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Analysis of the injection layer of PTCDA in OLEDs using x-ray photoemission spectroscopy and atomic force microscopy*

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Through the investigation of the sample surface and interface of 3, 4, 9, 10-perylenetetracarboxylic dianhydride (PTCDA)/indium-tin-oxide (ITO) thin films using atomic force microscopy, it has been found that the surface is complanate, the growth is uniform and the defects cover basically the surface of ITO. Furthermore, the number of pinholes is small. The analysis of the sample surface and interface further verifies this result by using x-ray photoemission spectroscopy . At the same time, PTCDA is found to have the ability of restraining the diffusion of chemical constituents from ITO to the hole transport layer, which is beneficial to the improvement of the performance and the useful lifetime of the organic light emitting diodes (OLEDs).

Keywords: atomic force microscopy, x-ray photoemission spectroscopy, PTCDA/ITO
PACC: 6116P, 2930K, 6165

1. Introduction

The organic light emitting diode (OLED) has developed into a kind of planar display devices with promising market potential, because it has the great advantages of low voltage drive, initiative luminescence, fast response and a great variety of colors. However, improving the light-emitting efficiency, useful lifetime and long-term stability of devices are very important for their applications. In order to gain a high light-emitting efficiency, we need to increase the carrier injection, improve the carrier level of balance and raise the probability of excitons formation and recombination. Many methods have proved to improve device performance, such as selecting fluorescence material with high efficiency,[1] multi-layer structure[2] and interface modification of cathode[3,4] and anode,[4−9] etc. A hole injection layer is added to modify the interface between indium-tin-oxide (ITO) anode and hole transport layer (HTL), therefore better electroluminescence efficiency is obtained for the same electroluminescence materials and structures as compared to the original device.

The organic semiconductor material 3, 4, 9, 10-perylenetetracarboxylic dianhydride (PTCDA), whose molecular formula is $C_{24}H_8O_6$, has a monoclinic structure and wide band gap.

The energy band gap between the lowest occupied molecular orbit (LOMO) and highest unoccupied molecular orbit (HUMO) is 2.2eV. Each PTCDA crystal cell contains two molecules with a separation of 3.21Å between adjacent molecules.[10] As PTCDA has unique characteristics of transporting electrons in the molecular plane and transporting holes in the vertical direction to the molecular plane,[11] it is usually used to fabricate p-Si/PTCDA heterojunction organic-on-inorganic photodetector[12] and used as a HTL in OLED.[13,14] In the organic inverse-light-emitting diode (OILED), PTCDA can be used as HTL and protecting layer when the ITO anode is sputtered.[14] According to the study of the struc-

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ture of TPD/PTCDA/ITO conducted by Chkoda *et al*,[15] the hole-injecting potential barrier is decreased because of the influence of dipole. That is to say, using middle energy level supplied by PTCDA can improve the hole injecting efficiency. Meanwhile, PTCDA can also be grown as a self-organization monomolecular layer on the ITO film, which can restrain the diffusion of chemical constituents from ITO to HTL.[16] This paper reports the influence of PTCDA in OLEDs using atomic force microscopy (AFM) and x-ray photoemission spectroscopy (XPS).

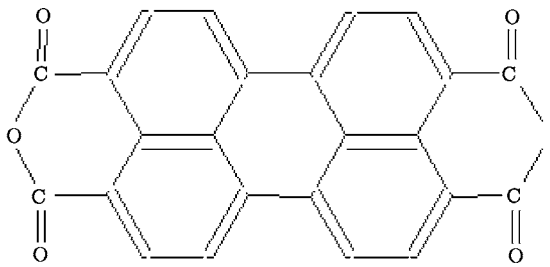


Fig.1. The molecular structure of PTCDA.

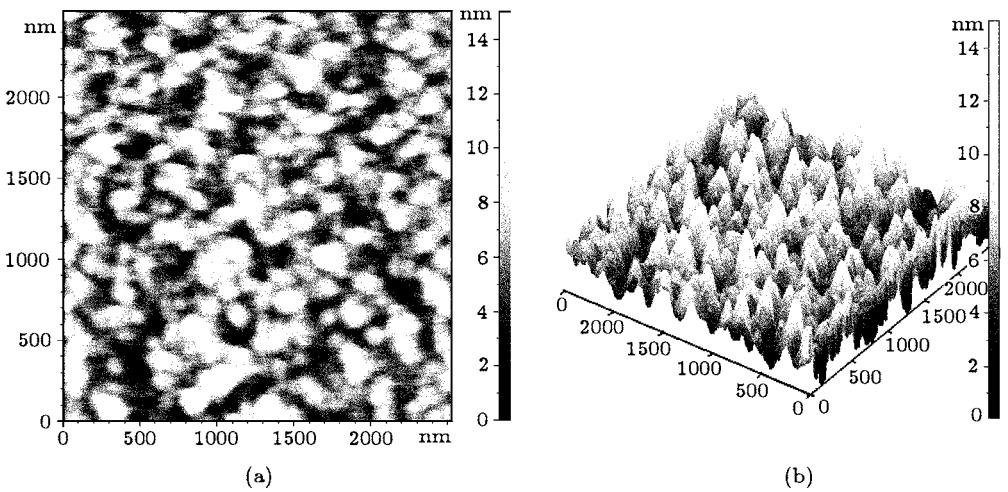


Fig.2. AFM micrographs of the PTCDA/ITO surface (a) Lateral force mode; (b) Topographic mode.

2. Experiment

Figure 1 shows the molecular structure of PTCDA. The substrate is an ITO coated glass. It was cleaned by ultrasonication in acetone and alcohol separately.

After being rinsed in hot and cold de-ionized water for several times, the substrates was dried in an infrared oven. In a vacuum better than 5×10^{-4}Pa, PTCDA was evaporated and deposited on the surface of the substrate. The thickness and square resistance of ITO film were about 300nm and 78Ω/□, respectively. The thickness of PTCDA film was 30nm.

The surface pattern of PTCDA /ITO was observed by a Topometrix Explorer atomic force microscope (AFM) with high resolution, and it was scanned in two modes of the topology and lateral force (see Fig.2). The scanning area of the AFM image was $3.0\times3.0\mu m^2$, and the height in the direction vertical to the surface was shown by grey scale. The weaker the grey scale, the larger the undulated height of microscopic outline in Z direction.

The x-ray photoemission spectroscopy (XPS) data were collected by an ESCALAB-220IXL x-ray photoemission spectroscopy with a base vacuum better than 1×10^{-8}Pa. Mg $K\alpha$ radiation ($h\nu$=1253.6eV) used as x-ray source was operated at 300W. In order to investigate the electron states of the interface, the PTCDA/ITO sample was sputtered by argon ion beam with 3.0keV kinetic energy for 20min in a vacuum chamber of 3×10^{-7}Pa. The sputtering area was $0.75\times0.75cm^2$ and the ion beam density was $1.0\mu A/0.75\times0.75cm^2$. Then the XPS results were treated with Scienta 300 data system and related software.

3. Results and analysis

3.1. The effect of defects in the surface of ITO film on film quality of hole-transport materials

The contact between crystal grains of ITO is quite tight, so dislocations are usually formed on grain boundaries.[17] Moreover, the surface atoms are more

active than bulk atoms and the activation energy of forming point defect is small,[18] thus the concentration of point defects such as the In vacancies in the surface is much higher than in the bulk.[19]

The uneven distribution of defects in ITO has great effect on film quality of the hole transport material. Because the binding ability of hole transport material with defects is stronger than with perfect surface, the deposited material will first combines with them and crystal nucleus are formed.[20] The uneven distribution of defects determines the uneven formation of crystal nucleus, therefore the hole transport layer deposited on ITO has many defects and pores, and the film quality is poor. All these immediately result in many effects: (1) The interfacial resistance of ITO/HTL rises, and the working voltage of the device becomes higher; (2) Oxygen atoms diffuse from ITO into HTL, causing the degeneration of the hole transport material, forming luminescence quenching centrals, and leading to the low efficiency of carriers injection and bad long-term stability of the device.

3.2. Analysis of the surface of PTCDA injecting layer deposited on ITO using AFM

Figure 2 shows the surface pattern of PTCDA / ITO by AFM. From this figure, we can see that PTCDA molecules form an island-like structure with a height of about 14nm on the ITO film, and the distribution of these islands is uniform, so the surface of PTCDA is complanate. Though the growth of PTCDA big-area islands appears on some places, it covers basically the defects on ITO and the number of pinholes is small.

The addition of PTCDA in OLEDs is of great advantage to even deposition of hole transport material and improve the film quality. The main reasons are as follows.

PTCDA molecules have transient polarity because of forming π electron clouds in the direction vertical to the molecular plane and many free floating π electrons. This not only produces interaction force between PTCDA molecules in adjacent layers, leading to slight overlapping of π electron clouds, but also causes PTCDA to easily interact quite strongly with the ITO substrate to form an ordered film. This PTCDA film covers the defects in the ITO surface, and causes the deposition of hole transport material on PTCDA better than on ITO, so the film quality is improved. Finally the island-like structure in the PTCDA thin film is formed.

3.3. Analysis of the surface and interface of PTCDA/ITO using XPS

Figure 3 gives the evolution of the whole XPS scanning spectrum recorded at the interface of PTCDA/ITO sample as sputtering time increases. Peaks associated with C1s, In3d, Sn3d and O1s emerge at 285, 444, 490 and 532eV, respectively. The facts that C1s and O1s peaks are significantly stronger than In3d peak, and the Sn3d peak is the weakest one on the raw surface (sputtering time t_s=0min) indicate a good coverage of PTCDA on ITO surface with almost no cracks.

It also can be seen from Fig.3 that the C1s peak intensity of the interface is much weaker than that in the case of raw surface. This indicates that the number of activated C atoms is significantly reduced. But the peaks of O1s, In3d and Sn3d are much stronger than those from the original surface, implying that most activated atoms in the interface come from ITO.

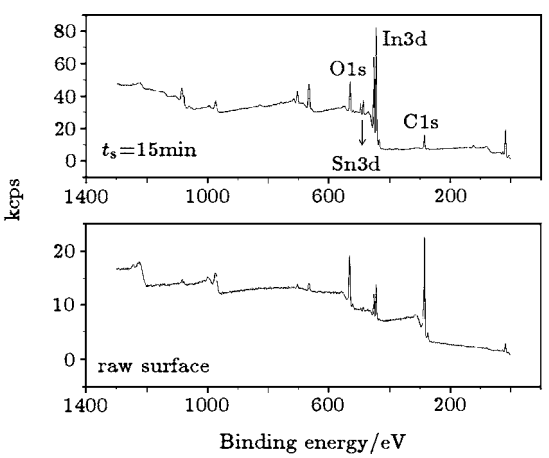


Fig.3. The evolution of the whole XPS scanning spectra recorded at the interface of the PTCDA/ITO sample as the sputtering time increases.

The C1s fine XPS spectrum of the PTCDA/ITO sample is given in Fig.4. In this figure, there are two main peaks and one weak shoulder peak, which are located at 284.6, 288.7 and 290.4eV, respectively. The peak at 284.6eV, corresponding to the binding energy of aromatic carbon atoms (C atoms bonding with C atoms and H atoms),[21,22] is considered to be activated by C atoms in perylene rings because the twenty C atoms in perylene rings all have the characteristics of aromatic carbon atoms. It is known that chemical shift of one element increases with the augment of electronegativity of the bonded atoms. The peak at 288.7eV, can be considered to be activated by C atoms in acid anhydride group, where C atoms bond

with O atoms.[23] The existence of a weak peak at 290.4eV indicates a slight oxidation of C atoms. The area ratio of the three peaks, which are located at 290.4, 288.7 and 284.6eV, respectively, is 3:7:52. If the area of oxidized C atoms is added to the area of C atoms in acid anhydride, the area ratio of peaks is 1:5.2, which agrees with the atomic number ratio of the two kinds of C atoms in perylene rings. It can be inferred that the oxidized C atoms only come from acid anhydride. The O atoms which oxidize the C atoms come from ITO and diffuse into PTCDA. This also proves the fact that the addition of PTCDA in multi-structured OLEDs can restrain the diffusion of chemical constituents from ITO to HTL, thus decreasing the number of luminescence quenching centres, and weakening the degeneration of hole transport material, so the carriers injection efficiency and long-term stability of devices are improved.

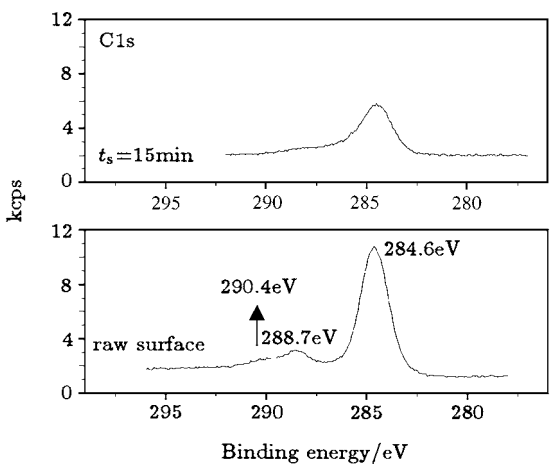


Fig.4. The evolution of the XPS fine spectra of C1s of the PTCDA/ ITO sample as the sputtering time increases.

From Fig.4 we can also find the disappearance of C1s peak at high binding energy and a chemical shift towards lower binding energy of C1s main peak. This indicates the reduction of C atoms activated by O atoms. There are many point defects of In vacancies, with which PTCDA molecules tend to combine at the surface of ITO, as the binding energy between PTCDA molecules and the defects is larger than that between PTCDA and perfect surface. From the disappearance of C1s peak at high binding energy, it can be concluded that it is the perylene rings rather than PTCDA molecules that combine with In vacancy of ITO, then the defects on ITO surface are covered.

Figure 5 shows the evolution of the XPS fine spectrum of O1s of the PTCDA/ITO sample as the sputtering time increases. The fine spectrum of the raw surface is composed of two peaks with a main peak at 531.5eV and a shoulder peak at 533.4eV. In PTCDA molecules, there are two kinds of O atoms, one of which combines with C atoms through double bonds and the other combines with diploid number of C atoms through single bonds. So the two peaks at 531.5 and 533.4eV correspond to the binding energies of O atoms in C═O bonds and C–O–C bonds, respectively.

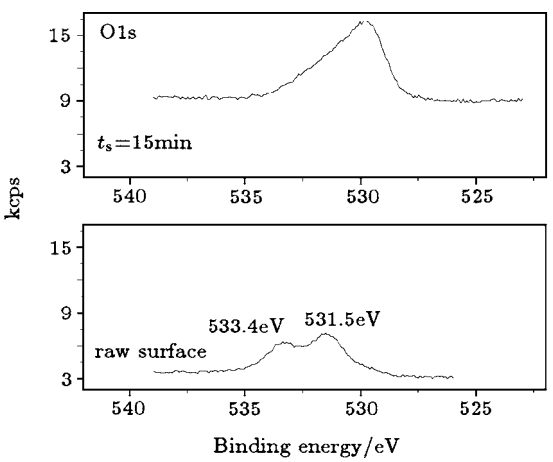


Fig.5. The evolution of the XPS fine spectra of O1s of the PTCDA/ITO sample as the sputtering time increases.

We can also find a chemical shift towards lower binding energy in Fig.5. It is caused by the stimulated emission of hypo-outside electrons of O atoms in ITO. The binding energy of O atoms in In_2O_3 and SnO_2 are 529.8 and 530.1eV respectively, which are both much lower than that in PTCDA molecules. The fact further demonstrates that the addition of PTCDA can restrain the diffusion of chemical constituents from ITO to HTL in multi-structure OLEDs.

Figures 6 and 7 show the evolution of the XPS fine spectra of In3d and Sn3d of the PTCDA/ITO sample as the sputtering time increases. The peak intensities of In3d and Sn3d are both weak for the raw surface, which further accounts for the covering effect of PTCDA to the defects on ITO surface. In the two figures, In3d and Sn3d interface spectra both have an increase of peak area and a chemical shift towards lower binding energy. The reduction of O atoms in ITO,[24] which is caused by selective sputtering effect of argon ion, leads to the chemical shift, because In_2O_3 and SnO_2 are partially deoxidized to suboxides, which have relatively lower binding energy.

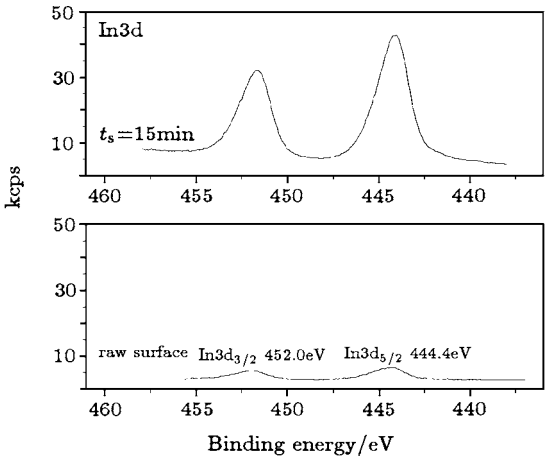


Fig.6. The evolution of the XPS fine spectra of In3d of the PTCDA/ITO sample as the sputtering time increases.

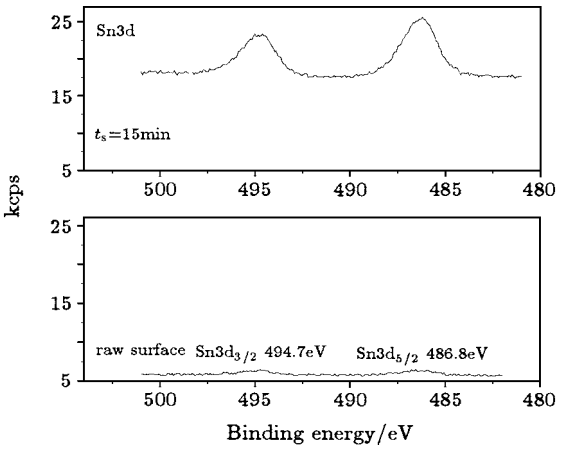


Fig.7. The evolution of the XPS fine spectra of Sn3d of the PTCDA/ITO sample as the sputtering time increases.

4. Conclusion

From the investigation of PTCDA/ITO sample surface, the growth of PTCDA is found to be uniform, which covers the defects of ITO surface basically, and the number of pinholes is small. In XPS spectra of raw surface, the C1s and O1s peaks are significantly stronger than In3d peak, and the Sn3d peak is the weakest one. The PTCDA is proved to cover the defects on ITO surface, basically. Through the evolution of the XPS whole scanning spectrum recorded at the surface of the sample as the sputtering time increases, the layer of PTCDA is found to behave as an obstacle to the diffusion of O atoms from ITO film. So the addition of PTCDA injection layer can restrain the diffusion of chemical constituents from ITO to HTL, decreasing the number of luminescence quenching centres, and weakening the degeneration of hole transport material, so the carriers injection efficiency and long-term stability of the devices are improved, which benefits the improvement of the performance and useful life time of devices.

References

[1] Tang C W, VanSlyke S A and Chen C H 1989 *J. Appl. Phys.* **65** 3610

[2] Era M, Adachi C, Tsutsui T and Saito S 1991 *Chem. Phys. Lett.* **178** 488

[3] Hung L S, Tang C W and Mason M W 1997 *Appl. Phys. Lett.* **70** 152

[4] Kurosaka Y, Tada N, Ohmori Y and Yoshino K 1998 *Jpn. J. Appl. Phys.* **37** L872

[5] Lou Z D, Xu Z, Xu C X, Yu L, Teng F and Xu X R 1998 *Acta Phys. Sin.* **47** 139 (in Chinese)

[6] Liu M, Yi L X, Teng F, Xu Z and Xu X R 2003 *Acta Phys. Sin.* **52** 1013 (in Chinese)

[7] Deng Z B, Ding X M, Lee S T and Gambling W A 1999 *Appl. Phys. Lett.* **74** 2227

[8] Ou G P, Song Z, Gui W M, Zhang F J 2005 *Acta Phys. Sin.* **54** 5717 (in Chinese)

[9] Tokito S, Noda K and Taga Y 1996 *J. Phys. D: Appl. Phys.* **29** 2750

[10] Zhang F J, Shao J F and Zhang D J 1999 Chinese *J. Luminescence* **20** 351 (in Chinese)

[11] Ostrick J R, Dodabalapur A, Torsi L, Lovinger A J, Kwock E W, Miller T M, Galvin M, Berggren M and Katz H E 1997 *J. Appl. Phys.* **81** 6804

[12] Forrest S R, Kaplan M L and Schmidt P H 1984 *J. Appl. Phys.* **55** 1492

[13] Burrows P E and Forrest S R 1994 *Appl. Phys. Lett.* **64** 2285

[14] Bulovic'V, Tian P, Burrows P E, Gokhale M R and Forrest S R 1997 *Appl. Phys. Lett.* **70** 2954

[15] Chkoda L, Heske C, Sokolowski M and Umbach E 2000 *Appl. Phys. Lett.* **77** 1093

[16] Campbell I H, Rubin S, Zawodzinski T A, Kress J D, Martin R L, Smith D L, Barashkov N N and Ferraris J P 1996 *Phys. Rev.* B **54** 14321

[17] Taga N, Odaka H, Shigesato Y, Yasui I, Kamei M and Haynes T E 1996 *J. Appl. Phys.* **80** 978

[18] Yun Z Z, Wang E X and Wan L X 1993 *Surface and Interface Physics* (Chengdu: University of Electronic Science and Technology of China Press) p40 (in Chinese)

[19] Wu C C, Wu C I, Sturm J C and Kahn A 1997 *Appl. Phys. Lett.* **70** 1348

[20] WU Z Q and Wang B 2001 *Film Growth* (Beijing: Science Press) p179 (in Chinese)

[21] Le Q T, Avendano F M, Forsythe E W, Yan L, Tang C W and Gao Y 1999 *J. Vac. Sci. Tech.* A **17** 2314

[22] Watts J F and Castle J E 1984 *J. Mater. Sci.* **19** 2259

[23] Arias A C, Roman L S, Kugler T, Toniolo R, Meruvia M S and Hümmelgen I A 2000 *Thin Solid Films* **371** 201

[24] Wagner C D 1977 *Handbook of X-ray and Ultra-violet Photoelectron Spectroscopy* (London: Heyden Press)