Thin Film
Room: B4 - Session TF-FrM

Transparent Electronic Materials and Applications

Moderator: M. Creatore, Eindhoven University of Technology, The Netherlands

8:20am **TF-FrM1 Thin-film Barrier on Foil for Roll-to-Roll OLEDs**, ***F.J.H. van Assche***, *E.W.A. Young, J.J. Michels,* TNO Holst Centre, The Netherlands, *G.H. Rietjens, P. van de Weijer, P.C.P. Bouten,* Philips Research Laboratories, The Netherlands, *A.M.B. van Mol*, TNO Holst Centre, The Netherlands

A flexible multi-layer ultra-barrier stack consisting of stacked silicon nitride layers interleaved by planarization layers has been developed for encapsulation of OLEDs on foil.

For this purpose a low temperature (<120°C) silicon nitride, deposited using a RF-driven parallel plate plasma reactor, has been optimized both on c-Si and on PEN foil by using spectroscopic ellipsometry (SE) and Fourier transform infrared spectroscopy (FTIR).

However, while intrinsically very low water vapour transmission rates (WVTR $<<10^{-5}$ g/m$_2$/day at room conditions) of the SiN can be achieved, the total flux of water through the barrier stack is eventually determined by the presence of local defects or pinholes. To gain insight in the transport mechanism of water in the barrier stack, both modelling and a method to trace pinholes in the barrier stack has been applied. On samples (both Ca-mirrors and OLEDs) excellent correspondence of local decay to local presence of water in the barrier stack has been shown.

Ca mirror tests of these barriers on PEN foil have yielded spotless devices after several weeks of accelerated lifetime testing at 60°C and 90% RH and even at 85°C/85% climates. Accelerated lifetime testing at 60°/90% of encapsulated OLEDs resulted in a significant yield of 6 cm^2 OLED devices without visible black spots due to cathode oxidation for over 3 weeks in this harsh climate.

Mechanical compatibility of the barrier coating with respect to R2R processing has been verified by means of bending tests of SiN layers on foil. As a next step towards R2R processing of barriers, the feasibility of R2R compatible plasma deposition by means of in-line microwave driven plasma sources is investigated. Barrier layer quality is monitored as a function of deposition rate and thickness.

8:40am **TF-FrM2 Study on MoO_{3-x} Films Deposited by Reactive Sputtering for Organic Light-Emitting Diodes**, ***N. Oka***, *H. Watanabe, Y. Sato,* Aoyama Gakuin University, Japan, *N. Ito, H. Tsuji,* Panasonic Electric Works Co., Ltd., Japan, *Y. Shigesato*, Aoyama Gakuin University, Japan

Molybdenum trioxide (MoO_3) films have been expected as a material that accelerates the hole-injection from the anode to the organic layer in organic light-emitting diodes (OLEDs) [1], where the hole-injection mechanisms into the organic layer have been discussed actively. It has been reported that the hole-injection performance of MoO_3 films would be dependent on stoichiometry of the MoO_{3-x} [2] and forming a charge-transfer complex between the MoO_3 layer and the hole-transport layer (HTL) for OLEDs [3,4]. In this study, MoO_{3-x} ($x \leq 1$) films were deposited by radio frequency (rf) magnetron sputtering using a Mo metal target at a power of 200 W. Total gas pressure of the mixture of argon (Ar) and oxygen (O_2) was maintained at 1.0 Pa. The O_2 gas flow ratio (f_{O2}) [O_2/(Ar+O_2)] during the sputtering process was varied 0-100%. The electronic state of the MoO_{3-x} films near the surface was analyzed by X-ray photoelectron spectroscopy (XPS) and photoelectron spectrometry in air (PESA). The chemical shift of the XPS Mo3d peak revealed that the valence electron numbers of Mo were four or six for the film deposited at 10 % f_{O2}, whereas it was approximately six for the films deposited at f_{O2} of higher than 15%. Furthermore, the PESA characteristics indicated that localized defect levels, caused by oxygen defects in MoO_{3-x}, should be generated between the Fermi level and the valence band, the amount of which varied with f_{O2}. These results suggest that the amount of oxygen in the films was controllable by appropriate adjustment of f_{O2}. In order to evaluate the chemical reaction between each MoO_{3-x} layer and HTL by Raman spectroscopy, bilayer films was fabricated by subsequent vacuum evaporation of N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (α-NPD) as HTL. The Raman spectra indicate that a charge transfer complex should be generated at an interface of the bilayers and the amount varied slightly with f_{O2}, which could be expected to promote hole-injection and thereby enhance the device performance of OLEDs.

<Acknowledgment>

This work was supported by New Energy and Industrial Technology Development Organization (NEDO) as a project of "Development of High-efficiency Lighting Based on the Organic Light-emitting Mechanism".

[1] T. Matsushima, G-H. Jin, H. Murata, J. Appl. Phys. 104, 054501 (2008).

[2] K. Sakanoue, Device Physics, Material Chemistry, and Device Application of Organic Light Emitting Diodes, CMC Publishing, 129 (2008) (in Japanese).

[3] W.-J. Shin, J.-Y. Lee, J. C. Kim, T.-H. Yoon, T.-S. Kim, O.-K. Song, Organic Electronics 9, 333 (2008).

[4] G. Xie, Y. Meng, F. Wu, C. Tao, D. Zhang, M. Liu, Q. Xue, W. Chen, Y. Zhao, Appl. Phys. Lett. 92, 093305 (2008).

9:00am **TF-FrM3 Amorphous and Crystalline Metaloxide Semiconductors for Transistor Applications**, ***A. Facchetti***, Northwestern University **INVITED**

In this presentation I will discuss our latest results in developing semiconductor metal oxide (SMO) formulations for solution-processed thin-film transistors based on crystalline and amorphous metal metaloxide films. Solution-processed amorphous semiconductor film fabrication by spin-coating and eventually printing is advantageous because of process simplicity, low cost, high reproducibility, chemical composition/stechiometry control, and possible high throughput enabling inexpensive electronics. Regarding crystalline SMO films, In_2O_3 thin-film transistors (TFTs) were fabricated on various dielectrics [SiO_2 and self-assembled nanodielectrics (SANDs)] by spin-coating In_2O_3 film precursor solutions consisting of methoxyethanol (solvent), ethanolamine (EAA, base), and $InCl_3$ as the In^{3+} source. Importantly, an optimized film microstructure characterized by the high-mobility In_2O_3 004 phase, is obtained only within a well-defined base: In^{3+} molar ratio after annealing at 400 C. The greatest electron mobilities of ~ 44 cm^2, for EAA :In^{3+} molar r atio = 10, $V^{-1}s^{-1}$, is measured for n^+-Si/SAND/In_2O_3/Au devices. This result combined with the high I_{on}:I_{off} ratios of ~ 10^6 and very low operating voltages (< 5 V) is encouraging for high-speed applications. We have also developed amorphous Sn-In-O and Zn-Ga-In-O formulations in which the corresponding films can be annealed at far lower temperatures (< 250 ºC). For instance, solution-processed amorphous tin-doped indium oxide (ITO) films for TFT fabrication at temperatures <250 °C can be achieved by controlling film precursor solution In^{+3} vs. Sn^{+4} molar ratio resulting in electron mobilities > 2 cm^2 $V^{-1}s^{-1}$ and I_{on}:I_{off} > 10^4 for TFTs using SiO_2 as the gate dielectric. Furthermore, w e demonstrate that hybrid integration of solution-processed ITO semiconductor films SAND enables m ~ 20 cm^2 $V^{-1}s^{-1}$.

9:40am **TF-FrM5 Permittivity-Engineered TCOs Studied by *In Situ* Spectroscopic Ellipsometry**, ***J. Burst***, National Renewable Energy Laboratory, *T.J. Peshek,* Arizona State University and National Renewable Energy Laboratory, *X. Li, T.A. Gessert, D.H. Levi,* National Renewable Energy Laboratory, *B.R. Rogers, S. Weiss*, Vanderbilt University

Recently, Gessert *et al* have reported on improved infrared optical transmittance of indium oxide-based transparent conductive oxides (TCOs) by addition of zirconia [1]. Their results show that zirconia addition allows for deposition conditions with a wider range of oxygen partial pressures while maintaining suitable optical performance. Here we report on our real-time spectroscopic ellipsometry (SE) sputter deposition studies of permittivity-engineered TCOs. *In situ* ellipsometry gives information on the growth dynamics and optical functions during film deposition. We map out the phase space of this system with regard to temperature, partial pressure of oxygen and zirconia content. Temperature-dependent Hall measurements indicate a critical point at which the films are non-degenerate. We further correlate the optical and electrical data with structural and compositional analysis.

[1] T.A. Gessert, Y. Yoshida, C.C. Fesemaier, and T.J. Coutts, *J. Appl. Phys.*, **105** (2009).

10:20am **TF-FrM7 Reactive Magnetron Sputter Deposition of Al-doped ZnO Films with Unipolar Pulsing and Impedance Control System**, ***Y. Nishi***, *K. Hirohata, N. Tsukamoto, Y. Sato, N. Oka, Y. Shigesato*, Aoyama Gakuin University, Japan

Transparent conductive oxide (TCO) is a highly degenerated wide band-gap semiconductor with low electrical resistivity and high transparency in the visible and near-infrared regions. Al-doped ZnO (AZO) should be promising potential alternative to In-based TCO, such as ITO or IZO. AZO films have been prepared by magnetron sputtering using ceramic targets because of the various advantages for uniform depositions in large area. In general the deposition rate for the sputtering using the oxide ceramic targets

is not so high and also the cost for the high quality ceramic targets is high. On the other hand, reactive sputtering using Zn-Al alloy targets is considered to be one of the most promising techniques to achieve much higher deposition rate for various industrial applications because sputtering yield of the metallic surface is much larger than oxide surface and also the higher sputtering power density can be applied for metallic targets because of their higher thermal conductivity. The reactive sputtering process, however, is strongly affected by the O_2 flow ratio; the deposition rate exhibits hysteresis with respect to the O_2 reactive gas flow rate. Such behavior originates in the oxidation state of the target surface, resulting in the marked decrease in deposition rate with the increasing O_2 flow. Therefore, the sputtering conditions should be precisely controlled so as to obtain high-quality AZO films by reactive sputtering with a high deposition rate and with high reproducibility. In this study, AZO films were deposited on quartz glass substrates, unheated and heated at 200ºC, using reactive sputtering with a specially designed feedback system (Fraunhofer Institut fur Elektronenstrahl-und Plasmatechnik, FEP) of discharge impedance combined with mid-frequency (mf) pulsing [1] . A planar Zn-Al alloy target (Al: 1.5wt.%) was connected to the switching unit, which was operated in a 50 kHz unipolar pulse mode [2] . Oxidation of the target surface was precisely controlled by the feedback system control the entire O_2 flow ratio in the "transition region". The deposition rate was about 10-20 times higher than the one deposited by conventional sputtering depositions using oxide ceramic targets. For the AZO films deposited on the glass substrates heated at 200ºC with a discharge power of 4000 W, the deposition rate was 390 nm/min, where the resistivity of the films was 3.8×10^{-4} Ωcm and transmittance in the visible region was 85 %.

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[2] S. Ohno, N. Takasawa, Y. Sato, M. Yoshikawa, K. Suzuki, P. Frach and Y. Shigesato, Thin Solid Films 496, 126 (2006).

10:40am **TF-FrM8 Study on Spatial Distribution of Electrical Properties for Al-doped ZnO Films Deposited by DC Magnetron Sputtering using Various Inert Gases**, ***Y. Sato***, *K. Ishihara, N. Oka, Y. Shigesato*, Aoyama Gakuin University, Japan

Due to recent shortages [1] and toxicity issues [2] of indium, Al-doped ZnO (AZO) have attracted much attention as alternatives to transparent conductive materials, such as Sn-doped In_2O_3 (ITO) films and indium zinc oxide (IZO). In general, AZO films deposited by magnetron sputtering showed large spatial distributions of electrical properties. Several investigations have suggested that such electrical property distributions should originate in the bombardments of the high-energy negative oxygen ions accelerated in cathode sheath region [3] or the oxidation enhancement by the activated oxygen sputtered from the oxide target and reaching at the growing film surface [4], both of which should take place at the locations in front of the erosion area of the magnetron cathode. In order to clarify the mechanisms of the degradation in the electrical properties, we investigated the dominant factors determining the electrical property distributions of AZO films deposited by dc magnetron sputtering using various sputtering gases, such as Ar, Kr or Xe. The spatial distributions clearly showed the dependence on a variety of the sputtering gases when the films were deposited on unheated glass substrate. In the cases of using Kr or Xe gases, the tendency to increase in the resistivity at the location in front of the erosion area was enhanced extremely compared with the case of using Ar. This could be attributed to the bombardment damages enhanced by the increasing sputtering voltages, because the plasma impedance increased by the smaller secondary electron emission coefficients for Kr or Xe impingements. We will also discuss on the oxidation effect of the activated oxygen or the bombardment effects by the high energy neutrals (Ar, Kr or Xe) on the electrical property distribution of AZO films. This work was partially supported by a High-Tech Research Center project for private universities with a matching fund subsidy from the Ministry of Education, Culture, Sports, Science, and Technology (MEXIT) of Japan.

[1] III-Vs Review 18 (8) (2005) p12.

[2] T. Homma et al., J. Occup . Health, 45 (2003) 137; T. Hamaguchi et al., Occup. Environ. Med. 65 (2008) 51.

[3] K. Tominaga et al., Jpn. J. Appl. Phys. **27**, 1176 (1988).

[4] T. Minami et al., J. Vac. Sci. Technol. A **18**, 1584 (2000)

11:00am **TF-FrM9 Multilayer Active Coatings on Flexible Polymer Sheet using High Rate, Closed Field Reactive Sputtering**, ***J.M. Walls***, Loughborough University, UK, *D.R. Gibson, S. Stanley, A.R. Waugh*, Applied Multilayers Ltd, UK

There is an increasing requirement for depositing complex multilayer active coatings on to surfaces of flexible polymer sheet. Applications include thin film photovoltaics, electrochromic coatings and displays. Coating materials include transmitting conducting oxides such as ITO, dielectric metal-oxides, refractory metal-oxides and metal conductors. Coating flexible polymer sheet presents a challenge since it requires a low temperature process that deposits thin films that are spectrally stable but also low in stress to prevent cracking.

This paper describes a flexible reactive sputtering process in which adjacent unbalanced magnetrons are constructed of opposite magnetic polarity. The resulting closed magnetic field maintains a high density reactive plasma. In contrast to previous reactive sputtering strategies, the process does not require an auxiliary ion or plasma source and the associated use of high Voltage ion acceleration. As a result, the deposition energy is optimized and insufficient to cause damage in the growing thin film. The substrate temperature is typically maintained below 100ºC without the need for direct cooling. The thin films exhibit bulk optical properties, they are also dense and super-smooth (<1nm rms roughness). The thin films also have typically low compressive stress. The magnetron targets are simple metals and are converted to compound thin films by using the appropriate reactive gas. The deposition process is high rate using pulsed dc power.

This paper provides data derived from a high throughput batch system with a 0.75m diameter drum substrate carrier and eight 1.2m linear magnetrons. The process geometry

is scaleable and adaptable to roll to roll deposition. Examples of both active coatings using on polymer substrates including polycarbonate, PET and Polyimide will be included. Details and examples of a novel final stage metal patterning process will also be presented .

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