ALD Applications
Room 116-118 - Session AA1-WeM

Display Device and Material

Moderators: Kwang Soo Lim, LG Display, Chang-Yong Nam, Brookhaven National Laboratory

8:00am **AA1-WeM-1 Growth Of Indium Oxide Thin Films Based On A Plasma Enhanced Atomic Layer Deposition Technique*, Joaquin Alvarado,*** *L Martinez,* University of Puebla, Mexico*; M Chavez,* CINVESTAV-IPN, Mexico*; S Alcantara, D Cortes,* University of Puebla, Mexico*; S Gallardo,* CINVESTAV-IPN, Mexico

Indium oxide is a wide band-gap transparent n-type semiconductor with a body centered cubic structure (a=1.012 nm) and relatively high electrical conductivity, in its non-stoichiometric form it has been widely used in the microelectronic field for gas sensors, window heaters, solar cells, memory devices, transistors, chemical and biosensors, transparent conducting electrodes, some types of batteries, hot mirrors, and also for transparent electronics [1].

It is expected that lowering the film dimensions or increasing the surface-to-volume ratio of the material can improve the performance of those applications; thus, several researchers worldwide have dedicated considerable efforts to the synthesis of In_2O_3 nanostructures such as nanowires, nanoparticles and thin films with a few nanometers of thickness [2].

Considering a homogeneous deposition, in this work we present a comparison of the growth of In_2O_3 thin films by thermal ALD and plasma enhanced atomic layer deposition PEALD at different temperatures, where we expect to get optical and/or electrically favorable layers to improve the performance of solar cells as well as a capacitor in order to use it as the base of a cost effective thin film transistor (TFT) suitable for radiation sensors (x-rays, alpha and gamma radiation) at low temperatures.

Figure 1 left shows that quite similar transmittance is obtained between In_2O_3 layers deposited by both ALD methods at the same temperature, where the ones deposited at 150ºC shows high transparent layers. Also, Figure 1 right depicts the absorbance of these layers as well as its band-gap, which is close to 3.2eV. Furthermore, Tauc plot calculation allows extracting a correct band-gap for each sample, being the layers grown by thermal ALD the ones that present higher band-gap that the ones grown by plasma. We will also present optical, electrical and elemental characterizations such as XRD, SEM, Transmittance, Reflectance, SIMS, AFM, Profilometry, C-V Curves and I-V Curves to explain the characteristics and applications of the material.

[1] G.F. Pérez-Sánchez et al., (2014), Synthesis of In-In_2O_3 microstructures by close-spaced vapor transport (CSVT) and their transformation to In_2O_3 nanobelts at low temperature, Vacuum 107, 236-241

[2] D. Cortés-Salinas, F. Chavez, G.F. Pérez-Sánchez, P. Zaca-Morán, A. Morales-Acevedo, R.Peña-Sierra, O. Goiz, A. T. Huerta. Synthesis and Characterization of In2O3 Micro- and Nano-Structures at Low Temperatures by the CSVT Technique. 386-390. ISBN: 978-1-4673-2168-6.

8:15am **AA1-WeM-2 Large-Area Atmospheric Pressure Spatial ALD for Display Applications***, C Frijters, F van den Bruele, A Illiberi,* ***Paul Poodt,*** Holst Centre - TNO, Netherlands **INVITED**

Atmospheric pressure Spatial ALD (sALD) is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. First industrial applications of Spatial ALD include passivation of c-Si solar cells and roll-to-roll manufacturing of flexible barrier foils. An emerging application for Spatial ALD is flat panel (OLED) displays. Examples include semiconducting and dielectric layers for use in thin-film transistors, and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated using glass panels in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

We are developing large-area Spatial ALD technology, and as a first step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates. With this tool we are able to deposit uniform films across a deposition width of 400 mm. The whole tool is operated under an atmospheric pressure but inert N_2 environment. The tool can be used to deposit a variety of materials using both thermal and plasma-enhanced Spatial ALD.

We will present the basic deposition performance of the tool in terms of thickness- and compositional uniformity. Large-area thickness non-uniformities of less than 1% are achieved for several oxide materials. Next, we will focus on two display-related applications: thin-film encapsulation of OLED devices, and high mobility InZnO and InGaZnO semiconductors for thin-film transistors. We will explain the requirements, the deposition process and the performance of the deposited films. Finally, the challenges in up-scaling Spatial ALD to plate sizes of 1.5 m and beyond will be discussed.

8:45am **AA1-WeM-4 Amorphous Indium Zinc Tin Oxide (IZTO) Semiconductor Materials and the Associated Thin Film Transistor Properties Deposited by Atomic Layer Deposition*, Jiazhen Sheng,*** *T Hong,* Hanyang University, Republic of Korea*; J Lim,* Samsung, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

Oxide semiconductor thin film transistors (TFTs) have been extensively researched as a backplane technology in display industry. Comparing to the indium gallium zinc oxide (IGZO) which has been widely used as TFT active layer ma terial, indium zinc tin oxide (IZTO) has been suggested as a promising material due to its attractive performance, including relatively high mobility (>25cm^2/Vs) and superior stability. Relying on the self-limiting reaction, the atomic layer deposition (ALD) takes advantage of uniformly depositing the films over large areas with precisely controlled thickness that makes ALD become a promising technology to apply in thin film transistor, including of active layer fabrication. In this research, the ALD Sn doped IZO thin film was first investigated, which was deposited using the concept of "super-cycle" – IZO (1 cycle InOx – 1 cycle ZnO), IZTO111 (1 cycle InOx – 1 cycle ZnO – 1cycle SnOx) and IZTO112 (InOx 1 cycle – 1 cycle ZnO – 2cycle SnOx). It is found, by doping with SnOx, the band gap structure, micro-structure as well as the electrical characteristics were changed. Then, the bottom gate top contact IZO, IZTO111 and IZTO112 thin film transistors were fabricated by ALD process. The devices with Sn doped IZO active layer exhibited increased mobility (27.8cm^2/Vs for IZTO111 and 22.7cm^2/Vs for IZTO112) and stability under positive bias temperature stress (threshold voltage shift of 1.8V and 0.7V) than IZO TFTs (mobility of 18.0cm^2/Vs and threshold voltage shift of 2.2V). The flexible ALD IZTO TFT also fabricated on the PI substrate, and 200,000 cycles bending test was processed to investigate the degradation mechanism of flexible ALD TFT under mechanical stress.

9:00am **AA1-WeM-5 Evaluation of Si precursor for SiO_2 OLED Encapsulation by PEALD*, GunJoo Park,*** *J Park, B Yang, S Kim, J Park, S Jang, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

OLED devices are made up of organic compounds, which are excited to emit light due to the nature of the material. In this excited state with high energy, it easily reacts with moisture and oxygen. When the OLED element reacts with moisture and oxygen, problems such as decrease in luminance, increase in voltage, and poor emission occur.

Recently, TFE (Thin Film Encapsulation) technology has been used to overcome this problem. The OLED encapsulation technology using a thin film can provide the display flexibility and effectively prevent the infiltration of air and moisture into the organic layer of the OLED device, which is suitable as a next generation display encapsulation film.

In this paper, NSi-01 and 1N5 precursors were applied to thin film encapsulation technology for next generation OLED devices, and low-temperature SiO_2 deposition process by PEALD method was developed. In both precursors, SiO_2 deposition conditions were similar, and RF dosage experiments confirmed their suitability as ALD precursors.

High growth rate of 1.95 Å / cycle and 2.65 Å / cycle (Fig.2) and formation of pure silicon oxide film free of impurities were confirmed (Table.1).

The density of the SiO_2 thin film was 2.23 g / cm^3 (Table.2) for both precursors, and the bulk SiO_2 density was 2.6 g / cm^3, indicating that an amorphous SiO_2 thin film was formed. The encapsulation layer affects the image quality and brightness of the display when the visible light transmittance is decreased. In the case of the precursor used in this experiment, the visible light transmittance was 99% at a thickness of 700Å (Table.2). It can be seen that there is no difference in image quality or brightness after applying the encapsulation layer .

The moisture permeability, which is the core of the encapsulation layer, varies with RF time and thickness. In case of NSi-01 with a thickness of 700Å, the RF time was 0.9 seconds at 4.6×10^{-3} g / m^2-day. In case of 1N5, the RF time was 1.5 seconds at 5.0×10^{-3} g / m^2-day Sufficient RF dosage is required compared to NSi-01. However, in case of 1N5, high film growth rate was confirmed compared to NSi-01, and the actual process time was confirmed to be similar. We also confirmed the excellent WVTR characteristics of 5.5×10^{-3} g / m^2-day even at a thin thickness 500Å (Fig.6), thus confirming the possibility of the next generation OLED element encapsulation film precursor.

9:15am **AA1-WeM-6 Hydrogen Barrier Properties of ALD Al_2O_3 with Different Oxidants***, H Kim, **Yujin Lee**, T Nam, S Seo, C Lee,* Yonsei University, Republic of Korea*; J Yang, D Choi, C Yoo, H Kim,* LG Display

Amorphous In-Ga-Zn-O (a-IGZO) semiconductors have been used as an active channel material in high mobility, flexible, and transparent thin film transistors (TFTs), but it is highly influenced by the external environment. To protect from it, plasma-enhanced chemical vapor deposition (PECVD) SiN_x deposited using SiH_4/N_2O is commonly used as the encapsulation film. In this process, however, the amount of hydrogen was introduced to backchannel.[1] It is well known that the hydrogen in an oxide semiconductor acts as a shallow donor by ionizing and bonding with oxygen to form hydroxyl bonds. It makes the oxide TFT very conductive and causes it not to show an on/off property.[2] Therefore, appropriate hydrogen barrier is required to prevent hydrogen incorporation into the IGZO channel, but there is a lack of systematic research on it.

In this study, Al_2O_3 was deposited on the a-IGZO TFT by atomic layer deposition (ALD) using trimethylaluminum(TMA) with water or O_3, as the precursor and oxidant, respectively, at low temperature (about 60°C). First, we fundamentally investigated the characteristics of Al_2O_3 according to the oxidant. The composition of the Al_2O_3 was different depending on the oxidant used in the ALD process. Based on this, we analyzed the effect of these characteristics on hydrogen barrier properties by using transfer curve and stress test of device. As a result, the device in which the Al_2O_3 was deposited exhibited excellent hydrogen barrier properties as compared with the bare device. There was no device degradation after the hydrogen treatment, which suggested the possibility of enhancing the device reliability in mass production in the future.

Reference

[1] A. Sato *et al.*, “Amorphous In-Ga-Zn-O thin-film transistor with coplanar homojunction structure,” *Thin Solid Films*, vol. 518, no. 4, pp. 1309–1313, 2009.

[2] S. I. Oh, G. Choi, H. Hwang, W. Lu, and J. H. Jang, “Hydrogenated IGZO thin-film transistors using high-pressure hydrogen annealing,” *IEEE Trans. Electron Devices*, vol. 60, no. 8, pp. 2537–2541, 2013.

9:30am **AA1-WeM-7 Flexible Al_2O_3/Organic Multilayer Moisture Barrier Films Deposited by Spatially Resolved ALD Processes in a Single Chamber***, **Sang Heon Yong**, S Kim, Y Choi, H Hwangbo, H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Thin film encapsulation (TFE) is one of essential technologies required for flexible organic light emitting diode (OLED) display devices. It is well known that organic materials are easily damaged by moisture and oxygen when plastic films are adopted for substrates. Atomic layer deposition (ALD) processes on plastic films demonstrated superior moisture barrier property to other inorganic barrier deposition processes.[1] However, extremely low throughput of ALD processes is a big huddle for commercialization and active research on ‘spatial ALD’ process is underway to enhance throughput. [2] To improve the barrier property further and to increase flexibility of barrier films simultaneously, various multilayer structures have been reported with various inorganic and organic layers. Since the multilayer structure consists of several thin films, the diffusion path of the barrier film can be increased and flexibility can be increased by reducing the bending stress of thin films. [3]

In this study, we deposited Al_2O_3 and organic layers in a single spatially-resolved processing chamber and demonstrated multilayer structures to achieve high barrier property and flexibility. The water vapor transmission rate (WVTR) of Al_2O_3 single thin films decreases significantly above 10nm thickness as shown in Figure 1. Organic layers were also deposited in the same chamber by plasma-enhanced chemical vapor deposition. About 20nm or thicker organic layers are required to improve the barrier film flexibility in this experiment. The total of 21 layers of Al_2O_3 and organic layers are deposited alternately and WVTR of 8.5 10^{-5} g/m^2·day was achieved. The WVTR increases by 10%, 21% and 32% in 3cm, 1.5cm and 1cm bending radius, respectively.

References

[1] J.S. Park, H. Chae, H.K. Chung, S.I. Lee, Semicond. Sci. Technol. 26, 034001, (2011)

[2] P. Poodt, D. C. Cameron, E. Dickey, S. M. George, V. Kuznetsov, G. N. Parsons, F. Roozeboom, G. Sundaram, A. Vermeer, J. Vac. Sci. Technol. A, 30, 010802, (2012)

[3] S.W. Seo, H.K. Chung, H. Chae, S.J. Seo, S.M. Cho, NANO, 8, 4, 1350041, (2013)

9:45am **AA1-WeM-8 Optimization of Film Structure by Stress Engineering for Flexible Thin Film Encapsulation***, **Ju-Hwan Han**, D Choi, J Lee, K Han, J Park,* Hanyang University, Republic of Korea

Flexible electronics are focused recently as future-oriented devices such as light emitting device, sensing device and photoelectric cell. One of critical issues is a rapid degradation by oxygen and water vapor in flexible organic light emitting diodes (OLEDs) devices. Thus, thin film encapsulation (TFE) process is highly recommended to protect the OLEDs from water vapor and also preserve their flexibility. The inkjet printing and PECVD methods have been comerciallized to make orgniac/inorganic hybride layer. Unfortunately, they have some limits on flexible OLEDs; not only poor step coverage and particle issues but also cracking films under mechanical stress conditons. Atomic Layer Deposition (ALD) can be a promising candidate to solve the above issues.

In this study, we optimized the TFE layer via the stress engineering using organic/Al_2O_3 ALD hybrid films. In order to suggest optimized structure for flexible gas diffusion barrier layer, we investigated water vapor transmission ratio (WVTR) of the layer under the bending stress as a function of thickness of substrate, thin film and additional layer on the thin film. With additional layer of similar thickness to the substrate, the degradation of TFE layer is minimum (W/W_0 ~ 1.08, bending radius of 2.5mm). And there was almost no degradation of TFE layer with more than 2 dyads of organic/Al_2O_3 layer (W/W_0 ~ 1.01, bending radius of 2.5mm). As a result, optimized TFE layer structure using inorganic/organic layer showed not only improved moisture barrier property, but mechanically robust behavior after bending stress.

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