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The effects of tetrafluoromethane (CF_4) plasma treatment of indium-tin-oxide (ITO) anode on indium diffusion into a poly(3,4-ethylene dioxythiophene):poly(styrene sulphonate) (PEDOT:PSS) layer were studied. Auger electron spectroscopy (AES) depth profile showed that 0.2 at. % indium was present in the PEDOT:PSS layer when ITO was not plasma treated. The plasma treatment of ITO increased the indium concentration to ~6 at. %. The increase in indium can be explained by an oxygen deficiency in the CF_4 plasma treated ITO. The presence of indium in the PEDOT:PSS layer showed a correlation with performance degradation of polymer light-emitting diodes. © 2008 American Institute of Physics. [DOI: 10.1063/1.2939261]

I. INTRODUCTION

Polymer light-emitting diodes (PLEDs) are considered promising candidates for full color, cheap, and flexible displays, which are easy to process.[1,2] A PLED consists of an emitting polymer layer that is sandwiched between an anode and a cathode. A great deal of effort has been made towards improving the performance of the PLEDs.

One approach is to modify the surface properties of indium tin oxide (ITO) with various techniques, such as plasma treatment,[3,4] ultraviolet-ozone cleaning,[5] mechanical polishing,[6] and coating treatment with a self-assembled monolayer.[7] Plasma treatment is regarded as the most promising technique, since it results in high work function as well as smooth surface. Another approach is to insert carrier injecting/transport material in between the electrode and emissive polymer layer, so that the carriers can be effectively transported to the emission zone.[8–10] Poly(3,4-ethylene dioxythiophene):poly(styrene sulphonate) (PEDOT:PSS) is one of the best known hole injecting material, mainly because of its excellent electrical conductivity and eletro-optic properties as well as processability. However, it has been shown that the interface between ITO and PEDOT:PSS is not stable, with indium contaminating the polymer.[11,12] Due to the strong acidic nature of PSS, a typical aqueous PEDOT:PSS solution has an acidity of $pH=1.2$, and In_2O_3 has a relatively high solubility in acid.[13] For PEDOT:PSS on ITO, it is reported that the acidic PEDOT:PSS solution can etch ITO during the polymer spin coating process. It is, therefore, important to investigate the ITO/PEDOT:PSS interface property in order to achieve a higher performance in PLEDs, especially when the ITO is plasma treated. However, among existing studies on ITO/PEDOT:PSS interfaces, only a few have considered the effects of plasma treatment on indium

diffusion. This report is on the effects and influence of plasma treatment on indium diffusion and the electrical properties of PLEDs.

II. EXPERIMENTAL

ITO coated glass was used as the substrate and it was approximately 200 nm thick with a sheet resistance of approximately 15 Ω/square. The ITO was first cleaned in trichloroethylene, acetone, and isopropyl alcohol in an ultrasonic bath, rinsed in de-ionized water, and finally dried in a high purity N_2 gas stream. The ITO substrate was then tetrafluoromethane (CF_4) plasma treated in a capacitance-coupled-plasma etcher for 5 min at rf power of 100 W. The electrodes were made of Cu and had dimensions of 5 $\times$ 10 cm^2. The upper electrode was grounded and the rf power was connected to the bottom electrode. The pressure of the chamber and the flow rate of the CF_4 were 150 mTorr and 15 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively.

PEDOT:PSS was spin coated approximately 50 nm thick as a hole transport layer. The residual solvent was removed by drying at 200 °C on a hot plate or suction under vacuum at room temperature. Directly afterwards, poly(9,9-dioctyl-fluorene) (PFO) was spin coated from its toluene solution at a concentration of 1 mg ml^{-1} onto the PEDOT:PSS films as a light-emitting layer. A bilayer cathode consisting of a LiF layer and an Al layer was deposited at 10^{-6} Torr by thermal evaporation. The device structure consists of ITO (200 nm)/PEDOT:PSS (50 nm)/PFO (80 nm)/LiF (3 nm)/Al (100 nm). The emitting area was defined to be 9 mm^2. The current-voltage (*I-V*) measurements were all carried out in air using a Keithley 2400 source meter, and the luminescence-voltage (*L-V*) characteristics were measured with a calibrated silicon photodiode using a Keithley 487. The dependence of the indium diffusion on the heat treat-

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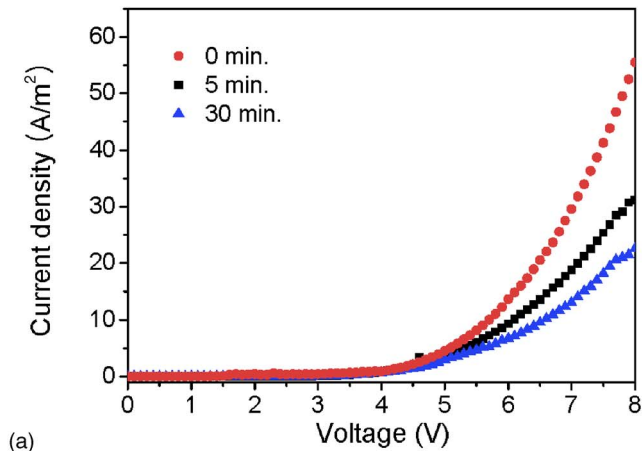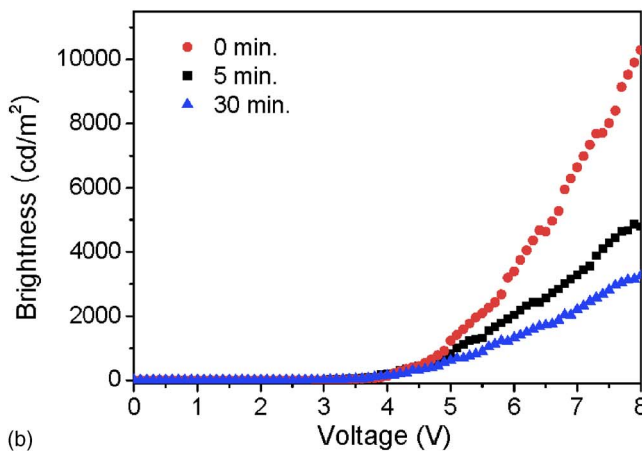
FIG. 1. (Color online) Effects of baking time of PEDOT:PSS on the performance of PLEDs when ITO was CF_4 plasma treated: (a) current density vs applied voltage and (b) EL intensity vs applied voltage.
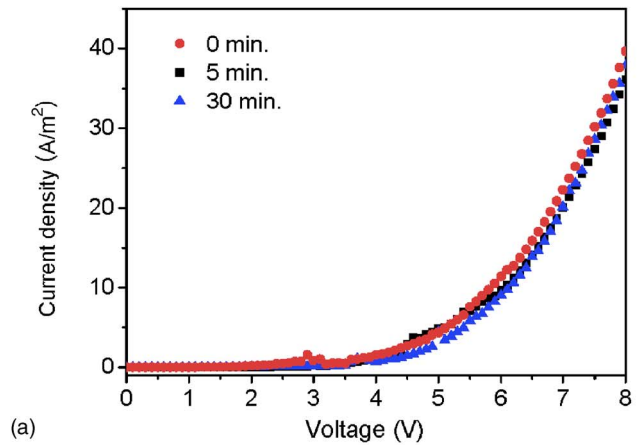

FIG. 2. (Color online) Effects of baking time of PEDOT:PSS on the performance of PLEDs when ITO was not CF_4 plasma treated: (a) current density vs applied voltage and (b) EL intensity vs applied voltage.
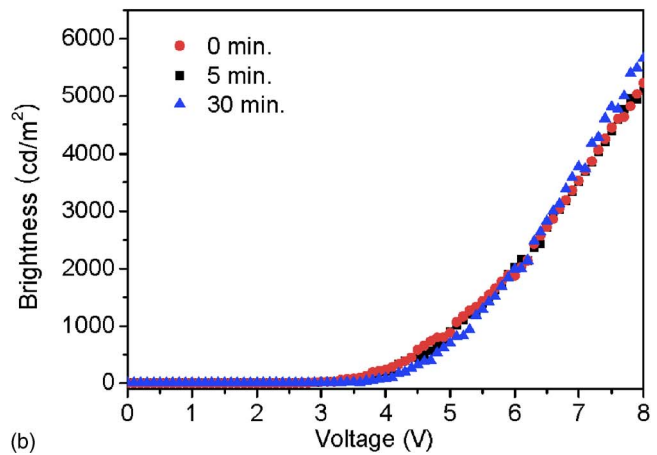
ment time was determined by the Auger electron spectroscopy (AES) depth profile. AES measurements were performed on a PHI 610 scanning Auger microprobe. The base pressure in the analysis chamber was 3×10^{-10} torr. A primary electron beam with energy of 10 keV and a current of 0.02 ΩA was incident on the sample surface.

III. RESULTS AND DISCUSSION

Figure 1 shows the *I-V-L* characteristics of PLEDs with various baking times of PEDOT:PSS when ITO was CF_4 plasma treated. The *I-V* performance of the device was found to be strongly dependent on the baking time of PEDOT:PSS. The device with vacuum dried PEDOT:PSS exhibited the maximum current density. With further increment in baking time, the current density was gradually decreased. The corresponding *L-V* measurement presented a similar behavior because luminance intensity was determined by current density. The device with vacuum dried PEDOT:PSS revealed the maximum brightness at the same driving voltage. Figure 2 shows the characteristics of *I-V-L* for PLEDs with various baking times of PEDOT:PSS when ITO was not CF_4 plasma treated. No obvious change in the performance was observed after the baking, which indicated that the PEDOT:PSS layer was not damaged in the baking process. In addition, these experimental results showed that the ITO anodes treated with

CF_4 plasma resulted in significant differences in the electrical characteristics, which became even worse as the baking time increased.

In typical PLED with ITO/PEDOT:PSS/PFO/LiF/Al structure, the barriers for the electron and hole injections are important because the barriers determine the *I-V* characteristic of the device.[14] In our previous work, the work function of CF_4 plasma treated ITO was increased from 4.81 to 5.35 eV. The increase in work function was due to the removal of carbon contaminants as well as adsorption of fluorine on the ITO surface by CF_4 plasma treatment.[15] This led to a decrease in the barrier height of the anode between ITO and PEDOT:PSS. As a result, the current and luminescence for the device fabricated on CF_4 plasma treated ITO were much higher than those of the untreated ITO. However, the performance of the device fabricated with CF_4 plasma treated ITO was worse than that of the untreated ITO as the baking time of PEDOT:PSS increased. The hole injection barrier is believed to be affected by the baking time of the PEDOT:PSS layer. AES measurements were performed to investigate the effects of the baking time. Figures 3 and 4 show the AES depth profile of ITO/PEDOT:PSS, and the inset indicates the indium concentration in the PEDOT:PSS layer. A depth profile was taken from the PEDOT:PSS toward the ITO. The change in the most abundant element
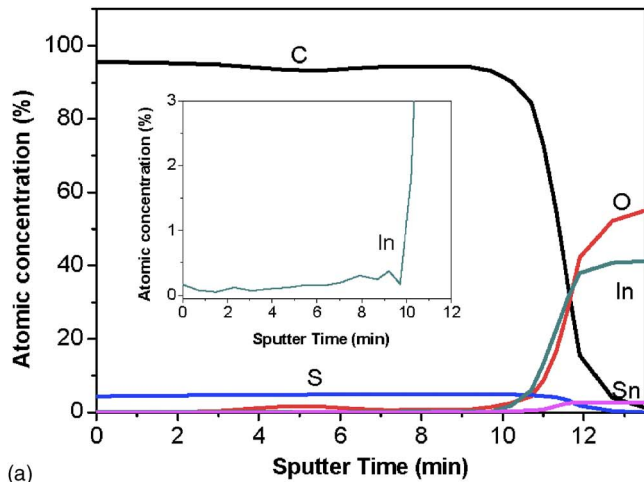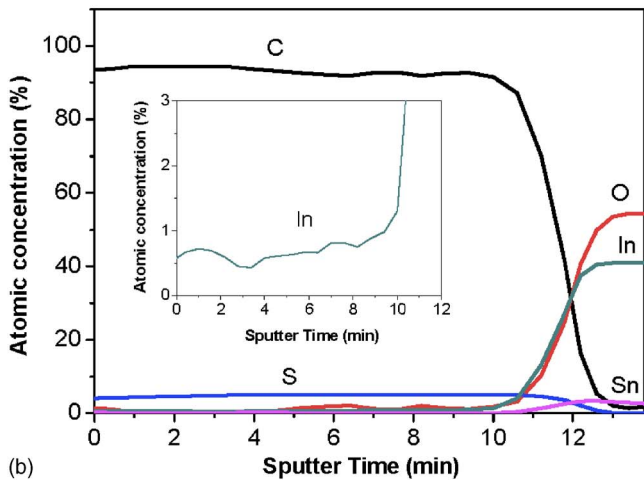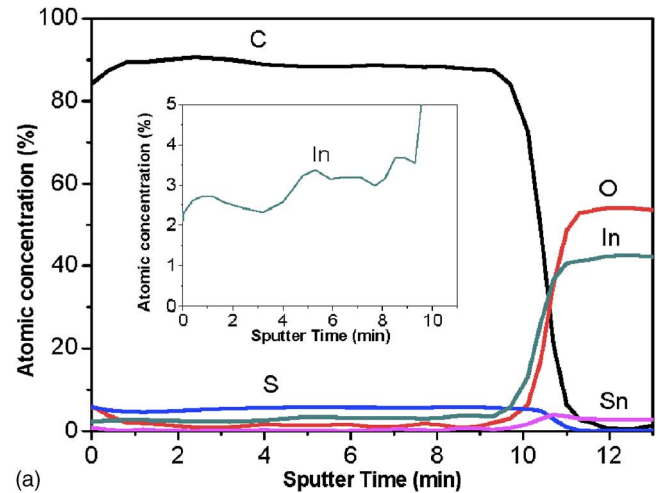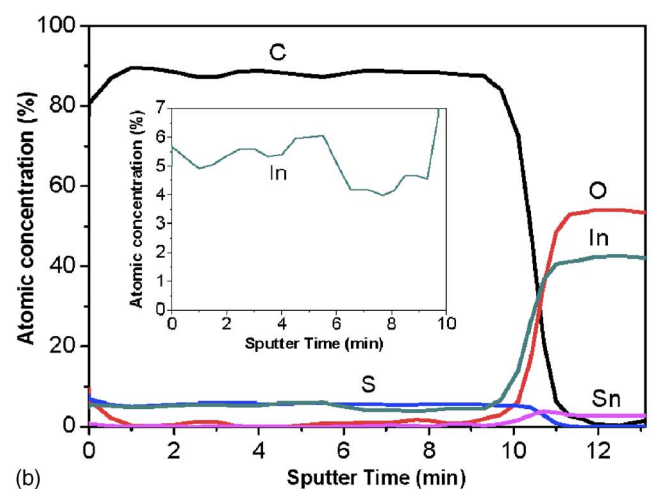
FIG. 3. (Color online) AES depth profile of ITO/PEDOT:PSS sample when ITO was not CF$_4$ plasma treated: (a) without baking and (b) 30 min baking.

FIG. 4. (Color online) AES depth profile of ITO/PEDOT:PSS sample when ITO was CF$_4$ plasma treated: (a) without baking and (b) 30 min baking.

from C to O determined the location of the PEDOT:PSS/ITO interface region. AES measurements showed that about 0.2 at. % indium was present in the PEDOT:PSS layer and that the concentration increased slightly as the baking time increased. A comparison between Figs. 3 and 4 shows that there was a considerable increase in the amount of indium in the PEDOT:PSS layer when ITO was CF$_4$ plasma treated. The CF$_4$ plasma treated sample gave an indium content of about 3 at. % and the indium content was raised to about 6 at. % by prolonged heat treatment. Prolonged heating induced a further intake of indium in the PEDOT:PSS layer, either due to a continued etching reaction or the diffusion of previously formed etch products from the ITO/PEDOT:PSS interface.[16,17] Indium diffusion may be related to the surface state of ITO. It is likely that indium diffusion under heat treatment is associated with indium migration of indium atoms from oxygen-deficient ITO. In our previous work, oxygen deficiency was observed in CF$_4$ plasma treated ITO.[18] Indeed, we found that CF$_4$ plasma treatment of ITO led to an increase in indium incorporation by a factor of 10.

The presence of indium in the PEDOT:PSS may change the electrical properties, especially the charge injection, of the PLED.[19] In order to understand the influence of the indium diffusion on device performance, hole-only devices

(ITO/PEDOT:PSS/PFO/Au) were made. Hole-only devices are particularly useful to study hole injection from various PEDOT:PSS layers. The barrier for hole injection is given by the difference between the PEDOT:PSS Fermi energy and the light-emitting polymer highest occupied molecular orbital level. *I-V* characteristics for the hole-only device are shown in Fig. 5. As the baking time increases, the IP of PEDOT:PSS decreases and the hole injection barrier increases. The hole-only current decreases markedly as the indium content in PEDOT:PSS increases. Since all the components of the hole-only device except PEDOT:PSS are the same, the lower current should be correlated with an increased barrier of the PEDOT:PSS. Thus, the hole-only device can prove the influence of indium diffusion on the device performance. This is in good agreement with the results shown in Fig. 1 for plasma treated PLEDs.

A possible cause for device degradation is considered to be the dedoping of PEDOT in PEDOT:PSS due to reaction of ITO with protons in PSS and those in doped PEDOT. Recently, Chang and Chen showed that protons in PEDOT:PSS can react with ITO in the presence of water to yield indium salt, leading to a change in its ionization potential, and that the indium ions can diffuse into the PEDOT:PSS layer.[20]
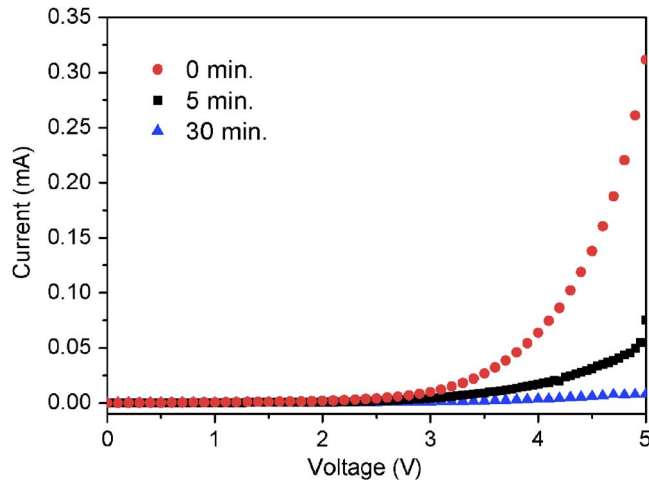
FIG. 5. (Color online) Current-voltage characteristics for hole-only devices (ITO/PEDOT:PSS/PFO/Au).

Thus, the indium content in PEDOT:PSS is related to the charge injection property and is a possible cause for device degradation.

IV. CONCLUSION

AES depth profile shows that the indium diffused almost throughout the entire PEDOT:PSS layer and that prolonged heating further induced the intake of indium in the PEDOT:PSS layer. We also found that the oxygen deficiency in CF_4 plasma treated ITO led to an increase in indium incorporation. It is shown that the charge injection property is affected by indium content in the PEDOT:PSS. The presence of indium in the PEDOT:PSS layer showed a correlation with performance degradation of PLEDs. Therefore, drying of the spin cast PEDOT:PSS by vacuum suction is a more desirable process when ITO is CF_4 plasma treated. Also, remote

plasma treatment and plasma polymerization of fluorocarbon are possible methods to improve work function properties without degrading the device.

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