Appl. Phys. A 68, 447–450 (1999) / DOI 10.1007/s003399900968

Applied Physics A
Materials
Science & Processing

Surface preparation and characterization of indium tin oxide substrates for organic electroluminescent devices

S.K. So[1,*], W.K. Choi[1], C.H. Cheng[1], L.M. Leung[2], C.F. Kwong[2]

[1] Department of Physics and Center for Surface Analysis, Hong Kong Baptist University, Kowloon Tong, Hong Kong
[2] Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong

Received: 10 March 1998/Accepted: 21 September 1998/Published online: 24 February 1999

Abstract. The cleanliness of indium tin oxide (ITO) substrates used in organic light-emitting diodes (OLEDs) is investigated by contact angle measurement and by X-ray photoemission spectroscopy (XPS). It was found that ultraviolet (UV) ozone treatment is quite effective in removing organic contamination on the ITO surface. The degree of surface contamination was checked by changes in contact angles and by XPS. Strong correlation can be established between these two techniques. OLEDs fabricated from UV-irradiated ITO substrates exhibit low turn-on voltage and superior brightness.

There are now widespread interests in using organic or polymeric fluorescent thin films for fabricating electroluminescent (EL) devices [1, 2]. The basic structure of an organic EL device consists of one or more layers of organic fluorescent materials sandwiched between an anode and a metal cathode. In most cases, a thin film of indium tin oxide (ITO), with a thickness in the order of 0.1 μm, is used as the anode material. The ITO layer can be prepared by standard sputtering techniques onto a glass plate or a plastic substrate. Since ITO is a transparent conductor, it also functions as the viewing side for the EL device. Although there are now numerous reports on EL devices fabricated by many different materials, few reports have been devoted to the preparation of ITO for EL devices. Since organic EL devices are thin film devices, a small amount of contamination on the surface of the anode can severely alter the work function, or the interfacial barrier height between the organic layer and the anode. Unless the anode is thoroughly cleaned, the electrical and optical characteristics can be highly unstable and unpredictable. It is, therefore, of utmost importance that the ITO substrate is carefully cleaned before deposition of the organic layers.

A variety of methods [3–8] have been developed in the preparation of ITO surfaces for organic light-emitting diodes (OLEDs). A summary of these methods is shown in Table 1.

* To whom correspondence should be addressed. E-mail: skso@hkbu.edu.hk

Table 1. Common cleaning procedure for ITO used in thin film organic electroluminescent devices

ITO sheet resistance/ Ω/□	Cleaning procedure	OLED structures	Reference
15	Sequentially boiling in 1,1,1-trichloroethane, acetone, methanol; drying in N_2 gas, between each step	ITO / TPD / Alq_3 / Mg:Ag	[3]
less than 30	Sonication sequentially in acetone and isopropyl alcohol, drying in N_2 gas and further drying by heating at 100 °C	ITO / MEH-PPV[a] / Al	[4]
about 100	Sonication in detergent, rinsing in deionized water and isopropanol, degreasing in toluene vapor and irradiation in a UV-ozone chamber	ITO / CuPc[b] / NPB[c] / Alq_3 / LiF / Al or Mg:Ag	[5]
20	Sonication in a surfactant, rinsing in distilled water, dipping in isopropanol, sonication in acetone, rinsing in isopropanol bath, and drying in N_2 gas	ITO / TPD / Alq_3 / Al_2O_3 / Al	[6]
20	Scrubbing, sonication and vapor degreasing	ITO / PVK[d] / Pu complex[e] / Al	[7]
10–20	Sonication in detergent, acetone, isopropyl alcohol baths, 10-min exposure to ozone in a glass chamber	ITO / PVK / Bu-PBD[f] / Mg:Ag	[8]

[a] PPV = poly(phenylene vinylene)
[b] CuPc = copper phthalocyanine
[c] NPB = naphthyl-substituted benzidene derivative
[d] PVK = poly(N-vinylcarbazole)
[e] Pu complex = polyurethane metal complex
[f] Bu-PBD = 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole

Irrespective of the complexities of these methods, which involve ultrasonic cleaning of the ITO surface in aqueous and organic solutions, the final step often invokes an exposure of the precleaned ITO to either ultraviolet (UV) irradiation or oxygen plasma treatment. The basic idea behind the last step is simple. UV irradiation (180–260 nm) photolyses molecular oxygen in air leading to formation of ozone. Since ozone is a very effective oxidizing agent, it reacts rapidly with residual organic molecules on the ITO surface. The oxidized products are volatile. Thus, a clean surface can be produced. A similar argument can be applied to oxygen plasma treatment of ITO.

In this study, we report a simple, low-cost, and yet efficient method of assessing the cleanliness of ITO surfaces based on the technique of contact angle measurement. Such a method has been used to examine surface contamination on inorganic surfaces before encapsulation in plastic packages [9]. The effectiveness of the contact angle assessment can be demonstrated by complementary X-ray photoemission spectroscopy (XPS). The electrical and optical characteristics of OLEDs fabricated from ITO substrates under different preparation conditions are examined.

1 Experimental

The ITO thin films under assessment were grown on soda glass. They have thicknesses of 250 and 1250 Å, and sheet resistances of 80 and 12 Ω/□, respectively. For the preparation of OLEDs, the ITO glasses were cut into square plates (25 mm × 25 mm). These plates were first cleaned by scrubbing in detergent and then in distilled water. Then, they were immersed sequentially in ultrasonic baths of ethanol and acetone, each for about 15 minutes. The ITO plates were then blown dry in a clean hood equipped with a class 10 000 filter. Finally, each ITO plate was exposed to a 30-W deuterium lamp (Oriel Model 63613) in an enclosed housing for UV irradiation. The deuterium lamp has a continuous emission spectrum starting at about 300 nm and with increasing intensities up to 190 nm. Based on the measured spectrum of the lamp, each ITO plate is estimated to have been exposed to about 9 mW/cm^2 of UV in the same range. Following the cleaning procedure, each sample was subjected to three tests for the inspection of its surface cleanliness. The first is the contact angle measurement technique. The contact angle is the angle formed between a liquid droplet and a flat surface when the liquid droplet is at rest and in thermal equilibrium with the surface (Fig. 1, inset). All contact angle measurements were performed at 18 °C under 60% relative humidity. A pipette was used to deliver a constant volume of about 0.045 cm^3 of pre-filtered distilled water on the ITO surface. A traveling microscope with a miniature protractor eyepiece was used to determine the contact angle. Under the same surface treatment, the contact angle was found to be insensitive to the exact volume of the water droplet. The second test on the ITO surface was by means of X-ray photoemission spectroscopy (XPS). XPS spectra were taken inside a Leybold–Shenyang system using Mg K_α radiation as the X-ray source. After UV exposure, ITO substrates were immediately transferred to vacuum for XPS analysis. The carbon, oxygen, indium, and tin intensities in the XPS spectra were monitored. The last test involves a systematic study of the effects of contamination on the organic EL devices. ITO substrates, with selected UV exposure time, were used as the anodes for bilayer organic LEDs using N,N′-diphenyl-N,N′-bis(3-Methylphenyl)(1,1′-biphenyl)-4,4′-diamine (TPD) and tris(8-hydroxyquinlonine) aluminum (Alq_3) as the hole transporter and the light emitter, respectively. The basic structure of the device was reported elsewhere [10]. An evaporated silver electrode is used as the cathode. Each OLED has an emission area of about 3 mm^2. The current and light intensity of the organic LEDs were measured against the driving voltage.

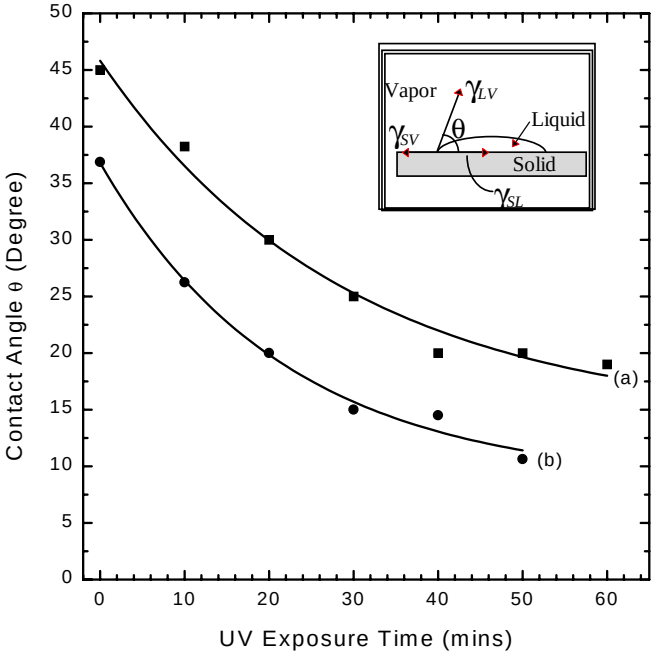

Fig. 1. Contact angles between water droplets and ITO substrates with sheet resistances of (a) 80 Ω/□, and (b) 12 Ω/□ under different UV exposure times

2 Results and discussion

The contact angle (θ) between a flat surface and a liquid droplet is given by the Young equation as follows:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \,,$$

where γ_{SV}, γ_{SL}, and γ_{LV} denote the surface tensions between the various interfaces (S = solid, L = liquid, V = vapor). On the ITO substrates for OLED fabrication, residual organics from the cleaning procedure are suspected to be the major source of contamination. If the ITO surface is contaminated, γ_{SV} is substantially reduced since organics are known to have low surface tensions. The contact angle should decrease as the quantity of organic residues decreases. Hence, contact angle measurement can provide an effective means of evaluating the cleanliness of a surface. The change of contact angle versus UV irradiation time is shown in Fig. 1 for two sets of ITO substrates with sheet resistances of 12 and 80 Ω/□ (curves (a) and (b), respectively). Each data point in Fig. 1 is the average of four independent measurements on the same ITO substrate. In Fig. 1a, the initial contact angle starts at about 45°, decreases monotonically as the UV exposure time increases, and levels off to about 20° after about 40 minutes

of UV irradiation. Similar results can be observed in Fig. 1b. In both cases, the decrease in contact angle suggests that residual organic contamination on the ITO substrate has been significantly reduced after the UV ozone treatment.

Surface contamination can be detected directly by complementary XPS experiments. In general, reduced carbon contamination and enhanced substrate signals were observed after UV irradiation. Figure 2 shows the XPS spectra of a batch of ITO substrates subject to different durations of UV exposure. The corresponding composition of each element (in percent) is also shown. Without UV exposure, a relatively large carbon peak is present, and peaks relating to the substrates: In3$d_{5/2}$ at 445 eV, Sn3$d_{5/2}$ at 482 eV, and O1s at 532 eV can be observed (spectra (a)). The $C1s$ peak becomes smaller while the substrate peaks gradually grow in intensity as the UV exposure increases. From spectra (c), the stoichiometric ratios of In:Sn:O (after UV exposures times of 20 minutes) are determined to be $2-x{:}x{:}3$ where $x = 0.24$. Further exposure to UV does not substantially alter the XPS spectra. It was found that the ultimate ratios of In:Sn:O remain relatively constant for different samples with the same resistivity. However, some residual carbon contamination remains despite long UV exposure. The residual carbon contamination (around 20%–30%) may originate from a brief exposure to air when the sample was transferred from air to vacuum, or from small amount of contamination in the preparation chamber of the XPS system. From the XPS analysis above, the decrease in contact angle after UV exposure is clearly related to the reduction in carbon contamination. It is also possible that some organic contamination may become more hydrophilic after UV exposure. Whereas XPS provides quantitative chemical information on the surface, the contact angle method provides a very simple, yet efficient technique for checking the cleanliness of an ITO substrate for OLED fabrication.

The effects of the UV ozone treatment on the ITO substrates and the subsequent influence on the performances of the OLEDs can be clearly seen in Figs. 3–5. Figure 3 shows a series of current–voltage (I–V) characteristic curves for a set of bilayer OLEDs fabricated from TPD and Alq_3. The inset indicates the structure of a typical device where the thicknesses of the TPD and Alq_3 layers are 150 and 380 Å, respectively. All OLEDs were prepared by the same procedure with the exception of the durations of UV ozone treatment on the ITO substrates prior to organic evaporation. With increasing UV irradiation times, the I–V curves tend to shift to the left with lower turn-on voltages. For UV exposures of 10 min or less, the turn-on voltage is between 16–20 V. The turn-on voltage decreases rapidly to about 10 V for longer UV exposure, and reaches an ultimate value of about 8 V after long time. The corresponding light intensity versus current (L–I) characteristics are shown in Fig. 4. As usual, linear dependences can be observed in such plots. The slope of a L–I curve in Fig. 4 is a measure of the relative external quantum efficiency of the OLEDs. It is clear that UV treatment enhances the quantum efficiency of the OLEDs. The dependence of the relative quantum efficiency versus irradiation time is shown in Fig. 5. The quantum efficiency is enhanced by 10 times after 40 min of UV ozone treatment on the ITO substrates.

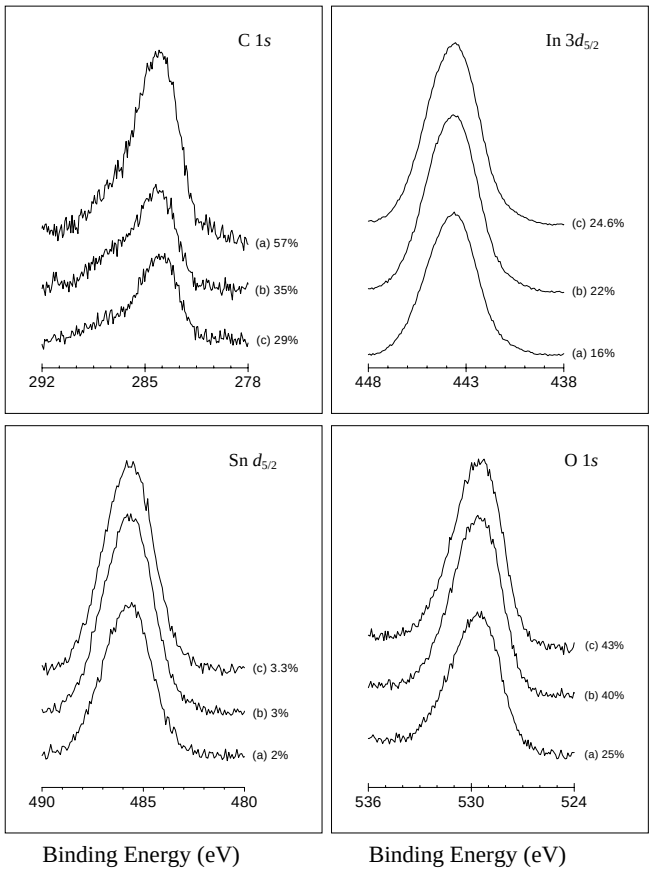

Fig. 2. XPS spectra of ITO substrates (80 Ω/□) after subjecting to UV exposure times of (a) 0, (b) 10, and (c) 20 min, respectively. The surface composition of each element is also shown. The spectra have been offset for clarity

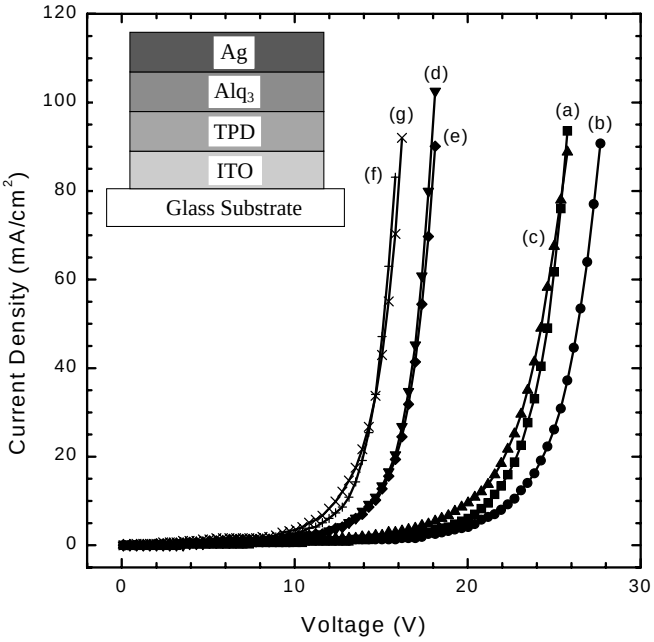

Fig. 3. Current–voltage plots of Alq_3-based OLEDs. The ITO substrates (80 Ω/□) used in these OLEDs were exposed to UV irradiation for: (a) 0, (b) 5, (c) 8, (d) 10, (e) 20, (f) 30, (g) 40 min prior to organic evaporation. The inset indicates the structure of an OLED

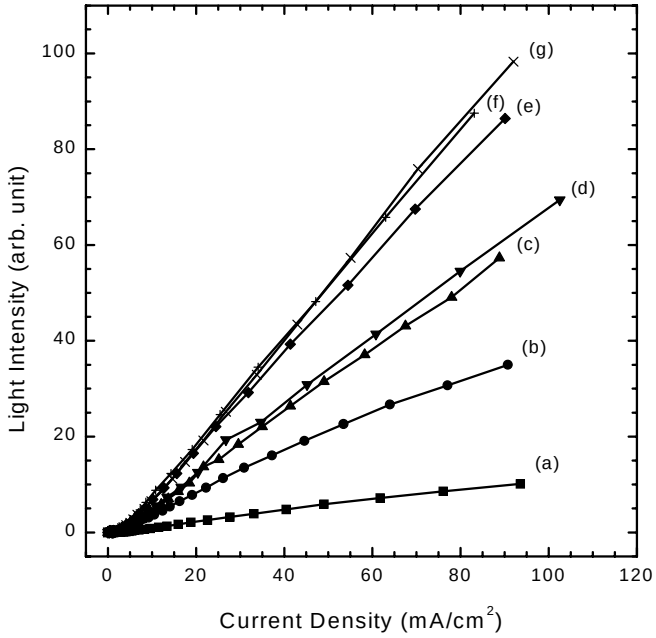

Fig. 4. Light intensity versus current for the same set of OLEDs used in Fig. 3

For ideal and clean interfaces, electrons are injected from the Ag cathode into the electron transporting layer (Alq_3) under large forward bias. Similarly, holes are injected from the ITO layer into the TPD layer (Fig. 3, inset). Under the external applied electric field, both electrons and holes migrates to the Alq_3/TPD interface where they recombine to yield singlet excitons. A small fraction of these excitons decay radiatively to produce light. For an ITO surface with a thin layer of organic contamination, an additional energy barrier is created for hole injection. Holes can be injected into the TPD layer by tunneling provided that the thickness of the contamination layer is of the order of a few Å. A reduction of surface contamination is then equivalent to reducing the thickness of the organic contamination, leading to smaller turn-on voltages in the I–V characteristics.

It should be noted that for short UV exposure times (0–10 min), both the I–V and the corresponding L–I curves are not highly reproducible. The uncertainties can be attributed to the difficulty in controlling the initial states of the anode surface by mere mechanical scrubbing or ultrasonic cleaning in organic solvents. On the other hand, for prolonged UV exposures (>30 min), both the I–V and the L–I characteristics become stabilized. In addition, an OLED fabricated from an ITO substrate with insufficient UV exposure exhibits uneven light-emitting areas. The results show that UV ozone treatment is a critical step for the fabrication of electroluminescent devices with reproducible and optimum characteristics.

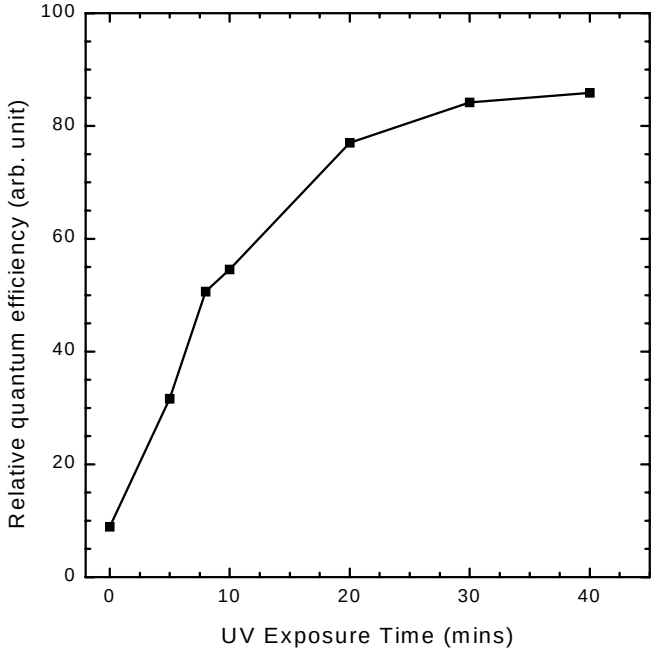

Fig. 5. Relative quantum efficiencies of OLEDs derived from Fig. 4

3 Conclusions

The effects of UV ozone treatment on ITO substrates used for OLED fabrication have been investigated. A contact angle technique was successfully developed to assess the cleanliness of the substrates before and after UV ozone treatment. The cleanliness can also be monitored by complementary XPS. UV ozone treatment can significantly enhance the quantum efficiencies of organic electroluminescent devices.

Acknowledgements. Support of this research by the Research Grant Council of Hong Kong under Grant No. RGC/96-97/12 and the Research Committee of Hong Kong Baptist University under Grant No. FRG/95-96/II-41 are gratefully acknowledged. We would like to thank ShenZhen Wellight Conductive Company for generously providing us the ITO samples.

References

1. J.R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman, A. Stocking: Science **273**, 884 (1996)
2. T. Tsutsui: MRS Bulletin **22**(6), 39 (1997), and references therein
3. P.E. Burrows, S.R. Forrest: Appl. Phys. Lett. **64**, 2285 (1994)
4. T. Zyung, J. Kim, I. Kang, D. Hwang, H.K. Shim: Mater. Res. Soc. Symp. Proc. **413**, 103 (1996)
5. L.S. Hung, C.W. Tang, M.G. Mason: Appl. Phys. Lett **70**, 152 (1997)
6. F. Li, H. Tang, J. Andergg, J. Shinar: Appl. Phys. Lett. **70**, 1233 (1997)
7. X.T. Tao, H. Suzuki, T. Watanabe, S.H. Lee, S. Migata, H. Sasaabe: Appl. Phys. Lett. **70**, 1503 (1997)
8. G.E. Johnson, K.M. McGrane: In *Electroluminescent Materials, Devices and Large-screen Displays*, ed. by E.M. Conwell, M. Stolka, M.R. Miller: SPIE Proc. **1910**, 6 (1993)
9. G.S. Ganesan, G. Lewis, H.M. Berg: Int. J. Microelectron. Electron. Pack. **17**, 152 (1994)
10. C.W. Tang, S.A. Vanlsyke: Appl. Phys. Lett. **51**, 913 (1987)