Improved performance of organic light-emitting devices with plasma treated ITO surface and plasma polymerized methyl methacrylate buffer layer

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Abstract

Transparent indium-tin-oxide (ITO) anode surface was modified using O₃ plasma and organic ultra-thin buffer layers were deposited on the ITO surface using 13.56 MHz rf plasma polymerization technique. A plasma polymerized methyl methacrylate (ppMMA) ultra-thin buffer layer was deposited between the ITO anode and hole transporting layer (HTL). The plasma polymerization of the buffer layer was carried out at a homemade capacitively coupled plasma (CCP) equipment. N,N′-Diphenyl-N,N′-bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine (TPD) as HTL, Tris(8-hydroxy-quinolinato)aluminum (Alq₃) as both emitting layer (EML)/electron transporting layer (ETL), and aluminum layer as cathode were deposited using thermal evaporation technique. Electroluminescence (EL) efficiency, operating voltage and stability of the organic light-emitting devices (OLEDs) were investigated in order to study the effect of the plasma surface treatment of the ITO anode and role of plasma polymerized methyl methacrylate as an organic ultra-thin buffer layer.

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1. Introduction

In organic light-emitting devices (OLEDs) [1], indium-tin-oxide (ITO) is used as an anode or a hole injecting electrode because its high work function reduces the energy barrier for hole injection between anode and hole transporting layer (HTL), so that the operating voltage of OLEDs decreases. Injection may proceed by thermionic emission over a barrier, or by tunneling though a barrier, or a combination of both processes [2]. The work function of ITO was sensitive to the cleaning technique and there have been several studies to clarify its role [3,4]. Conventionally, the ITO surface has been treated by plasma in O₂ atmosphere, so that the surface organic contaminants would be removed and the surface would be then oxidized, which resulted in an enhanced hole injection due to elevated work function level. In this study, we took notice of the report that more oxygen content was observed in an O₃ plasma [5], then treated the ITO surface rather with that than with an O₂ plasma.

One of the main problem the current OLEDs are their relatively poor stability, namely, the half-lifetime, defined as the time elapsed before the luminance of the OLED is limited to only few thousand hours. It is widely recognized that unbalanced charge carriers due to higher hole mobility in the hole transporting layer and slower electron mobility in the electron transporting layer (ETL) leads to reduced efficiency of OLEDs. It is thus important to balance the injected charges to improve device performance. Recently, some organic materials and inorganic insulating materials have been adopted as hole-injection buffer layers inserted between the ITO anode and the organic layer, such as copper phthalocyanine (CuPc), polyaniline, SiO₂, Al₂O₃, and so on [6–10].

In this study, transparent ITO anode surface was modified using O₃ plasma and organic ultra-thin buffer layers were deposited on the ITO surface using plasma polymerization technique. We investigated the effect of the rf plasma surface treatment and role of plasma polymerized buffer layer on the high efficiency, low operating voltage, and stability of OLEDs. Plasma polymerized methyl methacrylate (ppMMA) was deposited on the ITO anode as ultra-thin buffer layer between anode and hole transporting layer. The plasma polymerization
of the organic buffer layers was carried out using a homemade capacitive-coupled rf plasma equipment. \( \text{N,N'-Diphenyl}-\text{N,N'-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine (TPD)} \) as hole transporting layer, \( \text{Tris(8-hydroxyquinolinato)aluminum (Alq}_3\text{)} \) as both emitting layer (EML)/electron transporting layer, and aluminum layer as cathode were deposited using thermal evaporation technique. Effects of the plasma surface treatment of ITO and plasma polymerized ultra-thin buffer layer on the OLED performance were discussed.

2. Experimental

The substrates used in this study were ITO-coated glasses with the ITO film thickness of 200 nm and a sheet resistance of 12 kΩ. The as-received substrates were chemically cleaned by using acetone, ethanol, and DI-water with ultrasonic wave, which removed most of the ITO surface organic contaminants. After N\(_2\) gas blow-drying, the cleaned ITO substrate was moved into a vacuum. A homemade plasma polymerization equipment was used for the plasma surface treatment. A schematic diagram of the plasma polymerization apparatus used in this experiment is shown in Fig. 1.

13.56 MHz rf plasma generator (AUTO ELEC. ST-500 m 600 W) was used for creating plasma and matching box (Load coupler LC-1000) was installed for impedance matching. Also, rf power meter (Collins 30K-3) was connected to measure electric discharge power. A vacuum gauge (PG-1S 23593 Okano, 10 to 10\(^{-3}\) Torr) was used to detect the vacuum. Also, cold trap with liquid nitrogen was installed to protect the rotary pump from the attack of methyl methacrylate (MMA) monomer.

The ITO was treated for various period of time in an O\(_3\) plasma before depositions of buffer layer. An inductively coupled plasma (ICP) was used in the plasma polymerization apparatus for the surface treatment of the ITO. O\(_3\) plasma treatment was carried out at the pressure of 0.1 Torr, Ar flow rate of 10 sccm, and the rf power of 50 W, respectively. Without a vacuum break directly after the plasma surface treatment of ITO anode, the ultra-thin organic insulating layer was formed by plasma polymerization technique. Plasma polymerized methyl methacrylate (ppMMA) was deposited under the following experimental condition: 100 W power, 0.1 Torr system pressure, and a deposition time of 30 s with a MMA monomer vapor supply. The film thicknesses with these conditions were approximately 2.0 nm. While Ar gas was introduced into the reaction tube (3 sccm) to generate the capacitively coupled plasma (CCP), the MMA monomer was then introduced in the Ar plasma and the ppMMA buffer layer was deposited [11]. The OLEDs fabricated in this report had structures of ITO/PPMMA/TPD/Alq\(_3\)/Al and ITO/TPD/Alq\(_3\)/Al. Fig. 2 shows a schematic diagram of the OLEDs.

Surface morphology/roughness, chemical composition, surface energy, and electrical properties of the plasma treated ITO anode and ultra-thin buffer layer were investigated using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle measurement system, and four-point probe, respectively. For the purpose of investigating performance of the OLEDs, current and luminance change according to applied voltage change were measured by a source measurement unit (SMU; Keithley2400) and luminance meter (Topcon, BM-8). Using a personal computer as a measurement process control system, the SMU controlled the supply of voltage through serial interface (RS-232C) and measured the current. At the same time, the luminance meter measured the luminance through serial interface (RS-232C). In addition, time–voltage–luminance (T–V–L) characteristics were investi-
gated at constant current source and voltage reading mode. For the current–voltage–luminance (I–V–L) measurement, time delay for each measurement was 0.5 s, and sampling width was 0.1 V. In the T–V–L measurement for investigating lifetime, constant current of 1 mA was applied.

3. Results and discussion

Since the hole transporting layer of the device is directly deposited on the ITO anode, the surface properties of the ITO would affect the characteristics of the OLED.

Fig. 3 shows XPS spectra of the not-treated and O3 plasma treated ITO surface. The photoelectron peaks at about 531.0, 493.0, 485.0, 452.0, and 444.0 eV correspond to O 1s, Sn 3d3/2, Sn 3d5/2, In 3d3/2, and In 3d5/2, respectively. The peak at about 284.6 eV corresponds to C 1s, suggesting that carbon is the only major contaminant. Fig. 3 presents that O 1s peak increases (a), C 1s peak decrease (b), and Sn 3d3/2, Sn 3d5/2, In 3d3/2, and In 3d5/2 peak have slight change after the O3 plasma treatment. The XPS analysis results of these spectra are presented in Table 1. The concentrations of [O]/[In] ratio and [C]/[In] ratio in ITO surface change from 1.52, 0.88 to 1.77, 0.28, respectively, after the O3 plasma treatment. Due to the O3 plasma treatment, the oxygen concentration increased, and surface contaminating carbon concentration decreased. It is reported that the plasma treatment caused the change of surface work function of ITO [12], which would result in the hole-injection change.

Table 1 presents the surface resistivity and chemical composition of ITO films after the O3 plasma treatment. The sheet resistances of different samples were measured using a

<table>
<thead>
<tr>
<th>ITO anode surface</th>
<th>Sheet resistance (Ω/□)</th>
<th>Chemical composition (at.%)</th>
<th>O/In</th>
<th>C/In</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>O</td>
<td>In</td>
</tr>
<tr>
<td>Not-treated ITO</td>
<td>12.11</td>
<td>24.8</td>
<td>43.0</td>
<td>28.2</td>
</tr>
<tr>
<td>O3 plasma treated ITO</td>
<td>11.55</td>
<td>8.8</td>
<td>55.1</td>
<td>31.1</td>
</tr>
</tbody>
</table>
four-point probe method for O3 plasma treated ITO films. After the plasma treatment, the film surface resistivity decreases. It can be proposed that the smaller the sheet resistance of ITO is, the smaller is the turn-on voltage of the sample. In addition, the ppMMA thin film was found to be an insulating film after the sheet resistance measurement using four-point probe method.

Fig. 4 shows the AFM images of O3 plasma treated ITO surface and ppMMA buffer layer. The plasma treated ITO surface shows a relatively flat surface with a root mean square (RMS) surface roughness of about 2.1 nm compared to the bare ITO with an RMS of 2.8 nm. Besides, the surface roughness decreases from about 2.1 to 1.6 nm for the deposited ppMMA layer on the ITO. It is shown that RMS surface roughness of the ITO tends to decrease after the O3 plasma treatment with a limited treatment time. In addition, the enhancement is attributed to the ppMMA layer giving a conformal coverage of the ITO spikes and pinhole, has a smooth morphology interface with good contact for the HTL deposition, resulting hole-injection current is increased. It can be implied from this experiment that both O3 plasma treatment and ppMMA buffer layer would cause an improvement of ITO surface condition in a good way.

This smooth morphology of deposited ppMMA on ITO surface in contact with HTL layer would provide better organic–organic adhesion compared with the inorganic–organic contact at the plasma treated ITO/HTL interface. The hole-injection efficiency related to molecular contact at the interface and interfacial adhesion between organic layer and anode plays an important role in improving the OLEDs performance, thus it is specially needed to investigate the interfacial adhesion. Contact angle measurement is probably the most common method that gives information on the surface energy of outmost surface layer. Fig. 5 shows how the ITO surface treatment and inserted ppMMA buffer layer affect the contact angle and surface energy. The surface energy was calculated from the contact angle. The contact angle (surface energy) decreases (increases) for the samples with the plasma treated ITO and ppMMA layer. The increase of surface energy implies that the good adhesion between organic layer and anode, which could be related to an improvement of OLED performance.

In the luminance–voltage (L–V) and luminance–current density (L–J) measurements for the OLED samples with the ITO treated in O3 plasma for various period of treatment time, the sample with ITO treated for 3 min showed the best performance. Figs. 6 and 7 show L–V and L–J characteristics of
the fabricated OLEDs with the structure of ITO/ppMMA/TPD/Alq3/Al and ITO/TPD/Alq3/Al, where the ITO is either not-treated, or O3 plasma treated for 3 min. The best L–V and L–J characteristic for the device with the plasma treated ITO surface is presented together to compare. Among the OLED samples, the effect is most remarkable, when ppMMA buffer layer is inserted in the OLED structure. The ppMMA buffer layer deposited on ITO substrate causes the hole-injection efficiency increased due to the roughness of surface is improved. As regards characteristics of the device, the increase of hole-injection efficiency will reduce the operation voltage. An improved balance of hole and electron injections is a consequence one may expect from the inclusion of the ultra-thin ppMMA buffer. It is shown that the luminance of device is higher under the same voltage by inserting the ppMMA buffer layer. In addition, the OLED sample with the ppMMA buffer layer reveals an impressive brightness of more than 6800 cd/m², in contrast to the value of only 5600 cd/m² for the OLED sample without ppMMA. It is considered that the holes seem to move through the ppMMA layer by the tunneling effect [9]. In this work, ppMMA was prepared as an ultra-thin buffer layer, and the effect of ppMMA on the device efficiency have been investigated.

Fig. 8 shows initial stability curves of the devices with/without ppMMA layer. In order to accelerate the stability-degradation, the measurements were performed in atmosphere for the OLEDs without encapsulation. Luminance change with time was monitored at constant current of 1 mA, which gives information of the device operation stability. It is believed that stability of device with inserted ppMMA layer was improved due to retarded In, Sn, and Oxygen migration/diffusion from ITO anode and reduced pinhole on the ITO surface. It can be seen that the OLED with the ppMMA buffer layer reveals more stable characteristics than that of the OLED without ppMMA.

4. Summary and conclusion

Efficient OLEDs were fabricated with different device structures of O3 plasma treated ITO/ppMMA/TPD/Alq3/Al and ITO/TPD/Alq3/Al. Improvement of the device performance could be realized either by a rf plasma surface treatment of the ITO anode or by an ultra-thin layer of ppMMA inserted between ITO anode and TPD. After O3 plasma treatment, ITO surface was oxidized, and surface contaminating carbon concentration decreased. The plasma treatment consistently caused decrease of the roughness at the ITO surface and sheet resistance. In addition, contact angle at the ITO substrate decreased and surface energy increased. Increase of surface activation energy would cause modification of adhesion characteristics between ITO and other thin films. The increase of surface energy implies that the good adhesion between organic layer and anode, which could be related to an enhancement of OLED performance. The best conditions for O3 plasma surface treatment was 50 W, 10 sccm, 0.1 Torr, and treating time was 3 min, which was confirmed by enhanced luminance and decreased turn-on voltage. The OLED with the ppMMA buffer layer showed decreased turn-on voltage and the highest luminance of 6800 cd/m². It is suggested that enhanced hole injections was resulted from increase of work function of the ITO which reduces energy barrier for the hole injection into the other thin films, and that stability of device with inserted ppMMA layer were improved due to retarded In, Sn, and Oxygen migration/diffusion from ITO anode. Consequently, the stability of the OLED with ppMMA buffer layer was improved.

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References