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ARTICLE *in* CHEMICAL PHYSICS LETTERS · MARCH 2003

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# Photoelectron spectroscopic study of iodine- and bromine-treated indium tin oxides and their interfaces with organic films

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Received 25 June 2002; in final form 15 January 2003

## Abstract

Work function variations of indium tin oxide (ITO) treated with solutions of iodine and bromine as well as bromine vapor were studied by ultraviolet and X-ray photoelectron spectroscopies. Interfaces between the treated ITO and NPB were also investigated. Treatments by iodine and bromine solutions, and bromine vapor led to work function increase by as much as 0.6, 0.7, and 0.9 eV, respectively. After the halogen treatments, the hole-injection barrier for the NPB/ITO contact was remarkably decreased. A light-emitting device fabricated with bromine vapor-treated ITO as anode clearly demonstrated better hole injection at the ITO/NPB interface and a lower drive voltage.

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Organic light-emitting devices (OLEDs) have drawn considerable attention since Tang and van Slyke reported the first high efficiency multi-layered device in 1987 [1]. To enhance operation efficiency and to lower driving voltage, a large number of studies have been done on the modification of interface between electrodes and organic materials, especially at the cathode side [2–8]. Recently, studies on improvement of hole injection by surface treatment of indium tin oxide (ITO) and

modification of the ITO/organic interfaces have attracted tremendous interest [9–21]. The hole-injection efficiency of ITO is an important parameter influencing the OLED performance. Improving the work function of ITO to match the energy level of the highest occupied molecular orbital (HOMO) of the hole transport layer is a simple and effective way to decrease the energy barrier height for hole injection. Several studies have dealt with the increase of the work function of ITO by various surface treatments, such as plasma treatments [9], oxygen glow discharge (O-GDT) or ultraviolet (UV)-ozone [10–12], grafting molecules [13,14], and adsorption of acid [15,16].

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In this Letter, we report the results on ITO surface treatments with two highly electronegative elements – iodine and bromine. Photoelectron spectroscopy was used to assess work function shift and chemical composition changes caused by the various halogen treatments. We also investigated the interface formation between the treated ITO substrates and *N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB), a widely used hole transport material. A device with bromine vapor-treated ITO as anode was fabricated and its performance was measured and compared with that of the device with untreated ITO substrate.

The ITO glass substrates used in the experiments had a sheet resistance of 50  $\Omega$ /square. The substrates were first cleaned by mechanical scrubbing in water using a Decon detergent and ultrasonically cleaned in de-ionized water. The ITO samples were then UV ozone-treated for 20 min before the halogen treatments. The ozone-treated samples are referred to as 'standard' ITO. Iodine and bromine solutions with different concentration were prepared by dissolving iodine (>99.8% purity) and bromine (>99.5% purity) in ethanol (>99.9% purity). The iodine and bromine solutions were applied onto the surface of the standard ITO substrates by spin-coating. For bromine vapor-treated sample, standard ITO substrates were exposed to bromine vapor evaporated from bromine solutions of different concentrations for 5 min. The standard and the halogen-treated samples were immediately loaded into a fast entry load-lock chamber, which was attached to a VG ESCALAB 220i-XL photoelectron spectrometer system consisting of an analysis chamber and an evaporation chamber. Base pressures in the evaporation chamber and the analysis chamber were  $4 \times 10^{-10}$  and  $1 \times 10^{-10}$  mbar, respectively. For the study on the NPB/ITO interface, NPB overlayers were grown by sequential vacuum deposition onto the ITO substrates. NPB thickness was monitored by a quartz crystal oscillator. After different thicknesses of NPB were deposited, the ITO/NPB interfaces were characterized with ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) in the analysis chamber. The HeI excitation line (21.2 eV) from a

He discharge lamp was used for the UPS measurements and a monochromatic Al  $K_{\alpha}$  excitation line (1486.6 eV) was used for the XPS measurements. The UPS spectra were recorded with a sample bias of  $-4.00$  V to allow for the observation of the inelastic cut-off. Work function of the samples was taken as the excitation energy less the difference between the Fermi level and the low energy cut-off [22]. The resolution of UPS measurements was better than 0.02 eV. A nickel foil and a silver foil were used for the Fermi level ( $E_F$ ) and the binding energy calibration. The work function of the standard ITO was measured to be 4.5 eV. The effect of ethanol as a solvent was monitored by measuring the work function of ethanol-treated ITO, which showed a mere difference of 0.1 eV from that of the standard ITO. The OLED with the bromine vapor-treated ITO as anode, NPB as hole transport layer, Alq<sub>3</sub> as electron transport layer, and Mg:Ag as cathode was fabricated. A multi-layer structure of NPB (80 nm)/Alq<sub>3</sub> (60 nm)/Mg:Ag (200 nm) was sequentially vacuum deposited on the ITO glass substrate by thermal evaporation. A control device, with the same configuration, was made on a standard ITO substrate.

The work function of the ITO samples treated with iodine and bromine solutions of different concentrations is shown in Fig. 1. The work function of the iodine-treated ITO (curve a) increases with increasing iodine concentration, and reaches 5.2 eV when the concentration is 0.15 M.

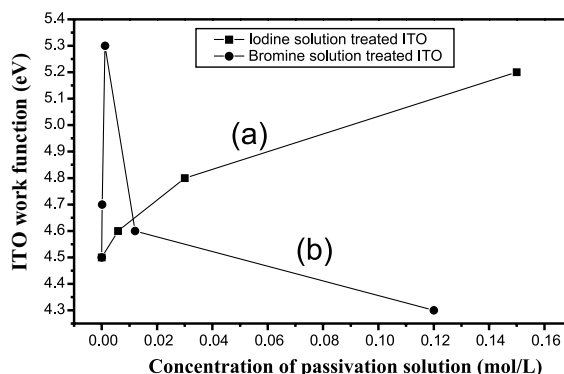


Fig. 1. Work function of ITO after treatment with solutions of different concentrations of (a) iodine and (b) bromine.

XPS analysis revealed that there was no chemical shift in the position of the In3d, Sn3d, and O1s peaks upon the iodine treatment (not shown here). Curve b in Fig. 1 shows a maximum work function of 5.3 eV for the ITO treated with a bromine solution of  $1.2 \times 10^{-3}$  M. Above this concentration, the work function decreases rapidly. XPS analysis showed that Sn3d, O1s, and In3d peaks from the ITO exhibited large chemical shifts upon the treatment with  $1.2 \times 10^{-3}$  M bromine solution, while treatment with less concentrated solutions caused no discernable chemical shifts. It is thus considered that the bromine solutions with concentrations higher than  $1.2 \times 10^{-3}$  M have reacted with the ITO and changed the surface structure and chemistry of the ITO film, giving rise to the work function decrease. For the bromine vapor-treated ITO, ITO substrates were exposed to bromine vapor evaporated from bromine solutions of different concentrations (0.5 M, 1.0 M, 2.0 M, and pure liquid bromine) for 5 min (30 s only for pure liquid bromine). A maximum work function of 5.5 eV was obtained by exposing to the vapor from the 2.0 M bromine solution. It was noted that the ITO surface was heavily damaged by the vapor from the pure liquid bromine even for an exposure of 30 s. Thermal stability of the iodine-treated ITO was studied in an annealing experiment. ITO surface treated with a 0.15 M iodine solution was annealed at different temperatures up to 400 °C. The work function and chemical composition (Sn:In ratio, In:O ratio, and I<sub>2</sub>:O ratio) of the ITO surface showed little changes up to 200 °C. It indicates that the iodine-treated ITO is stable annealing at this temperature.

The ITO/NPB interface was formed by deposition of NPB on the differently treated and the standard ITO samples. Fig. 2a shows the position of the highest occupied molecular orbital (HOMO) of NPB relative to the Fermi level (this represents the hole injection barrier), as a function of NPB thickness. ITO substrates treated with standard, 0.15 M iodine solution,  $1.2 \times 10^{-3}$  M bromine solution, and bromine vapor (from 2.0 M bromine solution) were compared for the difference in hole-injection barrier energy as measured by the difference between the Fermi level and the NPB HOMO edge of the ITO/NPB contact. The results

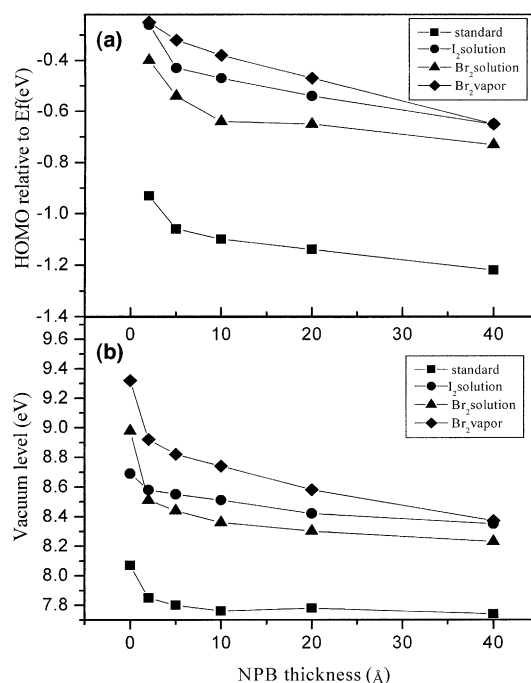


Fig. 2. (a) Position of the highest occupied molecular orbital (HOMO) relative to the Fermi level and (b) evolution of the secondary cut-off or vacuum level as a function of NPB thickness, respectively, for standard ITO (square) and ITO substrates treated with a 0.15 M iodine solution (circle),  $1.2 \times 10^{-3}$  M bromine (triangle) solution, and bromine vapor (from 2.0 M bromine solution) (diamond).

clearly indicate that the barrier height for hole injection depends on the work function of the ITO substrate. The higher is the ITO work function, the smaller is the barrier height for the hole injection. When 20 Å NPB was deposited, the barrier heights for iodine solution-, bromine solution-, and bromine vapor-treated ITO substrates were 0.5, 0.6, and 0.4 eV, respectively, comparing to 1.1 eV for the standard ITO. Table 1 shows the work functions and barrier heights for the standard ITO and the halogen-treated ITO. The increase of work function in the iodine- and bromine-treated ITO substrates can be explained by the formation of a dipole layer at the surface of ITO. Upon the halogen treatment, due to the large electronegativity of iodine and bromine, a dipole layer would form on the ITO surface. The negatively charged iodine and bromine molecules on the ITO surface hinder

Table 1

Work function of ITO and barrier height at the NPB/ITO interface upon different treatments

Treatment	Work function (eV)	$E_F$ -HOMO (eV)
Non-treated ITO	4.4	1.2
Ex situ ozone exposure	4.5	1.1
In situ oxygen plasma exposure [23]	5.2	0.7
I <sub>2</sub> solution (0.15 M)	5.2	0.5
Br <sub>2</sub> solution ( $1.2 \times 10^{-3}$ M)	5.3	0.6
Br <sub>2</sub> Vapor (2.0 M)	5.4	0.4

the escape of electrons from the surface and hence increases the work function.

Fig. 2b shows the variation in the secondary cut-off position (vacuum level) as a function of NPB thickness. Since the Fermi level is fixed, the change of the secondary cut-off corresponds directly to the

modification of the ITO work function. The decrease of secondary cut-off energy represents a decrease of ITO work function. We found that as the NPB was deposited onto the treated ITO surface; the work function of ITO dropped rapidly. This is attributed to the fact that the potential of dipole layer at the interface was changed by deposition of NPB and is confined to the interfacial region. XPS measurements of binding energy changes after NPB deposition showed that while the XPS In3d, Sn3d, and O1s core-level spectra for the treated and standard ITO remained similar; the C1s and N1s peaks showed dramatic differences. The C1s and N1s peaks of the NPB film on the treated ITO are at lower binding energies comparing to those of the NPB on the standard ITO substrate. Fig. 3 shows the evolution of C1s and N1s core level spectra for NPB deposited on the iodine-treated ITO. The C1s and N1s core level for NPB deposited onto the

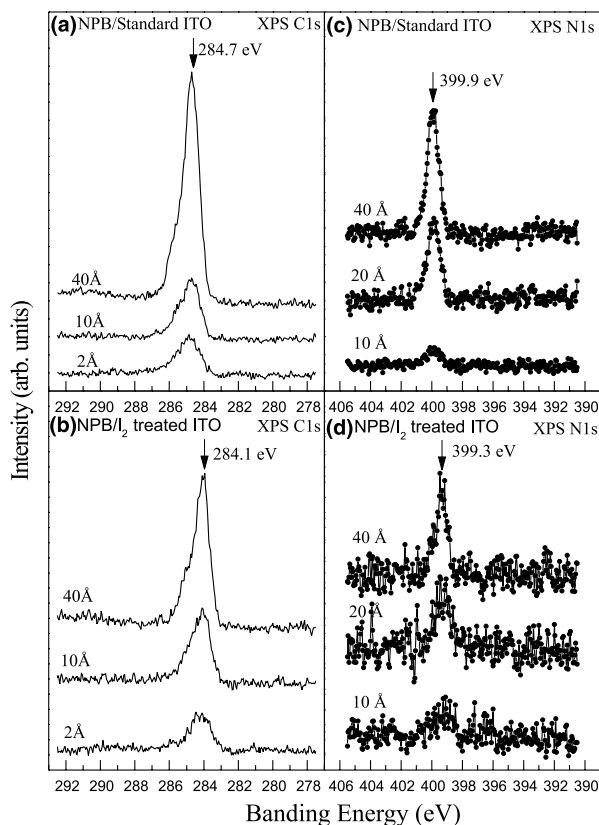


Fig. 3. Variation of C1s and N1s core level spectra for NPB deposited onto standard ITO and iodine treated ITO.

bromine-treated ITO (not shown here) showed similar changes as the iodine-treated ITO. We consider that when the NPB was deposited on the treated ITO surface, the conjugated bonds in NPB molecule conjugate with the negative charge of iodine and bromine molecules. This would decrease the density of negative charge in the iodine and the bromine molecules, and result in a decrease in the dipole moment of the iodine and the bromine molecules, leading to a work function decrease. As the electronegativity of bromine is larger than that of iodine and the radius of bromine is smaller than that of iodine, the dipole moment of bromine molecule is easier to be weakened by NPB molecules. In Fig. 2b, we may find that the work function of bromine-treated ITO abruptly decreases for about 0.5 eV, when 2 Å NPB was deposited on ITO surface. For the NPB/standard ITO interface, the UV ozone-treated ITO is rich in negatively charged oxygen [12], they might also conjugate to the NPB molecule during the early stage of the NPB/ITO interface formation. This would also lead to a decrease in the work function of the standard ITO as shown in Fig. 2b.

The current density–voltage and luminescence–voltage characteristics obtained from a device made with bromine vapor-treated ITO and standard ITO are shown in Fig. 4. It shows that the bromine-treated device has higher current density and greater luminescence comparing to the device made on standard ITO. The onset voltage decreased to 3.2 V in the bromine-treated device as compared to 3.6 V in the standard device. This decrease of onset voltage matches well to the decrease (0.4 eV as shown in Table 1) in the hole-injection barrier between the ITO/NPB interface upon bromine vapor treatment. The increase of work function of ITO and decrease of barrier height improve the hole injection efficiency between ITO anode and NPB, and lead to the high current density and luminescence and low drive voltage.

In conclusion, we studied the effect of surface treatment of ITO with iodine solution, bromine solution, and bromine vapor of different concentrations. In particular, the influence on the ITO work function and the properties of the ITO/NPB interface were studied with UPS and XPS analysis. The ITO treated by the suitable concentrations of

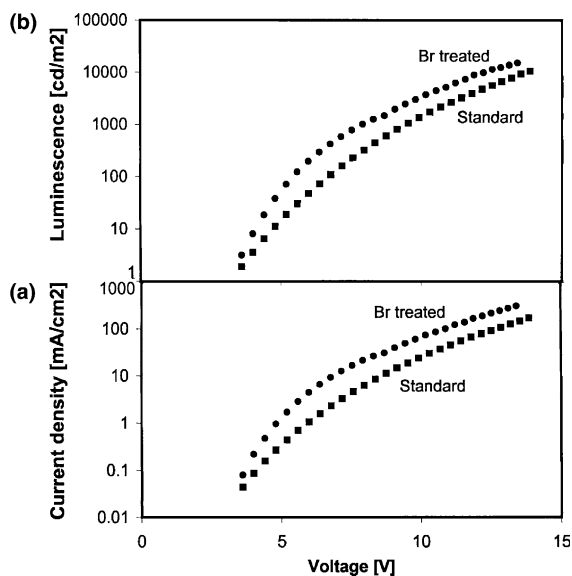


Fig. 4. (a) Current density vs. voltage and (b) Luminescence vs. voltage characteristics of two EL devices with bromine vapor-treated ITO (circle) and standard ITO (square).

iodine solution and bromine solution led to a significant increase in work function and reduction of hole injection barrier height for the ITO/NPB interface. These changes were attributed to the dipole moment induced by the negative charge of iodine and bromine on the surface of the ITO substrates. The OLED made on the treated ITO showed that the halogen treatment is a practical way to reduce the injection barrier height between ITO and NPB. This approach might be extended to other ITO/organic interfaces and would lead to performance enhancement especially when the device performance is limited by the hole injection.

### Acknowledgements

We are grateful to the financial support from the Research Grants Council of Hong Kong [Nos. CityU 1028/00E (9040496)].

### References

- [1] C.W. Tang, S.A. van Slyke, *Appl. Phys. Lett.* 51 (1987) 913.

- [2] L.S. Hung, C.W. Tang, M.G. Mason, *Appl. Phys. Lett.* 70 (1997) 152.
- [3] F. Li, H. Tang, J. Anderegg, J. Shinar, *Appl. Phys. Lett.* 70 (1997) 1233.
- [4] G.E. Jabbour, Y. Kawabe, S.E. Shaheen, J.F. Wang, M.M. Morrell, B. Kipplen, N. Peyghambarian, *Appl. Phys. Lett.* 71 (1997) 1762.
- [5] G.E. Jabbour, B. Kippelen, N.R. Armstrong, N. Peyghambarian, *Appl. Phys. Lett.* 73 (1998) 1185.
- [6] H. Tang, F. Li, J. Shinar, *Appl. Phys. Lett.* 71 (1997) 2560.
- [7] J. Kido, Y. Lizumi, *Appl. Phys. Lett.* 73 (1998) 2721.
- [8] J. Kido, T. Matsumoto, *Appl. Phys. Lett.* 73 (1998) 2866.
- [9] C.C. Wu, C.I. Wu, J.C. Sturm, A. Kahn, *Appl. Phys. Lett.* 70 (1997) 1348.
- [10] S.A. van Slyke, C.H. Chen, C.W. Tang, *Appl. Phys. Lett.* 69 (1996) 2160.
- [11] J. Shi, C.W. Tang, *Appl. Phys. Lett.* 70 (1997) 1665.
- [12] M.G. Mason, L.S. Hung, C.W. Tang, S.T. Lee, K.W. Wong, M. Wang, *J. Appl. Phys.* 86 (1999) 1688.
- [13] F. Nüesch, L. Si-Ahmed, B. François, L. Zuppiroli, *Adv. Mater.* 9 (1997) 222.
- [14] F. Nüesch, F. Rotzinger, L. Si-Ahmed, L. Zuppiroli, *Chem. Phys. Lett.* 288 (1998) 861.
- [15] F. Nüesch, K. Kamarás, L. Zuppiroli, *Chem. Phys. Lett.* 283 (1998) 194.
- [16] F. Nüesch, L.J. Rothberg, E.W. Forsythe, Quoc Toan Le, Y. Gao, *Appl. Phys. Lett.* 74 (1999) 880.
- [17] A.J. Heeger, I.D. Parker, Y. Yang, *Synth. Met.* 67 (1994) 23.
- [18] S.A. Carter, M. Angelopoulos, S. Karg, P.J. Brock, J.C. Scott, *Appl. Phys. Lett.* 70 (1997) 2067.
- [19] J.S. Kim, M. Granström, R.H. Friend, N. Johansson, W.R. Salaneck, R. Daik, W.J. Feast, F. Cacialli, *J. Appl. Phys.* 84 (1998) 6859.
- [20] A. Gyoutpku, S. Hara, T. Komatsu, M. Shirinashihama, H. Iwanaga, K. Sakanoue, *Synth. Met.* 91 (1997) 73.
- [21] Z.B. Deng, X.M. Ding, S.T. Lee, W.A. Gambling, *Appl. Phys. Lett.* 74 (1999) 2227.
- [22] Y. Park, V. Choong, Y. Gao, B.R. Hsieh, C.W. Tang, *Appl. Phys. Lett.* 68 (1996) 2699.
- [23] X.M. Ding, L.M. Hung, L.F. Cheng, Z.B. Deng, X.Y. Hou, C.S. Lee, S.T. Lee, *Appl. Phys. Lett.* 76 (2000) 2704.