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Electrical Properties of Organic Light-Emitting Diodes with an Insertion of CMTS Self-Assembled Monolayers

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Electrical properties of organic light-emitting diodes were studied in a device with an insertion of chloromethyl-trichlorosilane self-assembled monolayer (SAM) between the ITO anode and organic layer. Self-assembled monolayer is generally used for a surface reformation of ITO substrate to enhance the charge injection at the anode/organic interface. For a formation of SAM onto the ITO anode, the ITO substrate was immersed in a 20 mM solution of SAM material. SAM-treatment time on the ITO substrate was varied to be 0, 10, 15, 20, and 25 minutes. And then, the device was made in a structure of ITO(170 nm)/SAM/TPD(50 nm)/Alq_3(70 nm)/LiF(0.5 nm)/Al(100 nm). A device with properly treated self-assembled monolayer at the anode/organic interface gives an improvement in turn-on voltage, luminance, and efficiency compared to the one without SAM layer. A current efficiency and an external quantum efficiency of the device with 15 minutes treated SAM layer were increased by 2.6 times compared to the ones without the SAM layer. Fowler-Nordheim tunneling conduction mechanism was applied to the current density-voltage characteristics to obtain a hole injection barrier height. It was found that there is a reduction in barrier height by 25% for the device with 15 minutes SAM-treated compared to the one without SAM-treated.

Keywords Fowler-nordheim tunneling; ITO; organic light-emitting diodes; self-assembled monolayer

1. Introduction

Organic light-emitting diodes (OLEDs) are well developed for the industry of flat-panel displays, since Tang and Vanslyke reported a bilayer organic electroluminescent cell structure in 1987 [1–2]. However, there are still lots of studies going on to

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improve a performance of the device. It is still needed to optimize an operating voltage, device efficiency, compatibility with conventional integrated circuitry and device lifetime.

Transparent conductive oxide such as an indium-tin-oxide (ITO) is commonly used as an anode of photo-devices due to its high electrical conductivity and excellent transparency in the visible region [3]. And a performance of OLEDs is highly sensitive to the surface properties of the ITO substrate. Especially, a work function of the ITO is sensitive to a manufacturing process.

In general, the OLEDs have a device structure of "Metal/organic layer/Metal" [4]. At an interface between the anode and organic layer, hole carriers are injected into the organic layer from the anode [5]. However, the work function of ITO is not sufficiently large for the contact to be ohmic, so that there is an energy barrier that interferes hole injection from the ITO anode to the organic layer [6–8]. As a result, it gives a negative effect on the luminance, turn-on voltage, and the efficiency of the organic light-emitting diodes.

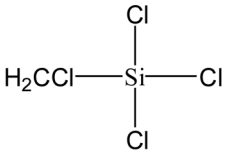
A reformation of the physical and the chemical properties of the ITO surface could change the work function of the electrode. Therefore, a reformation of the ITO surface is used to reduce the Schottky barrier at the ITO/organic interface, and to increase the adhesion of the organic semiconductor onto the electrode [7–8]. Zehner showed a change in work function of gold induced by chemisorbed self-assembled monolayers using arenethiols adsorbates [9–10]. Surface reformation of the ITO substrate can be done by treatment either by a wet or dry processing, including chemical processes (hydrogen passivation, hydrogen-bonded fluorinated monolayer, and self-assembled monolayer), and physical treatment (oxygen/argon plasma, E-beam, and UV ozone treatment) [11].

In this paper, we present electrical properties of organic light-emitting diodes due to a surface reformation of the ITO substrate in a device structure of ITO/TPD(50 nm)/Alq_3(70 nm)/LiF(0.5 nm)/Al(100 nm). And the ITO surface was reformed by wet processed chloromethyl-trichlorosilane (CMTS) self-assembled monolayer by varying a treatment time.

2. Experimental

The device was manufactured in a structure of ITO(170 nm)/TPD(50 nm)/Alq_3(70 nm)/LiF(0.5 nm)/Al(100 nm). The ITO substrate has a thickness of 170 nm and a surface resistance of 10 Ω/sq, which was purchased from Asahi Co. After patterning the ITO strip line with a 3 mm width from a $2 \times 2\,cm^2$ substrate, it was cleaned in chloroform ($CHCl_3$), ethyl alcohol (C_2H_5OH), and distilled water for 60 minutes each at 50°C in an ultrasonic bath. The cleaned ITO glass was dried with N_2 gas. The ITO glass dried with N_2 gas was dipped in a solution (hydrogen peroxide:ammonia:distilled water = 3:3:5) for 10 minutes to enhance the adhesion between the ITO glass and SAM material.

Figure 1 shows a molecular structure and chemical formula of the chloromethyl trichlorosilane SAM material. The formula weight is 183.92 and a boiling point is 117°C. The CMTS (95% purity) was purchased from Acros. The ITO substrate was immersed in a 20 mM SAM solution followed by thorough drying. The SAM solution was made using a methanol and chloroform with a weight ratio of 3:7. SAM-treatment time on the ITO substrate was varied to be 0, 10, 15, 20, and 25 minutes. After the SAM treatment, the substrate was dried by blowing nitrogen gas very



CH_2Cl_4Si (chloromethyl trichlorosilane)

Figure 1. Molecular structure and chemical formula of the chloromethyl trichlorosilane SAM material.

cautiously. N,N′-diphenyl-N,N′-di(m-tolyl)-benzidine (TPD) was used as a hole-transport layer and tri(8-hydroxyquinoline) aluminium (Alq_3) was employed as an electron-transport and emission layer. A lithium fluoride (LiF) serves as a buffer layer to enhance the electron injection. Both 50 nm thick TPD and 70 nm thick Alq_3 layer were deposited by thermal evaporation at a pressure of 10^{-6} torr. Deposition rates for organics were $1.0 \sim 1.5$ Å/s. The LiF was thermally evaporated at a deposition rate of 0.2 Å/s successively. A thickness of LiF layer was made to be 0.5 nm, and then a 100 nm thick Al layer was thermally evaporated for an electrode at a pressure of 10^{-6} torr.

Electrical properties of organic light-emitting diodes were measured using a Keithley 236 source-measure unit, Keithley 617 electrometer, and Si-photodiode at ambient conditions.

3. Results and Discussion

Figure 2 is a plot of (a) current density-voltage and (b) luminance-voltage characteristics of ITO/SAM/TPD/Alq_3/LiF/Al devices depending on a SAM treatment time on the ITO substrate. Here, the SAM treatment time means the time taken for the ITO substrate dipped in a 20 mM solution of chloromethyl trichlorosilane. As shown in the figure, SAM treatment on the ITO substrate lowers a turn-on voltage, and enhances a current density and a luminance of the device. Especially, for the

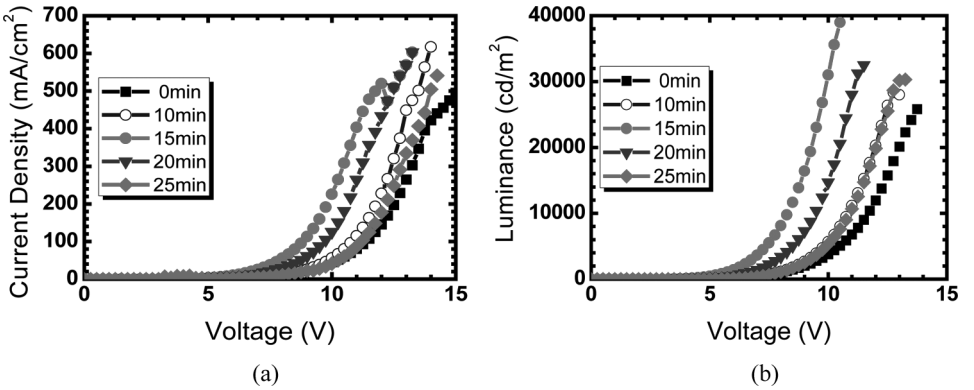


Figure 2. (a) Current density-voltage and (b) luminance-voltage characteristics of ITO/SAM/TPD/Alq_3/LiF/Al devices depending on a SAM treatment time on the ITO substrate. SAM treatment was processed for 0, 10, 15, 20, and 25 minutes.

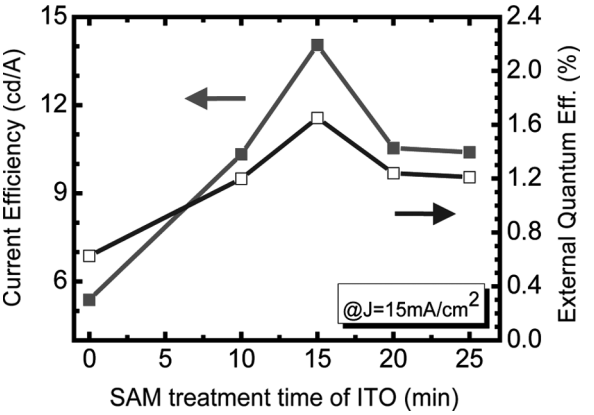


Figure 3. Current efficiency (■) and external quantum efficiency (□) of the device depending on SAM treatment time on the ITO substrate at the current density of 15 mA/cm^2. For the 15 minutes SAM-treated device, the efficiency reaches maximum.

15 minutes SAM-treated device, the turn-on voltage is lowered to about 4 V and the luminance is enhanced more than 40,000 cd/m^2 near 10 V. This enhanced performance of the device is thought to be due to a reduction of hole-injection barrier height at the anode interface by SAM layer. This reduction in energy barrier height was analyzed using a Fowler-Nordheim tunnel conduction mechanism. It will be explained later in Figure 4.

Figure 3 shows the efficiency of the devices as a function of SAM treatment time on the ITO substrate measured at the current density of 15 mA/cm^2. Solid square(■) and open square(□) in the figure represent the current efficiency and the external quantum efficiency of the device, respectively. As the SAM treatment time on the ITO substrate increases from 0 to 25 minutes, the efficiency of the device reaches maximum (14.4 cd/A, and 1.6%) at the 15 minutes SAM-treated device. The current efficiency and the external quantum efficiency of the device were increased

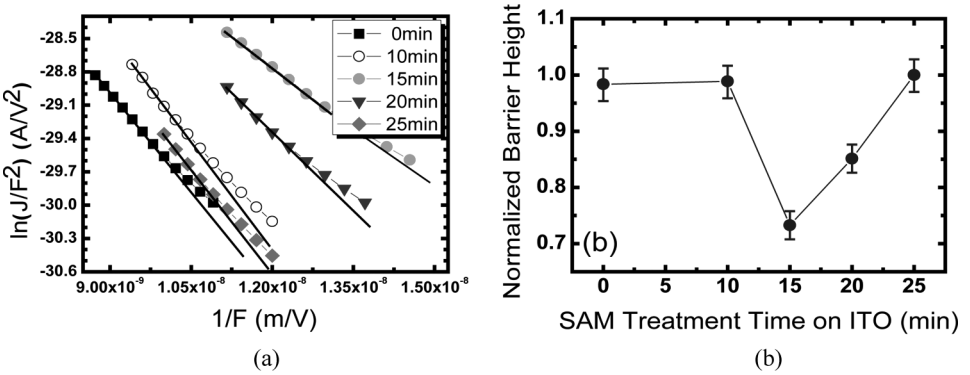


Figure 4. (a) Fowler-Nordheim plot of the current density-voltage characteristics. The injection barrier height can be obtained from the slope of this straight line. (b) Normalized barrier height as a function of SAM treatment time on the ITO substrate. It is normalized to that of the non SAM-treated device.

by 2.6 times for the 15 minutes SAM-treated device compared to the ones without SAM layer. Thus, it was found that a properly treated self-assembled monolayer at the anode/organic interface gives an improvement in turn-on voltage, luminance, and efficiency of the device compared to the ones without SAM layer.

To see how the SAM layer affects on the efficiency of the device, we tried to obtain a hole injection energy barrier height by employing a Fowler-Nordheim tunneling model to the current density–voltage characteristics. Fowler-Nordheim tunneling conduction mechanism strongly depends on the electric field and temperature independent. An electrical current density in this model is given by

$$J = AF^2 \exp\left(-\frac{B}{F}\right) \tag{1}$$

Here, J is a tunneling current density, F is an electric field, and B is a parameter depending on a shape of barrier. If injected charges tunnel though a triangular shaped barrier, the parameter B is given by the following.

$$B = \frac{8\pi(2m^*)^{1/2}\phi^{3/2}}{3qh} \tag{2}$$

Here, ϕ is an energy barrier height, q is a charge, h is a Planck constant, and m^* is an effective mass of charge carrier.

Figure 4(a) shows a Fowler-Nordheim plot of $\ln(J/F^2)$ as a function of $1/F$. From the linear relationship in high electric-field region, a hole injection barrier height can be obtained for each SAM-treated device. Normalized barrier height was plotted in Figure 4(b) as a function of SAM treatment time on the ITO substrate. Barrier height was normalized to that of the non SAM-treated device. It shows that the barrier height of the device for 15 minutes SAM-treated device is reduced by 25% compared to that of the non SAM-treated one. This result is consistent to the improvement of the device performance, which was explained in Figure 2.

4. Conclusion

Electrical properties of organic light-emitting diodes were studied due to a surface reformation of ITO substrate by treating the substrate with self-assembled monolayer. The device was made in a structure of ITO/SAM/TPD/Alq_3/LiF/Al. Self-assembled monolayer introduced at the anode/organic interface gives an improvement in turn-on voltage, luminance, and efficiency compared to the ones without SAM layer. For the 15 minutes SAM-treated device, the current efficiency and the external quantum efficiency were increased by 2.6 times compared to the ones without SAM layer. This improvement of the device performance is thought to be due to a reduction in hole injection energy barrier. An analysis of current density-voltage characteristics by employing a Fowler-Nordheim tunneling conduction mechanism shows that there is a reduction in barrier height by 25% for the device with 15 minutes SAM-treated compared to the one without SAM-treated. We are going to study further to improve the device performance by employing a proper choice of SAM materials.

Acknowledgment

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