the 0.90ZnO-0.10 In<sub>2</sub>O<sub>3</sub> phase in the bilayer film increased significantly, resulting from improvement of crystallinity of the phase.

**TF-ThP4 The Effect of Additive Oxide Material to the MgO Protecting Layer on the XPS Spectra and the Electrical Properties in AC-PDP, S.H. Moon, T.W. Heo, S.Y. Park, J.H. Kim, H.J. Kim,** Seoul National University, South Korea

A MgO layer reduces the discharging voltage of AC-PDP (Alternating current Plasma Display Panel) due to its high secondary electron emission coefficient and protects the dielectric layer from the ion bombardments during the discharge. The mechanism of secondary electron emission from MgO is basically understood by Auger neutralization and resonance neutralization. Considering the mechanism, it is a key factor to control the work function or the summation of band gap and electron affinity. This report focused on the effect of additive oxide material to the MgO protecting layer on the XPS spectra and the electrical properties. Some kinds of materials, which have a lower work function than MgO, were chosen for adding. The pellets for the source of e-beam evaporation were fabricated by mixing the additive oxide powder with the MgO powder. Then, the mixed powder was pressed and sintered. To evaluate the discharging property, 2-inch test panels were fabricated. The characteristics of the films were evaluated by SEM, XRD and XPS. In case of adding Gd<sub>2</sub>O<sub>3</sub>, the firing voltage was lower than that of the conventional MgO films by about 17 eV. Also, the firing voltage was reduced by about 19 eV for adding (Ba,Sr,Ca)CO<sub>3</sub>. The interesting results were that the firing voltage had a correlation with the XPS valence band spectra. The firing voltage was reduced as the valence band edge was shifted to lower binding state. It means that the secondary electrons can be ejected more easily and the ejected electrons have more energy. Consequently, the discharging property was improved. @FootnoteText@ @footnote 1@H. Uchiike et al., IEEE Trans. Elec. Dev., ED-23 1211 (1976). @footnote 2@Yasushi Motoyama et al., J. Appl. Phys., 95 (12), 8419 (2004). @footnote 3@ H. D. Hagstrum, Physical Review, 122 (1), 83 (1961) @footnote 4@M. O. Aboelfotoh et al., J. Appl. Phys., 48 (11), 4754 (1977). @footnote 5@T. J. Vink et al., Appl. Phys. Lett., 80 (12), 2216 (2002).

**TF-ThP6 Real Time Monitoring of Plasma-less Vacuum Process using Self-Plasma Optical Emission Spectroscopy (SP-OES), S.-H. Han, D. Lee, S.W. Hwang, Y. Kim, C. Shin, C.-J. Kang, H. Cho, J.-T. Moon,** Samsung Electronic Co. Ltd., Korea

As the semiconductor devices shrink, degradation of device characteristics caused by plasma damage, such as charge-up and UV exposure becomes more severe. To dissolve this kind of process damage issue, a plasma-less process in a process chamber has been recently introduced for semiconductor fabrication. On the purpose of monitoring this kind of plasma-less processes, there has been studied self plasma optical emission spectroscopy (SP-OES), which is installed at pumping line and generates plasma using a small discharge cell. The emission spectra from the cell discharge plasma are analyzed to give the information on the process change in the plasma-less vacuum process chamber. By using SP-OES, it was possible to monitor the change of process behavior such as a reaction mechanism and end point detection (EPD) for which, till lately, there were no proper real-time monitoring tools for plasma-less process. Additionally, we have confirmed a possibility of monitoring process drift over wafer to wafer as a function of fault detection and classification (FDC) tool.

**TF-ThP8 Leakage Current and Dielectric Loss of BLT Thin Film Capacitors Fabricated by Chemical Mechanical Polishing (CMP) with Changes of Polishing Pressure, P.-G. Jung, N.H. Kim, W.-S. Lee,** Chosun University, Korea

PZT thin films, which are the representative ferroelectric materials in ferroelectric random access memory (FRAM), have some serious problem

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such as the imprint, retention and fatigue which ferroelectric properties are degraded by repetitive polarization. BLT thin films have many advantages such as highly fatigue resistant characteristic, low processing temperature, and large remanent polarization. BLT thin film capacitors were fabricated by plasma etching, however, the plasma etching of BLT thin film was known to be very difficult. In our previous study, the ferroelectric materials such as PZT and BLT were patterned by chemical mechanical polishing (CMP) using damascene process to top electrode/ferroelectric material/bottom electrode. It is also possible to pattern the BLT thin film capacitors by CMP, however, the CMP damage was not considered in the experiments. The properties of BLT thin films were changed by the change of polishing pressure although the removal rate was directly proportional to the polishing pressure in CMP process. The structural property of BLT thin films after CMP with the change of the polishing pressure and then the behaviors of leakage current and dielectric loss were compared with the structural property. In view of the results so far achieved, the removal rate and the leakage current must be considered simultaneously when the polishing pressure of CMP process parameter were decided. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2004-005-D00007).

**TF-ThP9 High-Performance Pentacene Thin-Film Transistors with PEDOT:PSS S/D Electrodes and Polymer Gate-Insulators, J.-M. Kim, H.-J. Her, J. Kim, Y.J. Choi, C.J. Kang, Myongji University, Korea; D. Jeon, Seoul National University, Korea; Y.-S. Kim, Myongji University, Korea**

Organic thin-film transistors (OTFTs) have been studied with much interests over the last decade, due to their attractive features such as low cost, low temperature processing and mechanical flexibility. Among the various organic semiconductors, pentacene-based TFTs show the best results in terms of the electrical performance, if the OTFTs are fabricated using inorganic gate-insulators, metal electrodes and silicon substrates. The device performance of OTFTs made only from organic materials, which are ideal for low cost, flexible and large-area electronic applications, has yet to be improved. The fully organic OTFTs implies organic gate insulators, conducting polymer electrodes and flexible substrates. We have fabricated pentacene TFTs in which the conventional inorganic gate-insulators, S/D metal electrodes and substrates are replaced by organic material, Poly (3, 4-ethylenedioxythiophene)-Polystyrene Sulfonate (PEDOT:PSS) and plastic substrates, respectively. The PEDOT:PSS S/D electrodes are deposited by inkjet printing technique for low cost and simple process. We also fabricated pentacene TFTs with several kinds of polymers as gate insulators. The physical and electrical properties of the polymer gate insulator are measured by atomic force microscope (AFM) and I-V measurement. In this work, fully organic pentacene TFTs with PEDOT:PSS S/D electrodes and polymer gate insulators are successfully demonstrated by simple process on the plastic substrate and their electrical properties are compared with conventional pentacene-based organic TFTs with inorganic electrodes and/or inorganic gate insulators.

**TF-ThP10 Pb(Zr,Ti)O<sub>3</sub> Thin Film Capacitors by Damascene Process : Fabrication and Characterization, P.J. Ko, N.H. Kim, W.-S. Lee, Chosun University, Korea**

The ferroelectric materials of the PZT, SBT and BLT attracted much attention for application to ferroelectric random access memory (FRAM) devices. Through the last decade, the lead zirconate titanate (PZT) is one of the most attractive perovskite-type materials for the ferroelectric products due to its higher remanent polarization and the ability to withstand higher coercive fields. FRAM has been currently receiving increasing attention for one of future memory devices due to its ideal memory properties such as non-volatility, high charge storage, and faster switching operations. In this study, we first applied the damascene process using chemical mechanical polishing (CMP) to the fabricate the PZT thin film capacitor in order to solve the problems of plasma etching such as low etching profile and ion charging. The structural characteristics were compared with specimens before and after CMP process of PZT films. The P-E characteristics of PZT capacitors were examined at various voltages and room temperature. The properties of PZT capacitor were Current-voltage characteristics (I-V) and capacitance-voltage (C-V) measured with RT66A. The densification by the vertical sidewall patterning and charging-free ferroelectric capacitor could be obtained by the damascene process without remarkable difference of the characteristics. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2004-005-D00007).

**TF-ThP12 Formation of Magnetic Iron Oxide Films from Decomposition of Ferric Acetylacetonate on Cold Substrates, S. De Dea, D. Graziani, D.R. Miller, R.E. Continetti, University of California, San Diego**

Ferric acetylacetonate Fe(acac)<sub>3</sub> is known to undergo thermal decomposition to form either Fe<sub>3</sub>O<sub>4</sub> or  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> magnetically ordered materials when heated above 180°C. We have recently observed that magnetically ordered Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can be formed near room temperature conditions in an inert atmosphere when a supercritical solution of Fe(acac)<sub>3</sub> in CO<sub>2</sub> is sprayed in a supersonic free-jet onto a cold Si substrate. This process is referred to as Rapid Expansion of Supercritical Solutions (RESS), and we originally anticipated the need to grow the thin cluster films on a heated substrate in an oxygen environment. We have now grown films in background pressures from vacuum to atmosphere and in both air and inert gases. The resulting cluster films have particles in the range from 50 nm to 800 nm, depending on experimental conditions, and have been analyzed by SEM, SQUID, and Mossbauer spectroscopy. The measured coercivities for the thin films range from 50 Oe to 100 Oe. These data suggest that we have grown Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, even on cold substrates in both inert and oxidizing gas backgrounds. We were able to identify  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on the basis of the Morin transition and we are currently performing additional measurements to confirm that the other magnetically ordered phase is Fe<sub>3</sub>O<sub>4</sub>. In order to better understand the mechanism for the decomposition, we are in the process of introducing a time-of-flight mass spectrometer probe of the jet conditions before the solution impacts the substrate. To remove the effects of the free-jet expansion, which can provide considerable translational energy to the impinging Fe(acac)<sub>3</sub> molecules and clusters, we are also preparing to use the supercritical solution in a batch experiment in a closed cell.

**TF-ThP13 Surface Modification of Porous Nanocrystalline TiO<sub>2</sub> Films for Dye-Sensitized Solar Cell Application by Various Gas Plasma, Y.-S. Kim, K.-J. Kim, Korea University; Y.H. Lee, KIST, Korea**

Dye-sensitized solar cells (DSSCs) have been attracting much attention because solar cells are clean, renewable and of low-cost. Many research groups make an effort to enhance photocurrent by using the modification of dye, electrolyte, and TiO<sub>2</sub> films. In this study, cold plasma treatment was used in order to modify TiO<sub>2</sub> films. Cold plasma treatment is a very effective technology in the surface modification for a variety of materials because the surface can be modified without affecting the bulk properties of the materials. The influence of plasma treatment of TiO<sub>2</sub> film on the photoelectric performance of DSSC was investigated. Treatment parameters include kinds of gases, plasma power, and gas pressure. In order to modify TiO<sub>2</sub> surface, we used different ion species such as O<sub>2</sub>, N<sub>2</sub>, Ar, H<sub>2</sub> and CF<sub>4</sub>. After various gas plasma treatment, stoichiometric changes of TiO<sub>2</sub> films were observed. Short-circuit photocurrent (J<sub>sc</sub>), open-circuit voltage (V<sub>oc</sub>) and the amount of adsorbed dye for DSSCs were measured. As a result, the solar-to-electricity conversion efficiency of the O<sub>2</sub> and N<sub>2</sub> treated cell increased by 10-15% in comparison with untreated cell. On the other hand, solar energy conversion efficiency of CF<sub>4</sub> plasma treated cell decreased drastically. The increased amount of adsorbed dye on the TiO<sub>2</sub> film was measured by UV/Vis absorption spectroscopy. Modified TiO<sub>2</sub> surfaces by plasma treatment were characterized using analytical instruments such as X-ray photoelectron spectroscopy (XPS), Near-edge X-ray absorption fine structure (NEXAFS) and Raman spectroscopy. The improved performance of DSSCs by plasma treated TiO<sub>2</sub> film was attributed to the removal of carbon contaminants, reduction of oxygen vacancies, and the enhancement of bond strength between TiO<sub>2</sub> film and dye.

**TF-ThP14 Oxide-Nitride-Oxide (ONO) Deposition Mechanism and Modelling Study in a Batch Furnace for Sub-Micron Technology, E. Chiu, A. Kolessov, J. Bailey, Aviza Technology, Inc.**

A highly uniform oxide-nitride-oxide (ONO) dielectric film deposition is required to achieve reliable flash memory device performance in the sub-micron manufacturing realm. A vertical furnace was used to investigate the effects of thin thermal oxide (<17Å), oxy-nitride and high temperature oxide (HTO) on film formation; uniform film control and low particle performance were achieved in the entire ONO film stack. In a batch reactor, various chamber and gas injection geometries were found to have moderate impact on within-wafer uniformity (WiW), while controlled temperature zone gradient significantly impacted wafer-to-wafer uniformity (WtW) across the load. Thermal oxide growth in oxygen and

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oxy-nitride deposition with DCS, NH<sub>3</sub> and N<sub>2</sub> provided excellent WiW and WtW uniformities in the optimized chamber configuration from these reaction rate controlled processes. From the HTO process experiments, high chamber pressure and low N<sub>2</sub>/DCS gas ratio were found to be the contributing factors in improving WiW uniformity. A computer model and deposition reaction mechanism were developed to simulate flow, gas-phase and surface reactions to provide further understanding of the effects of HTO deposition with DCS and N<sub>2</sub>. Results demonstrated that both the reaction and diffusion rates of gas species play an important role in determining the deposition efficiency. In the model, process temperature and reactant concentration mostly determined the WiW and WtW uniformities. As the simulation showed, the current chamber hardware could be further adjusted to improve the process performance. With optimized control of temperature zone gradient and reactant concentration, high quality films were deposited to meet and exceed the requirements for WiW and WtW ONO stack uniformities.

**TF-ThP16 Characterization of TFT-LCD and OLEDs Devices by Phase Modulated Spectroscopic Ellipsometry for Display Applications, E. Teboul, Y. Ji, HORIBA Jobin Yvon Inc; N. Nabatova-Gabain, HORIBA Ltd.**

Accurate and reliable optical characterization of polymers, liquid crystals (LCs) and organic light emitting diodes (OLEDs) is a crucial step in the manufacturing process of flat panel display. Different methods for measuring the optical constants and multiple film thickness of solid materials are available. One of the most sensitive and accurate method that measure simultaneously optical constants and film thickness is the well established technique called Spectroscopic Ellipsometry. Beside the fact that only few optical data are available for LCs and OLEDs, these devices are formed by complex structure such as multi-layer stacks including anisotropy, absorbing and graded materials. Therefore, the correct use of spectroscopic ellipsometry to characterize complex materials such as the ones found in LCs and OLEDs, require a combination of the proper choice of hardware and the appropriate ellipsometric model to analyze the data. Compare to conventional ellipsometers technique, Phase Modulated Spectroscopic Ellipsometry (PMSE) provide significant advantages for display applications. Its technology is most suitable for accurate thin film measurements on transparent substrate. In this work, we presents ellipsometric results obtained by a commercially available phase modulated spectroscopic ellipsometer on full TFT-LCD structure characterized from UV to NIR. As expected, strong anisotropy and inhomogeneous optical properties were found respectively on LCs and ITO materials. We also introduce the results on OLEDs devices previously published by Tsuboi et al (IEICE Transact. Electronics, E87-C, No.12 (2004) 2039-2044). In this case, it was found that film thickness and optical constants of a single layer differs significantly from the measurements of the same materials in a multiple layer configuration.

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