

## Effects of HfO<sub>x</sub> treated indium tin oxide on organic emitting diodes

Sunyoung Sohn<sup>1</sup>, Keunhee Park<sup>1</sup>, Donggeun Jung<sup>1</sup>, and Hyungsub Kim<sup>2\*</sup>

<sup>1</sup>Dept. of Physics, Institute of Basic Science, Brain Korea 21 Physics Research Division, Sungkyunkwan University, Suwon, Kyungki-do, Republic of Korea

<sup>2</sup>School of Advanced Materials and Engineering, Sungkyunkwan University, Suwon, Kyungki-do, Republic of Korea

\* Phone: +82-31-290-7363 , E-mail: hsubkim@skku.edu

### Abstract

The surface of ITO in OLEDs was treated with HfO<sub>x</sub> deposition process using an atomic layer chemical vapor deposition system. The treatment at room temperature for 5 cycles exhibited significantly improved electroluminescent characteristics compared to the OLEDs without any treatment, which is believed to be caused by the increased holes injection efficiency.

### 1. Introduction

Organic light emitting diodes (OLEDs) have been attracting much interest as a next generation flat panel display due to many advantages, such as simple fabrication methods, wide view angel, and low power consumptions.<sup>1-3</sup> In fabricating OLED devices, indium tin oxide (ITO) film is widely used as an anode layer because of its high transparency in visible light range, low conductivity, and high work function.<sup>1-3</sup> Among many factors determining the performance of OLED device, the interface between the organic hole transport layer (HTL) and the anode plays an important role in controlling the charge carrier injection from electrodes into the emitting layer.<sup>1,2</sup> The modification of the work function of ITO surface was reported by doping with Hf atoms using a co-sputtering technique or inserting an conducting oxide layer, such as IrO<sub>x</sub>.<sup>4,5</sup> Recently, atomic layer chemical vapor deposition (ALCVD) technique is widely used in many application areas which require precise thickness controllability and low structural defects of ultra-thin films because the ALD process is based on the surface adsorption and saturation-controlled deposition kinetics.<sup>6</sup>

In this paper, we investigated the effects of treatments of ITO surface using ALCVD HfO<sub>x</sub>

process on the electrical and the optical properties of OLED device.

### 2. Results

The ITO coated glass with a sheet resistance of 20 Ω/□ was used as a substrate for the fabrication of 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<sub>2</sub> gas. For the surface modification of ITO, the ITO anode was treated with ALCVD-HfO<sub>x</sub> process at room temperature. The fabricated OLED device without any treatment on the ITO surface is referred as control and that having the ITO electrode treated with ALCVD-HfO<sub>x</sub> process for 5, 10, 20, 30 cycles at room temperature is referred to as RT-5C, RT-10C, RT-20C, and RT-30C, respectively. After various treatments, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine (TPD, 32 nm), tris-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>, 48 nm), LiF (0.5 nm), and Al (90 nm) were deposited as an HTL, an emitting layer (EML), a cathode interfacial layer, and a cathode, respectively, as depicted in Fig. 1.

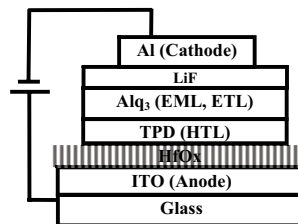
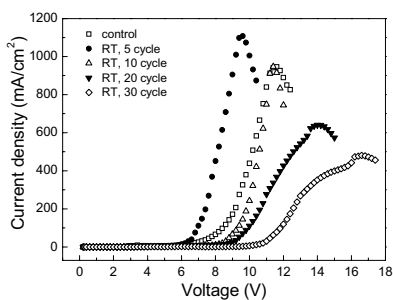


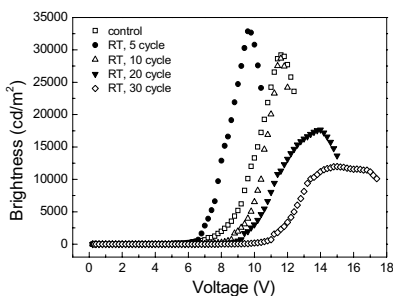
Figure 1. A schematic OLED structure having an HfO<sub>x</sub>-treated ITO.

The current density-voltage ( $J$ - $V$ ) characteristics were measured using a Keithley 2400 electrometer and the brightness was evaluated by measuring the photocurrent induced by the light emission from the OLEDs using a Keithley 485 picoammeter. In order to investigate the chemical bonding structure of the  $\text{HfO}_x$ -treated ITO surface, x-ray photoelectron spectroscopy (XPS) measurement was performed using a VG Microtech ESCA-2000 system having an  $\text{MaKa}$  source.

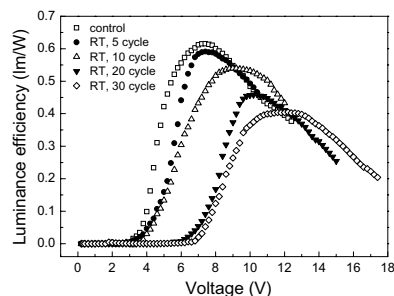
The current density and the brightness versus applied voltage with different treatment conditions on the ITO surfaces are shown in Fig. 2(a) and 2(b), respectively. Although the RT-5C sample shows a similar luminance efficiency compared to the control sample without any treatment, RT-5C sample exhibited a significantly improved OLED performance, i.e., the decrease of turn-on voltage, and the increase of brightness. Because the high current flow and the subsequent increase of brightness mainly originate from the increased holes injection efficiency from the ITO anode into the organic layer, it is believed that the RT-5C treatment by ALCVD process effectively improved the holes injection efficiency.<sup>7</sup>



(a)



(b)



(c)

**Figure 2. (a)  $J$ - $V$ , (b)  $B$ - $V$ , and (c) luminance efficiency characteristics without and with ALCVD- $\text{HfO}_x$  surface treatment.**

However, with the increase of number of ALD cycles, the turn-on voltage increased and the brightness decreased compared to the control sample, which is believed to be caused by the formation of a thick physical barrier layer and the subsequent retardation of holes injection. In order to investigate the chemical bonding status of the RT-5C, XPS measurement was performed on the ITO substrate after the  $\text{HfO}_x$  treatment, not shown here. The  $\text{Hf } 4d$  peaks exhibited two distinctive components, vis.  $\text{Hf } 4d_{3/2}$  and  $\text{Hf } 4d_{5/2}$ , with binding energies of 224 and 213 eV, respectively, which corresponds to  $\text{Hf-O}$  bonding formation.<sup>8</sup> According to the high resolution transmission electron microscopy (HRTEM) measurement, the  $\text{HfO}_x$  film thickness of the RT-5C sample deposited on Si substrate was approximately 0.5 nm, not shown here. Since the measured thickness of the  $\text{HfO}_x$  for RT-5C, it is quite possible that hole tunneling can easily happen without retarding the hole injection from the anode.

### 3. Conclusion

In summary, we investigated the electrical and the optical characteristics of OLED devices with  $\text{HfO}_x$ -treated ITO substrates using an ALD process. By treating the ITO substrate with  $\text{HfO}_x$  for 5 cycles at room temperature, the turn-on voltage was significantly decreased and the electroluminescent characteristics was improved up to  $7000 \text{ cd/m}^2$  due to the enhancement of hole injection efficiency compared to the OLED without any treatment. With the increase of

treatment cycle, the device characteristics were systematically degraded due to the growth of a physically insulating barrier layer, i.e.  $\text{HfO}_x$  film.

#### 4. Acknowledgements

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#### 5. References

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