©2007 The Japan Society of Applied Physics

Characteristics of Organic Light Emitting Diodes with Tetrakis(Ethylmethylamino) Hafnium Treated Indium Tin Oxide

Sunyoung SOHN, Keunhee PARK, Donggeun JUNG, Hyoungsub KIM^{1*}, Heeyeop CHAE², Hyunmin KIM³, Junsin YI³, Mann-ho CHO⁴, and Jin-hyo BOO⁵

Department of Physics, Institute of Basic Science, and Brain Korea 21 Physics Research Division, Sungkyunkwan University, Suwon 440-746, Republic of Korea

¹School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea

²Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea

³School of Information and Communication Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea

⁴Institute of Physics and Applied Physics, Yonsei University, 134 Shinchon-Dong, Seodaemun-Ku, Seoul 120-729, Republic of Korea

⁵Department of Chemistry, Institute of Basic Science, and Brain Korea 21 Chemistry Research Division, Sungkyunkwan University, Suwon 440-746, Republic of Korea

(Received December 11, 2006; accepted April 9, 2007; published online May 11, 2007)

The surface of indium tin oxide (ITO) in organic light emitting diodes (OLEDs) was treated using an atomic layer deposition with tetrakis(ethylmethylamino) hafnium (TEMAH) and O_2 precursors. The treatment for 5 cycles at room temperature resulted in a significant improvement in the electroluminescent characteristics resulting from the increased hole injection. According to the various characterizations, an ultra-thin HfO_x layer without any insulating properties was formed, which modified the electronic band structure of the ITO anode. When the number of cycles or temperature was increased, an electrically insulating HfO_x was formed, and the resulting OLED properties deteriorated. [DOI: 10.1143/JJAP.46.L461] KEYWORDS: organic light emitting diodes, ALCVD, TEMAH, hafnium oxide, impedance analysis, NEXAFS spectroscopy

Recently, organic light emitting diodes (OLEDs) have attracted a great deal of interest for their potential application in the next generation of flat panel displays, due to their simple fabrication process, a wide view-angle, and low power consumption.¹⁻⁷⁾ In fabricating OLED devices, indium tin oxide (ITO) film is widely used as an anode layer, because of its high transparency in the visible light range, low conductivity, and high work function ($\sim 4.8 \text{ eV}$).^{1–3)} Among the many factors determining the performance of OLED devices, the interface between the organic hole transport layer (HTL) and the anode layer plays an important role in controlling the efficiency of the charge carrier injection into the emitting layer.^{1,2)} The insertion of an organic interfacial layer such as CuPc or various thin insulating films such as WO₃, NiO, SiO₂, ZrO₂, Ta₂O₅, and TiO_2 between the ITO anode and the HTL was found to improve the performance of the OLEDs. This performance improvement was explained by the energy level alignment or tunneling effect.¹⁻⁸⁾ In addition, the modification of the work function of the ITO surface was reported by doping it with Hf atoms using a co-sputtering technique or inserting a conducting oxide layer, i.e., IrO_x , which increased the work function of the ITO surface through surface dipole formation.9,10)

Although many thin-film deposition techniques, such as sputtering or chemical vapor deposition, have been used to obtain an ultra-thin interfacial layer between the HTL and the anode, these methods are not suitable for obtaining a high quality ultra-thin interfacial layer with a sub-nm range thickness. Recently, atomic layer chemical vapor deposition (ALCVD) has been widely used in many application areas which require precise thickness controllability and low structural defects. This is because the ALCVD process is based on surface adsorption- and saturation-controlled deposition kinetics.^{11,12}

In this paper, we describe our investigation of the effects of the ALCVD treatment on the ITO surface on the electrical properties of an OLED device. The ALCVD treatment was performed both at room temperature (RT) and at various temperatures up to the typical HfO₂ deposition temperature (300 °C) using tetrakis(ethylmethylamino) hafnium (TEMAH; Hf[N(CH₃)C₂H₅]₄) as the precursor. The binding and molecular structure of the HfO_x layer formed on the ITO surface were analyzed by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

ITO (150 nm)-coated glass with a sheet resistance of $20 \Omega/\Box$ was used as a substrate for the fabrication of the OLED device. First, the ITO glass was cleaned successively in ultrasonic baths of trichloroethylene, acetone, and methanol. After sonicating the ITO glass in deionized water, the samples were dried by blowing them with high purity N_2 gas. For the surface modification of the ITO, some of the samples were treated with various ALCVD process conditions using TEMAH as an Hf precursor and O2 as an oxidizer, respectively. For the ALCVD treatment, each cycle was composed of four steps as follows. First, a mixture of TEMAH and Ar carrier gas (300 sccm) was introduced into the vacuum chamber for 10 s. The chamber was purged by flowing Ar (150 sccm) for 5 s. For the formation of the HfO_r layer, oxygen gas (300 sccm) was flowed for 5 s, and the resulting by-products or remnant gases were completely removed by the subsequent purging step using an Ar (150 sccm) gas for 5 s. The ITO substrates were treated in an ALCVD system for various number of cycles (3 to 30 cycles) from RT to 300 °C. After various treatments, *N*,*N*'-diphenyl-*N*,*N*'-bis(3-methylphenyl)-1,1'-diphenyl-4,4'diamine (TPD; 32 nm), tris-(8-hydroxyquinoline) aluminum (Alq₃; 48 nm), lithium fluoride (LiF; 0.5 nm), and Al (90 nm) were deposited as an HTL, an emissive material layer (EML), a cathode interfacial layer, and a cathode, respectively, as depicted in the inset of Fig. 1(a).

^{*}E-mail address: hsubkim@skku.edu



Fig. 1. (a) *J–V*, (b) *B–V*, and (c) power efficiency characteristics of OLEDs treated without and with ALCVD-HfO_x at room temperature as a function of deposition cycles.

Fig. 2. (a) J-V, (b) B-V, and (c) power efficiency characteristics of OLEDs treated with ALCVD-HfO_x at 100, 200, and 300 °C as a function of deposition cycles.

Following the OLED fabrication, the current density– voltage (J-V) characteristics of the OLED devices were measured using a Keithley 2400 electrometer and their brightness was evaluated by measuring the photocurrent using a Keithley 485 picoammeter. The capacitance characteristics were measured using an LF 4192A impedance analyzer at an applied voltage of 0 V with an AC frequency of 50 Hz. In order to investigate the chemical bonding structure of the HfO_x-treated ITO surface, some of the ITO samples, with the various HfO_x treatments without TPD, Alq₃, LiF, and Al layer, were analyzed by XPS and NEXAFS. The XPS measurement was performed using a VG Microtech ESCA-2000 system having a Mg K α source, and NEXAFS measurements were carried out using a thirdgeneration synchrotron radiation source located at the Pohang Accelerator Laboratory (beamline 8Al).

The current density, brightness, and power efficiency curves for the different treatment conditions on the ITO surfaces are shown in Figs. 1 and 2. In this study, the OLED without any treatment was referred to as a control sample. Compared to the control sample without any treatment, the sample treated for 5 cycles at RT, which was referred to as RT-5C, exhibited significantly improved OLED performance, i.e., a decrease in turn-on voltage as depicted in the inset of Fig. 1(a) and an increase in brightness. Because of the high current flow and subsequent increase in brightness mainly originating from the increased hole injection efficiency from the ITO anode into the organic layer,¹³⁾ we



believe that the 5 cycle treatment at RT by the ALCVD process is an effective method of improving hole injection efficiency. However, when the number of ALCVD cycles was increased at RT, the turn-on voltage increased and the brightness decreased as compared to the control sample as shown in Fig. 1. This is believed to be caused by the formation of an insulating layer and the consequent retardation of the hole injection. The power efficiency characteristics of the OLEDs, as a function of the current density, are also shown in Fig. 1(c). The efficiency of the RT-5C sample, compared to that of the OLEDs without any treatment, slightly increased and showed a saturating behavior with an increase of current density, which is desirable for passive matrix displays.¹⁴⁾ However, when the deposition cycles were increased, the power efficiency of OLEDs was reduced as an decrease of the current density. With the increase of the deposition temperature, the electrical and optical characteristics of the OLEDs showed similar or worse performance when compared to the control sample as a function of deposition cycles as shown in Fig. 2, which is also believed to be caused by the formation of an insulating layer with the increase of the deposition temperature.

Figure 3 shows the capacitance versus frequency (C-f)characteristics and Cole-Cole plots of the OLEDs prepared with different surface treatments on the ITO substrates, respectively. As shown in Fig. 3(a), the RT-5C sample exhibited the highest capacitance among the fabricated OLED devices, which also confirmed that it has the highest hole injection efficiency into the HTL, because the capacitance depends on the amount of charge injection into the organic layer from the electrodes.¹³⁾ However, in the case of the RT-30C and 300T-30C samples, the capacitance values were decreased, because of the formation of a thicker carrier injection barrier, as revealed by the previously mentioned OLED device characteristics shown in Figs. 1 and 2. The equivalent circuit of the OLED can be described as depicted in the inset of Fig. 3(b), consisting of a single parallel resistance (bulk resistance, $R_{\rm p}$) and capacitor (bulk capacitance, C_p) network with a series resistance (contact resistance, R_s).¹⁵⁾ The horizontal and vertical axes of the Cole–Cole plots represents the real (Y') and imaginary (Y'') parts of the total admittance of the OLED device, respectively. These values can be calculated from the following complex admittance equation.

$$Y = 1/Z = G + jB = G + j\omega C, \qquad (1)$$

where Y is the admittance, Z is the impedance, G is the conductance, B is the susceptance, and C is the capaci-

S. SOHN et al.

Fig. 3. (a) *C*-*f* characteristics and (b) Cole–Cole plots of OLEDs without and with surface treatment.

tance.¹⁶⁾ The values of R_s extracted from the Cole–Cole plots of the control, RT-5C, RT-30C, and 300T-30C samples are 85.0, 65.7, 150.4, and 297.9 Ω , respectively. The sample whose ITO surface was subjected to 5 cycles of the ALCVD- HfO_x process at RT exhibited a lower series resistance than the control sample without any treatment, because of the improvement of the hole injection efficiency between the organic layer and the ITO anode, which is in good agreement with the previously observed improvement of the current flow and brightness. It means that the interface property between the ITO and TPD layer was improved because of the HfO_x treatment, resulting in the improved device performance. Therefore, we believe that the performance enhancement of HfO_x treated OLEDs for 5 cycles at RT as an optimized condition, was due to the improvement of the interface property between the ITO and TPD layer considering its lowest contact resistance compared with other devices and/or the increase of ITO work function by a metal oxide with high dipole moment. However, when the number of cycles and process temperature were increased, the total capacitance decreased and the series resistance increased, because of the formation of a thick insulating HfO_x barrier layer.

In order to investigate the chemical bonding status of the HfO_x layer, XPS measurements were performed on the ITO substrates after the various HfO_x treatments, as shown in Fig. 4(a). For all the samples, the Hf 4*d* peaks exhibited two distinctive components, *viz*. Hf 4*d*_{3/2} and Hf 4*d*_{5/2}, with binding energies of 224 and 213 eV, respectively, which corresponds to Hf–O bonding formation.¹⁷⁾

Recently, NEXAFS measurement has been reported as one of the best methods of studying the electrical properties and orientation of the molecules in organic films.¹⁸⁾ In order to investigate the molecular structure of the HfO_x films in more detail, the NEXAFS spectra of the OK edge were obtained, as shown in Fig. 4(b). The peaks at 535.5, 533.5, and 529.2 eV correspond to the SnO_2 , In_2O_3 , and $SnO_2 + In_2O_3$ phases in the ITO film, respectively.¹⁹⁾ Although the RT-5C sample showed the existence of HfO_x according to the XPS measurements, the NEXAFS spectra of the O K edge was not changed as compared with that of the ITO film without any surface treatment and the peak caused by the electronic structure of the O K edge representing unoccupied hybridized orbitals of HfO2 was not detected. This indicates that the typical electronic structure of HfO₂ as an insulator was not formed in the adsorbed Hf layer on ITO. In summarizing the XPS, NEXAFS, and electrical results, we believe that the Hf precursor chemically adsorbed on the ITO surface formed Hf-O bonding



Fig. 4. (a) Hf 4*d* peak in the XPS peak spectra of the ITO surface as a function of the TEMAH deposition conditions and (b) NEXAFS spectra of the O *K* edge features as a function of TEMAH deposition conditions.

with the subsequent oxygen injection during the ALCVD process and additional air exposure during the sample transfer. In addition, the Hf precursor formed Hf-O bonding having a high dipole moment with the underlying ITO network, and the subsequent bias-induced realignment of the anode Fermi level and highest occupied molecular orbital (HOMO) of the HTL lowered the band offset with the top HTL by modifying the work function of the ITO surface. However, the existence of the ultra-thin HfO_x layer did not retard the hole injection from the anode due to the tunneling effect. When the number of cycles or deposition temperature was increased, the peaks caused by the unoccupied hybridized orbitals of Hf and O appeared in the lower photon energy range, which confirmed the formation of an electrically insulating HfO_x layer. The O K edge NEXAFS spectra of the 300T-30C sample were directly related to the oxygen *p*-projected density of states of ITO overlapped with that of HfO₂, which consists of the four unoccupied hybridized orbitals, Hf $5d + O 2p\pi$, Hf $5d + O 2p\sigma$, Hf 6s + O 2p, and Hf 6p + O 2p of the HfO₂ film.¹⁸⁾ The formation of an physically thick *insulating* HfO_x layer between the anode and HTL, as confirmed by the NEXAFS measurement, significantly deteriorated the OLED performance, as previously shown in Figs. 1 and 2.

In summary, we investigated the electrical and optical characteristics of OLEDs fabricated with TEMAH treated ITO substrates using an ALCVD process. By treating the ITO substrate with TEMAH using an ALD process for 5 cycles at RT, the turn-on voltage and electroluminescent characteristics were significantly improved, because of the modification of the work function of the ITO surface and the resulting enhancement of the hole injection efficiency as compared to the OLED without any surface treatment. According to the XPS and NEXAFS measurements, we believed that one or two layers of HfO_x were formed on the ITO surface, without exhibiting any insulating properties because of the hole tunneling effect. When the number of deposition cycles or deposition temperature was increased, insulating HfOx films were deposited and the OLED performance was severely deteriorated because of the thick carrier injection barrier.

Acknowledgement

This work was supported by the SRC program (Center for Nanotubes and Nanostructured Composites) of MOST/ KOSEF.

- J. Li, M. Yahiro, K. Ishida, H. Yamada, and K. Matsushige: Synth. Met. 151 (2005) 141.
- 2) I. M. Chan and F. C. Hong: Thin Solid Films 450 (2004) 304.
- C. Qiu, Z. Xie, H. Chen, M. Wong, and H. S. Kwok: J. Appl. Phys. 93 (2003) 3253.
- 4) C. J. Huang: J. Mater. Sci. Lett. 22 (2003) 1423.
- 5) A. Mitsui and K. Masumo: Thin Solid Films 442 (2003) 140.
- 6) H. T. Lu and M. Yokoyama: Solid-State Electron. 47 (2003) 1409.
- H. Ishii, K. Sugiyama, E. Ito, and K. Seki: Adv. Mater. 11 (1999) 605.
- S. A. VanSlyke, C. H. Chen, and C. W. Tang: Appl. Phys. Lett. 69 (1996) 2160.
- T. H. Chen, Y. Liou, T. J. Wu, and J. Y. Chen: Appl. Phys. Lett. 85 (2004) 2092.
- 10) S. Y. Kim and J.-L. Lee: Appl. Phys. Lett. 87 (2005) 232105.
- K. Kukli, M. Ritala, T. Sajavaara, J. Keinonen, and M. Leskela: Chem. Vap. Dep. 8 (2002) 199.
- 12) S. K. Park, J. I. Lee, Y. S. Yang, and S. J. Yun: Int. Meet. Information Display, 2002, p. 746.
- 13) V. Shrotriya and Y. Yang: J. Appl. Phys. 97 (2005) 54504.
- 14) L. S. Hung and C. H. Chen: Mater. Sci. Eng. R 39 (2002) 143.
- 15) J. R. Macdonald: Impedance Spectroscopy: Emphasizing Solid Materials and Systems (John Wiley & Sons, New York, 1987) Chap. 1.
- 16) Y. S. Lee, J.-H. Park, J. S. Choi, and J. I. Han: Jpn. J. Appl. Phys. 42 (2003) 2715.
- J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben: Handbook of X-ray Photoelectron Spectroscopy (Physical Electronics, Minnesota, 1995).
- 18) M.-H. Cho, H. S. Chang, Y. J. Cho, D. W. Moon, K.-H. Min, R. Sinclair, S. K. Kang, D.-H. Ko, J. H. Lee, J. H. Gu, and N. I. Lee: Appl. Phys. Lett. 84 (2004) 571.
- 19) C. McGuinness, C. B. Stagarescu, P. J. Ryan, J. E. Downes, D. Fu, and K. E. Smith: Phys. Rev. B 68 (2003) 165104.