

Analysis of PTCDA/ ITO Surface and Interface Using X-ray Photoelectron Spectroscopy and Atomic Force Microscopy*

Ou Guping¹, Song Zhen², Gui Wenming¹, and Zhang Fujia^{1,†}

(1 School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China)

(2 Beijing Mechanical Industry Institute, Beijing 100085, China)

Abstract: The electronic states of the surface and interface of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA)/indium-tin-oxide (ITO) thin film are investigated using X-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) is also applied to investigate the pattern of PTCDA/ITO film. XPS results show that there are two main peaks, which are associated with C atoms in the perylene rings and acid anhydride groups, located at 284.6 and 288.7 eV, respectively, in the C1s spectrum of the original surface. It can be deduced from the emergence of a small peak at 290.4 eV in the C1s spectrum that some C atoms are oxidized by O atoms from ITO. The binding energies of O atoms in C=O bonds and C—O—C bonds are 531.5 and 533.4 eV respectively. At the interface, the peak at the high binding energy in the C1s spectrum disappears, and the peak value shifts about 0.2 eV to lower binding energy. There is a significant 1.5 eV chemical shift to lower binding energy in the O1s spectrum. These observations indicate that perylene rings inside PTCDA molecules are combined with In vacancies in the ITO at the interface. The AFM results show that PTCDA molecules formed an island-like structure a height of about 14 nm. The sizes of the crystal grains are about 100 ~ 300 nm. The island-like pattern comes from the delocalized bonds of adjacent molecules in PTCDA and the combination of vacancies in ITO with perylene rings at the PTCDA/ITO interface.

Key words: AFM; XPS; PTCDA

PACC: 6116P; 2930K; 6165

CLC number: TN304

Document code: A

Article ID: 0253-4177(2006)02-0229-06

1 Introduction

Significant progress has been made in organic semiconductor materials and devices with the rapid development of optoelectronic technologies. New devices, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photosensitive field-effect transistors (OPFETs), have been fabricated and investigated. Thus the scope of organic optoelectronics has been enlarged. Compared to devices based on inorganic semiconductors, those based on organic semiconductors have many advantages such as a simple fabrication process, low cost, flexibility, and the realization of large-area planar processes^[1-4].

3, 4, 9, 10-perylenetetracarboxylic dian-

hydride (PTCDA), whose molecular formula is $C_{24}H_8O_6$, is a wide gap organic semiconductor (Fig. 1)^[5-7]. The energy band gap between the LOMO and HUMO is 2.2 eV. A PTCDA crystal is a monoclinic structure, in which each unit cell contains two molecules, with a distance of 0.321 nm between adjacent molecules. The hole concentration of highly ordered PTCDA film is $5 \times 10^{14} \text{ cm}^{-3}$, and the mobility is between 10^{-7} and $10^{-6} \text{ cm}^2 / (\text{V} \cdot \text{s})$ in the direction orthogonal to the molecular plane^[8]. The film is transparent for light with a wavelength of 632.8 nm.

ITO is composed of 90 %wt In_2O_3 and 10 %wt SnO_2 . It is used as anode material and windows for incident light in PTCDA/P-Si photodetectors. Its band gap, which depends on the deposition conditions and surface modifications, is between 3.75 and 4 eV^[9]. It is transparent for 80 % of visible

* Project supported by the National Natural Science Foundation of China (No. 60276026) and the Natural Science Foundation of Gansu Province (No. ZS031-A25-012-G)

† Corresponding author. Email: prof_zhangfj@sina.com

Received 23 August 2005, revised manuscript received 24 October 2005

© 2006 Chinese Institute of Electronics

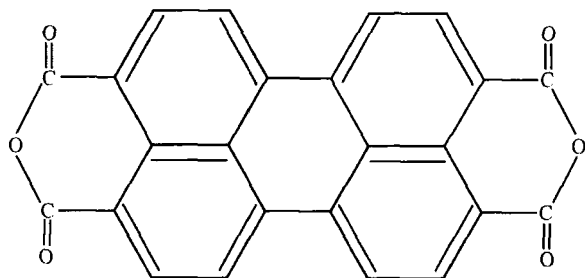


Fig. 1 Molecular structure of PTCDA

light ($\lambda = 360 \sim 780\text{nm}$) and has a reflectivity of over 90 % for infrared rays ($1 \sim 2\mu\text{m}$)^[10]. It is also a highly degenerate semiconductor and can form good Ohmic contact with PTCDA.

In this paper, the electron states of the surface and interface of PTCDA/ITO in PTCDA/P-Si organic-on-inorganic photodetectors are investigated using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

2 Experiment

ITO coated glass, with a resistance of 50Ω and thickness of 20nm, was boiled in de-ionized water for 10min, and was then ultrasonically treated in acetone and alcohol for 20min each. After being rinsed in de-ionized water several times, the substrates were dried in an infrared oven in nitrogen ambient, and were then transferred immediately into a vacuum chamber. In a vacuum of 10^{-5} Pa, a PTCDA film with a purity of 99.5 % and thickness of 150nm was thermally evaporated onto the surface of the substrate. The evaporating temperature and substrate temperature were controlled to about 450 and 256 °C, respectively.

The surface pattern of the PTCDA/ITO was observed with a high resolution Topometrix Explorer AFM. The size of the AFM images was 3.0mm \times 3.0mm. The film was also measured by an ESCALAB-220IXL XPS with a base pressure of over 1×10^{-8} Pa. Mg K radiation operated at 300W ($h\nu = 1253.6\text{eV}$) was used as an X-ray source. In order to investigate the electron states of the interface, the PTCDA/ITO sample was sputtered by an argon ion beam with a 3.0keV kinetic energy at 3×10^{-7} Pa for 20min. The sputtering area was very large (0.75cm \times 0.75cm), with an ion beam density of 1.0 $\mu\text{A}/0.75\text{cm} \times 0.75\text{cm}$, in order to decrease the damage induced by argon

ion sputtering. The XPS results were processed by a scienta300 data system.

3 Results and analysis

Figures 2 (a) and (b) show the surface pattern of PTCDA/ITO by AFM with ichnography and stereography, respectively. PTCDA molecules form island-like structures with a height of about 14nm. The sizes of the crystal grains are 100 ~ 300nm. According to the chemical structure of PTCDA, both the top and underside of PTCDA molecules are covered by a π electron cloud, in which a great deal of electrons can move freely a-

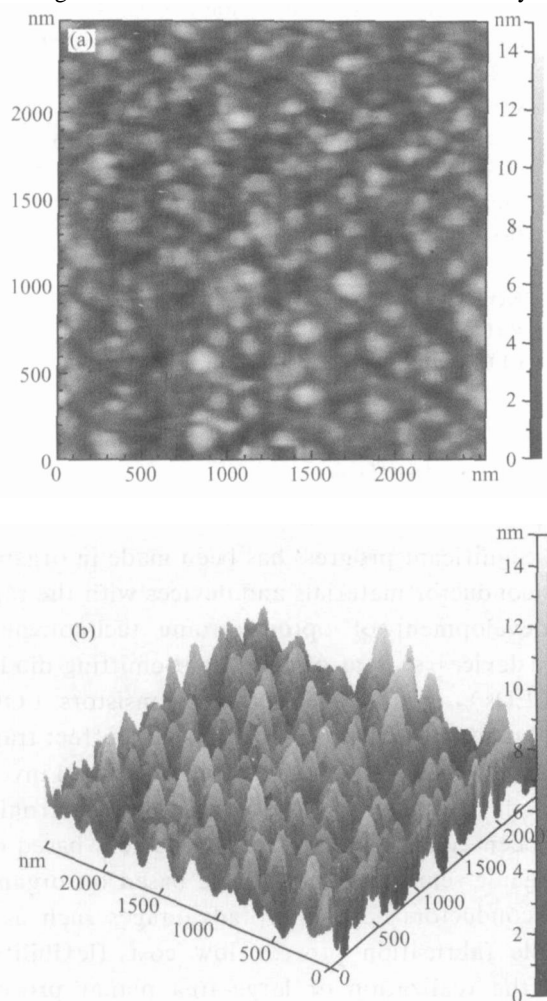


Fig. 2 AFM micrographs of the PTCDA/ITO surface (a) Ichnography; (b) Stereography

long the whole molecule. PTCDA molecules will exhibit transient polarity because of the transient asymmetry of π electrons, and produce an interaction force between PTCDA molecules in adjacent layers, leading

to a slight overlapping of electron clouds.

In ITO film, surface atoms are more active than bulk atoms because of close contact between crystal grains, and thus the concentration of In vacancies in the surface is much bigger than in the bulk. These electropositive vacancies will attract PTCDA molecules with transient polarity, so the combination of PTCDA molecules with surfaces with vacancies is stronger than with perfect surfaces. Thus, PTCDA molecules will first find these vacancies and combine with them. Small islands of PTCDA will first form at these vacancies and ultimately grow up to form an island-like pattern.

Figure 3 shows the whole XPS spectrum of the original surface of the PTCDA/ITO sample. Peaks associated with C1s, In3d, Sn3d, and O1s emerge at 285, 444, 490, and 532eV, respectively. The fact that the C1s peaks and O1s peaks are significantly stronger than the In3d peaks indicates a good coverage of PTCDA on the ITO surface with hardly any cracks.

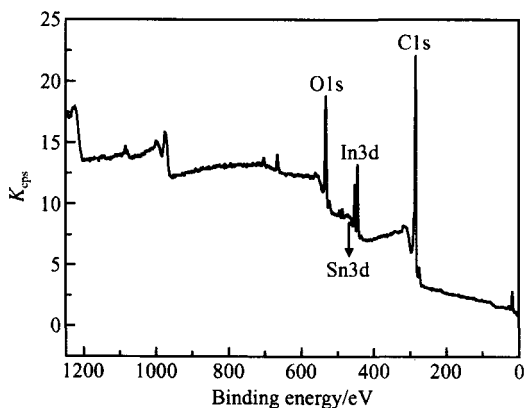


Fig. 3 Whole XPS spectrum at the raw surface of PTCDA/ITO

C1s, O1s, In3d, and Sn3d fine spectra of the PTCDA/ITO sample are given in Figs. 4 (a) ~ (d). One main peak at 284.6eV and two weak shoulder peaks, located at 288.7 and 290.4eV, are found in C1s spectrum. The peak at 284.6eV, which is activated by C atoms in the perylene rings, corresponds to the binding energy of aromatic C atoms (C atoms bonding with C atoms and H atoms)^[11,12]. It is known that the chemical shift of an element increases with the augment of the electronegativity value of the bonded atoms. The peak at 288.7eV, can be considered to be activated by C atoms in the acid anhydride

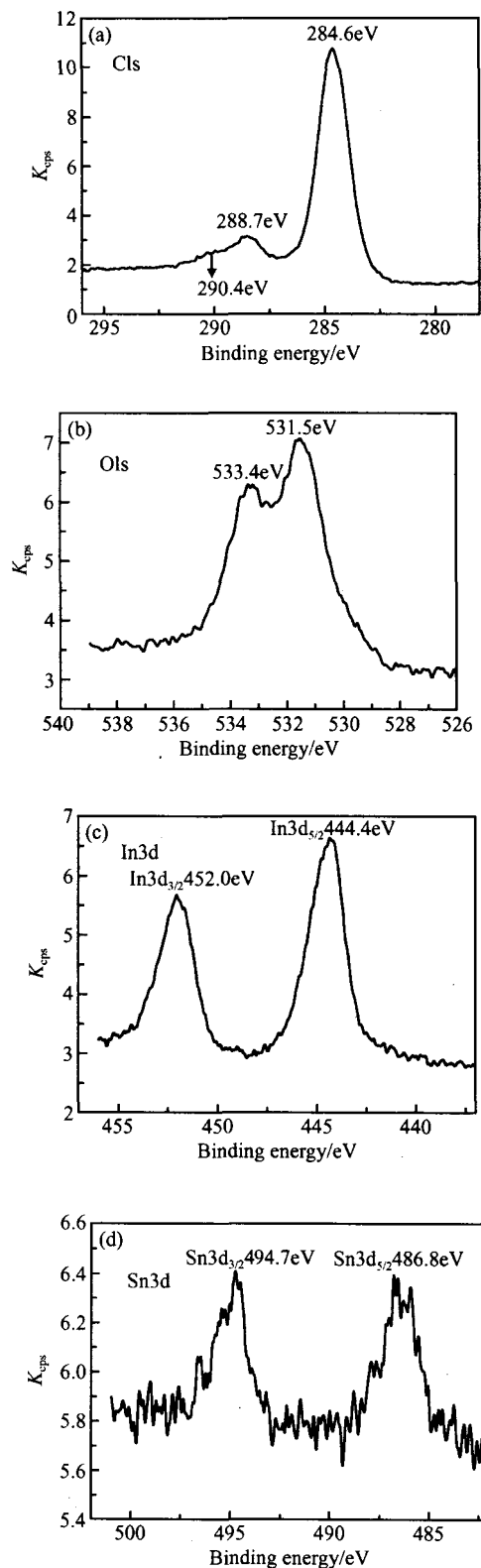


Fig. 4 Fine spectra at raw surfaces (a) C1s; (b) O1s; (c) In3d; (d) Sn3d

group^[13], where C atoms bond with O atoms. The existence of a weak peak at 290.4eV indicates a

slight oxidation of C atoms. The area ratio of the three peaks, located at 290.4, 288.7, and 284.6 eV, respectively, is 3 : 7 : 52. If the oxidized C atoms are added to the C atoms in the acid anhydride, the area ratio of the peaks is 1 : 5.2, which agrees with the ratio of the numbers of the two kinds of C atoms in perylene rings. It can be inferred that the oxidized C atoms come from the acid anhydride.

The fine spectrum of O1s is composed of two peaks, with a main peak at 531.5 eV and a shoulder peak at 533.4 eV. In PTCDA molecules, there are two kinds of O atoms, one which combines with C atoms through double bonds and one which combines with two C atoms through single bonds. Thus the two peaks at 531.5 and 533.4 eV correspond to O atoms in C=O bonds and C-O-C bonds, respectively.

Figure 5 shows the whole spectra and fine spectra of C1s, O1s, In3d, Sn3d at the PTCDA/ITO interface. The spectra of the original surface are also given in the figure for comparison. From Fig. 5 (a), C1s peaks are much weaker than in the original 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 in the original surface, indicating that most activated atoms in the interface come from ITO.

It can be seen from Fig. 5 (b) that the peak at high binding energy in the C1s spectrum disappears. Thus it can be inferred that only perylene rings are found at the PTCDA/ITO interface. Furthermore, the center of the main peak shifts about 0.3 eV to lower binding energy. It is reported

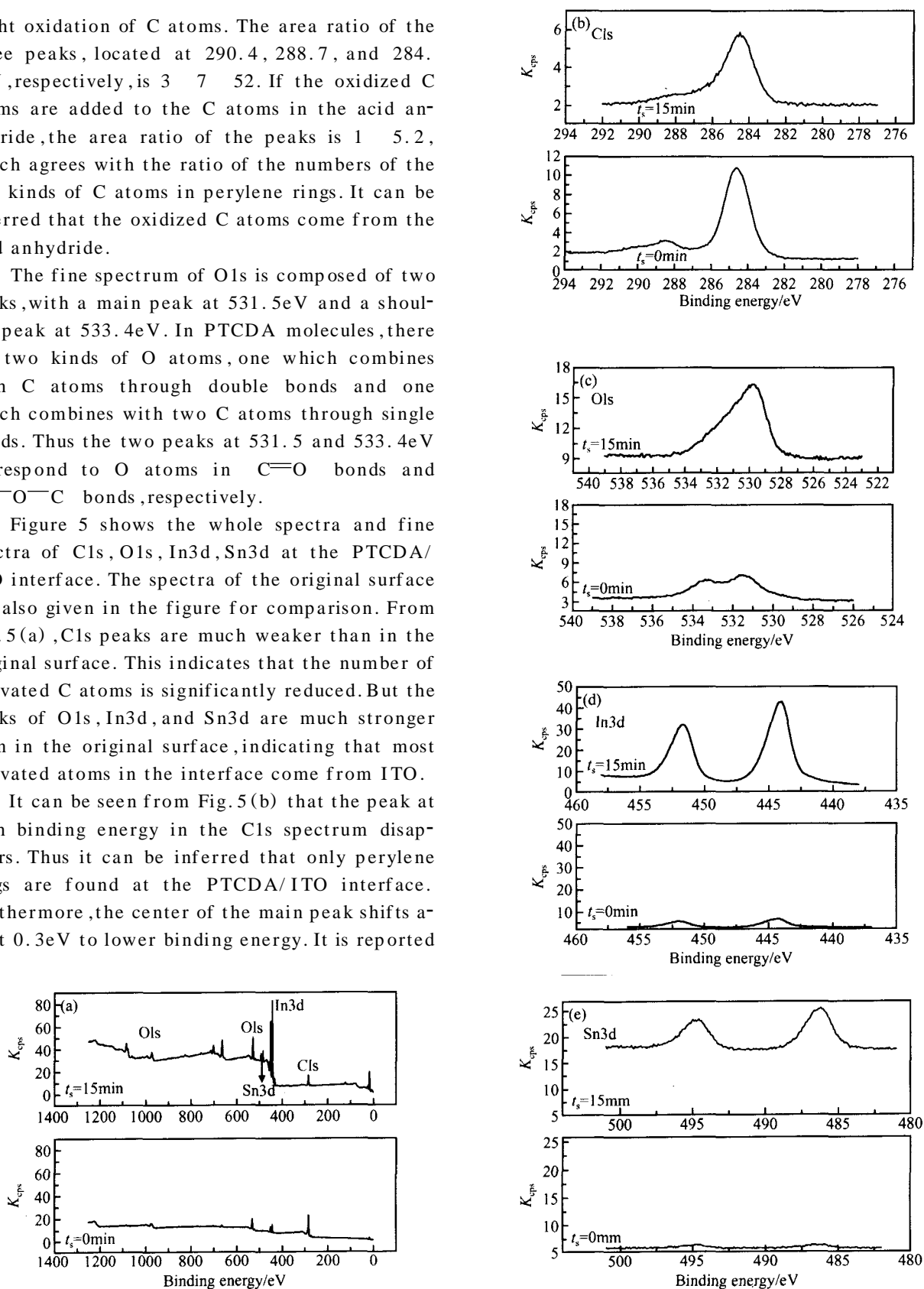


Fig. 5 Spectra at the interface (a) XPS whole spectrum; (b) C1s fine spectrum; (c) O1s fine spectrum; (d) In3d fine spectrum; (e) Sn3d fine spectrum

that there are many In vacancy defects^[14], with which PTCDA molecules tend to combine at the surface of ITO. As the binding energy between PTCDA and the defects is larger than that between PTCDA and a flawless surface, the C1s peaks shift to a lower binding energy. It can be concluded that perylene rings rather than PTCDA molecules combine with In vacancies in the ITO at the interface.

Figure 5(c) shows the O1s spectrum at the interface of the sample. A chemical shift of 1.5eV towards a lower binding energy is found. The binding energies of O atoms in In₂O₃ and SnO₂ are 529.8 and 530.1eV^[15], respectively, which are both much lower than in PTCDA molecules. Thus the activated O atoms at the interface come from the ITO rather than the acid anhydride. This fact further demonstrates that the combination of PTCDA and ITO is the combination of the perylene rings of PTCDA and ITO.

In3d and Sn3d spectra at the interface are given in Figs. 5(d) and (e), respectively. They both have an increase of peak area and a 0.4eV chemical shift toward lower binding energy. The reduction of O atoms in ITO, which is caused by the selective sputtering effect of argon ions^[15], leads to the chemical shift, because In₂O₃ and SnO₂ are partially deoxidized to suboxides, which have relatively lower binding energy.

4 Conclusion

In summary, we have investigated the electron states of the surface and interface of PTCDA/ITO in PTCDA/p-Si photodetectors. AFM results indicate that PTCDA molecules form an island-like film on the ITO. The binding energy of C atoms in perylene rings and acid anhydride are 284.6 and 288.7eV, respectively. Meanwhile, a slight oxidation of C atoms is found to be caused by O atoms from the ITO. At the interface, perylene rings, instead of PTCDA molecules, combine with In vacancies in ITO. This fact leads to the disappearance of the C1s peak at high binding energy and a chemical shift toward the lower binding energy of the C1s main peak. In the fine spectrum of O1s, peaks at 531.5 and 533.4eV correspond to O atoms in C=O bonds and C-O-C bonds, respectively. At the interface,

the O1s spectrum has a significant chemical shift to lower binding energy, due to the detachment of acid anhydride groups from PTCDA molecules at the interface.

References

- [1] Schön J H, Kloc C. Organic metal-semiconductor field-effect phototransistors. *Appl Phys Lett*, 2001, 78(22):3538
- [2] Huang Jinsong, Xie Zhiyuan, Yang Kaixia, et al. Highly bright yellow-emitting organic diode. *Chinese Journal of Semiconductors*, 2000, 21(1):76 (in Chinese) [黄劲松, 谢志元, 杨开霞, 等. 有机高亮度黄光发光二极管. *半导体学报*, 2000, 21(1):76]
- [3] Dimitrakopoulos C D, Purushothaman S, Kymissis J, et al. Low-voltage organic transistor on plastic comprising high-dielectric constant gate insulators. *Science*, 1999, 238:822
- [4] Wang Dongxing, Zhu Min, Kudo Kazuhiro, et al. Fabrication of organic semiconductor thin film transistor. *Chinese Journal of Semiconductors*, 2002, 23(6):463 (in Chinese) [王东兴, 朱敏, 工藤一浩, 等. 有机半导体薄膜三极管的研制. *半导体学报*, 2002, 23(6):463]
- [5] Tang C W, VanSlyke S A. Organic electroluminescent diodes. *Appl Phys Lett*, 1987, 51(12):913
- [6] Fuchigami H, Tanimura S, Uehara Y, et al. Deposited by organic molecular beam deposition method. *Jpn J Appl Phys*, 1995, 34:3852
- [7] Zhang Fujia, Shao Jiafeng, Zhang Dejiang. Preparation of organic semiconductor PTCDA and studies on its structure indication and specific property of light absorption. *Chinese Journal of Luminescence*, 1999, 20(4):351 (in Chinese) [张福甲, 邵佳峰, 张德江. 有机半导体 PTCDA 的制备及其结构表征和光吸收特性研究. *发光学报*, 1999, 20(4):351]
- [8] Mathine D L, Woo H S, He W, et al. Heterogeneously integrated organic light-emitting diodes with complementary metal-oxide-silicon circuitry. *Appl Phys Lett*, 2000, 76:3849
- [9] Liu S Y, Zhao Y, Li F. Advances in organic light-emission. *Physics*, 2003, 32(5):315
- [10] Kim H, Pique A, Horwitz J S, et al. Indium tin oxide thin films for organic light-emitting devices. *Appl Phys Lett*, 1999, 74:3444
- [11] Le Q T, Avenda F M, Forsythe E M, et al. X-ray photoelectron spectroscopy and atomic force microscopy investigation of stability mechanism of tris-(8-hydroxyquinoline) aluminum based light-emitting devices. *J Vac Sci Technol A*, 1999, 17(4):2314
- [12] Watts J F, Castle J E. The application of X-ray photoelectron spectroscopy to the study of polymer-to-metal adhesion. *J Mater Sci*, 1984, 19:2259
- [13] Arias A C, Roman L S, Kugler T, et al. The use of tin oxide thin films as a transparent electrode in PPV based light-emitting diodes. *Thin Solid Films*, 2000, 371:201
- [14] Wu C C, Wu C I, Sturm J C, et al. Surface modification of indium tin oxide by plasma treatment: an effective method to improve the efficiency, brightness, and reliability of organic light emitting devices. *Appl Phys Lett*, 1997, 70:1348
- [15] Wagner C D. *Hand book of X-ray and ultra-violet photoelectron spectroscopy*. London: Heyden, 1977

PTCDA/ITO 表面和界面的 AFM 和 XPS 分析*

欧谷平¹ 宋 珍² 桂文明¹ 张福甲^{1,†}

(1 兰州大学物理系, 兰州 730000)

(2 北京机械工业学院基础部, 北京 100085)

摘要: 利用 X 射线光电子能谱 (XPS) 对茈四甲酸二酐 [3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA)]/ 铟锡氧化物 (ITO) 表面和界面进行了研究. 用原子力显微镜 (AFM) 对 PTCDA/ITO 样品的表面形貌进行了分析. XPS 表明, 在原始表面的 C1s 精细谱存在两个主谱峰和一个伴峰, 主谱峰分别由结合能为 284.6eV 的花环中的 C 原子和结合能为 288.7eV 的酸酐基团中的 C 原子激发; 而结合能为 290.4eV 的伴峰的存在, 说明发生了来源于 ITO 膜中的氧对 C 原子的氧化现象. O 原子在 C=O 键和 C—O—C 键的结合能分别为 531.5 和 533.4eV. 在界面处, C1s 谱中较高结合能峰消失, 且峰值向低结合能方向发生 0.2eV 的化学位移; O1s 谱向低结合能方向发生 1.5eV 的化学位移. 由此可以推断, 在界面处 PTCDA 与 ITO 的结合是 PTCDA 中的花环与 ITO 中的 In 空位的结合. AFM 的结果显示, PTCDA 薄膜为岛状结构, 岛的直径约为 100~300nm, 表面起伏约为 14nm. 相邻两层 PTCDA 分子由于存在离域大 π 键而交叠和 PTCDA 分子中的花环与 ITO 的 In 空位的紧密结合是最终导致 PTCDA 岛状结构形成的原因.

关键词: 原子力显微镜; X 射线光电子能谱; PTCDA

PACC: 6116P; 2930K; 165

中图分类号: TN304

文献标识码: A

文章编号: 0253-4177(2006)02-0229-06

* 国家自然科学基金(批准号:60276026)和甘肃省自然科学基金(批准号:ZS031-A25-012-G)资助项目

† 通信作者. Email: prof_zhangfj@sina.com

2005-08-23 收到, 2005-10-24 定稿

© 2006 中国电子学会