Influence of oxygen plasma treatment on the surface properties of indium-tin oxide thin films

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Abstract The surfaces of indium-tin oxide (ITO) thin films were modified by oxygen plasma discharge. The effect of oxygen plasma treatment on the surface properties of ITO films and the changes in surface properties of treated ITO films with the ageing time were investigated through the measurements of chemical composition, contact angle, surface energy and polarity. Experimental results show that oxygen plasma treatment improves the stoichiometry of ITO surface, increases the surface energy and polarity, and enhances surface wettability of ITO, so as to improve the surface properties of ITO owing to the effective removal of the contaminants of the ITO surface. In addition, with the increment of ageing time after oxygen plasma treatment, the improved stoichiometry, surface energy and polarity of the ITO surface tend to decay, and the optimized ITO surface properties become worse and worse.

Keywords indium-tin oxide, oxygen plasma treatment, surface properties
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氧气等离子体处理对铟锡氧化物薄膜表面性质的影响

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摘 要 采用氧气等离子体处理对铟锡氧化物(ITO)薄膜进行表面改性,基于化学组分、接触角、表面能和极性度的测试表征,研究了氧气等离子体处理对 ITO 表面性质的影响以及表面性能随放置时间的变化.实验结果表明:氧气等离子体处理有效去除了 ITO 表面的污染物,改善了 ITO 表面的化学组分、提高了表面能、极性度和润湿性,从而优化了 ITO 的表面性能.但是随着处理后放置时间的增加,ITO 薄膜的表面能减小、极性度降低、润湿性退化,从而相应的表面性能也变差.

关键词 铟锡氧化物; 氧气等离子体处理; 表面性质

Indium-tin oxide (ITO) is a commonly used substrate for the construction of organic optoelectronic devices because ofits unique characteristics for instance low electric resistivity, high visible transmittance, excellent adhesion to substrates, chemical stability and easy patterning ability[1-3]. It is well known that the organic light-emitting device (OLED) usually consists of a sandwich structure with the organic thin film

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deposited onto the ITO transparent anode and covered by patterned top metal cathode contacts[4-8]. Since the organic thin film is in direct contact with the ITO anode, the surface characteristics of the ITO anode plays an important role in improving the OLED performance. Many studies have been reported on modifying the surface properties of the ITO. They include annealing process[9-11], oxygen or argon plasma[12-14], oxygen glow discharge[15], ultraviolet-ozone clearing[16,17], electro-chemical treatment[18], acid and base adsorption[19], SF_6 plasma[20], low energy ion beam treatment[21], and coating treatment with self-assembled monolayers[22,23]. Among them, oxygen plasma was considered as a promising and efficient treatment because it results in the highest work function, the lowest sheet resistance, and the smoothest surface[13,14]. In this work, oxygen plasma treatment was carried out on the ITO substrates. The influence of oxygen plasma treatment on the surface properties of ITO films and the changes in surface properties of treated ITO samples with the ageing time were studied by X-ray photoelectron spectroscopy (XPS), contact angle and surface energy measurements.

1 Theoretical

Surface energy is a direct manifestation of intermolecular forces. The surface of a solid, like that of a liquid, possesses additional free energy, but owing to the reduced molecular mobility this free energy is not directly observable, and it must be measured by indirect methods.

When a liquid drop is in contact with an ideally smooth, homogeneous, planar, and nondeformable surface, it exhibits an equilibrium contact angle that can be expressed by Young's equation[24]:

$$\gamma_L \cdot \cos\theta = \gamma_S - \gamma_{SL}, \quad (1)$$

where γ_L is the surface tension of the liquid, γ_S the surface energy of the solid, γ_{SL} the interfacial tension between the solid and the liquid, and θ the equilibrium contact angle formed by the liquid on the solid.

It was proposed that thesurface energy (γ) is composed of two components[24]: the polar component (γ^p) including three different intermolecular forces due to permanent and induced dipoles, and hydrogen-bonding, whereas the dispersion component (γ^d) is due to instantaneous dipole moments. Their relationship is given by the following equation:

$$\gamma = \gamma^p + \gamma^d, \quad (2)$$

The work of adhesion between the solid and the liquid (the negative of the Gibbs energy of adhesion), W_a, can be expressed by the Dupré equation:

$$W_a = \gamma_S + \gamma_L - \gamma_{SL}, \quad (3)$$

The Young-Dupré equation, therefore, is achieved by combining Eqs. (1) and (3):

$$W_a = \gamma_L \cdot (1 + \cos\theta), \quad (4)$$

This equation implies that the solid-liquid work of adhesion can be simply calculated from liquid surface tension and contact angle measurements.

According to the theory of fractional polarity[24], the work of adhesion between the solid and the liquid can also be expressed by the following equation:

$$W_a = 4\left(\frac{\gamma_S^p \cdot \gamma_L^p}{\gamma_S^p + \gamma_L^p} + \frac{\gamma_S^d \cdot \gamma_L^d}{\gamma_S^d + \gamma_L^d}\right), \quad (5)$$

Combination of the above with Eq. (4) yields

$$\gamma_L \cdot (1+\cos\theta) = 4\left(\frac{\gamma_S^p \cdot \gamma_L^p}{\gamma_S^p + \gamma_L^p} + \frac{\gamma_S^d \cdot \gamma_L^d}{\gamma_S^d + \gamma_L^d}\right), \quad (6)$$

Equation (6), known as the harmonic-mean approach, is one of the approaches of estimate the solid surface energy. The two components (γ_S^p, γ_L^p) of surface energy of any solid (γ_S) can be obtained by measuring the contact angles (θ_1, θ_2) of the two testing liquids (with known surface tension of γ_1 and γ_2) on the solid surface and solving the two simultaneous equations:

$$\gamma_1 \cdot (1+\cos\theta_1) = 4\left(\frac{\gamma_S^p \cdot \gamma_1^p}{\gamma_S^p + \gamma_1^p} + \frac{\gamma_S^d \cdot \gamma_1^d}{\gamma_S^d + \gamma_1^d}\right), \quad (7)$$

$$\gamma_2 \cdot (1+\cos\theta_2) = 4\left(\frac{\gamma_S^p \cdot \gamma_2^p}{\gamma_S^p + \gamma_2^p} + \frac{\gamma_S^d \cdot \gamma_2^d}{\gamma_S^d + \gamma_2^d}\right), \quad (8)$$

After having obtained the polar component (γ_S^p) and the dispersion component (γ_S^p), the total surface

energy (γ_S) and polarity (χ_p) of the solid can be readily achieved according to the following formulae:

$$\gamma_S = \gamma_S^p + \gamma_S^d, \quad (9)$$

$$\chi_p = \frac{\gamma_S^p}{\gamma_S}. \quad (10)$$

2 Experimental

2.1 Sample preparation

Commercial ITO-coated glasses with film thickness and sheet resistance of 150 nm and 30Ω/sq respectively were used and cut into 3.0 cm×3.0 cm plates in this experiment. Prior to their use, the ITO samples were routinely cleaned by rubbing in a detergent, rinsing in deionized water, successive ultrasonification with acetone and isopropanol each for 15 min, and finally dried in a flow of nitrogen. Then, the ITO samples were modified using oxygen plasma discharge (oxygen purity was 99.999%) at room temperature. The reaction chamber was evacuated to 10 Pa pressure and the working pressure during the plasma discharge was about 15 Pa. The gas flow rate, the discharge power and the treatment duration were 20 sccm, 35 W and 6 min, respectively.

2.2 Surface analysis

The XPS measurements were carried out by a XSAM-800 X-ray photoelectron spectrometer, using a monochromatic Al Kα ($h\nu$ = 1486.60 eV) as X-ray source. Typically the operating pressure in the analysis chamber was about 2×10^{-7} Pa. All binding energies were referenced to the binding energy of the carbon C 1s peak at 285.0 eV. For the calculation of the atomic concentrations, a linear background correction was done, and the peak areas were corrected with empirical sensitivity factors, the instruments transmission function and the specific mean free path lengths [23].

The contact angles were measured by the sessile drop technique [24] using a JY-82 type contact angle analyzer at 20° C in an environmental chamber. The reported values of contact angles are the mean of five measurements. Distilled water (H_2O) and methylene iodide (CH_2I_2, from Beijing Chemical Reagents Company) were used as the probe liquids [23], and their surface tension and surface tension components are listed in Table 1.

Tab.1　The surface tension components of probe liquids

表 1　测试液体的表面张力参数

Surface tension (mN/m)	γ_L^p	γ_L^d	γ_L
H_2O	50.7	22.1	72.8
CH_2I_2	6.7	44.1	50.8

3 Results and discussion

3.1 XPS analysis

Fig.1 shows the high-resolution O 1s XPS spectra for the ITO samples. The O 1s XPS spectrum exhibits an asymmetric peak that was fitted to two components: the main peak O(1) centred at about 530.4 eV can be assigned to O^{2-} ions in the tetrahedral interstices of the face-centred-cubic In^{3+} ion array, while the shoulder peak O (2) centred at about 532.0 eV is due to residual surface contaminants [24].

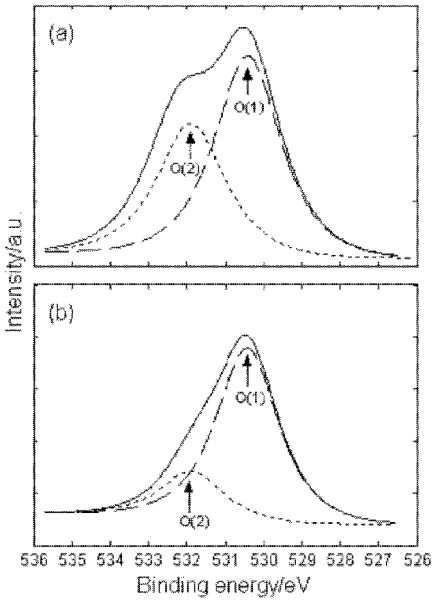

Fig.1　O 1s high-resolution XPS spectra for (a) untreated and (b) treated ITO samples

图 1　处理前后 ITO 样品 O 1s 的 XPS 能谱

The intensity of O (2) for the treated ITO is observed to largely decrease compared to that of the non-treated ITO, indicating the oxygen plasma treatment effectively removes the contaminants from the

ITO surface. The XPS analysis results of the ITO samples are summarized in Table 2. Note that the ratios of O/In and C/In respectively change from 1.132 and 0.342 on the non-treated ITO to 1.929 and 0.129 on the treated ITO, while the Sn/In ratio is hardly changed by the plasma discharge, remaining near 0.160. This means the oxygen plasma treatment used here does not etch the ITO surfaces. Note also that besides containing the elements of In, Sn and O, the carbon element also exists on the ITO samples, suggesting that carbon is the only major contaminant. Similar results have also been reported in the previously literatures [12,13,26]. The concentrations of In, Sn, O and C on ITO surface are observed to change from 38.0, 6.0, 43.0, 13.0 at.% to 31.0, 5.2, 59.8, 4.0 at.% respectively after the plasma discharge. The result demonstrates that the oxygen plasma treatment largely increases the oxygen concentration and decreases the carbon concentration, and improves the surface stoichiometry, and thereby effectively enhances the work function of the ITO, since the ITO work function is determined by the oxygen composition or by the carbon concentration [27-29].

Tab.2 XPS analysis results of the ITO surfaces

表2 ITO样品表面的XPS分析结果

ITO sample	Chemical composition/at.%				Ratio		
	In	Sn	O	C	Sn/In	O/In	C/In
untreated	38.0	6.0	43.0	13.0	0.158	1.132	0.342
treated	31.0	5.2	59.8	4.0	0.167	1.929	0.129

Fig. 2 gives the evolution of chemical composition of ITO surfaces as a function of the time after plasma discharge. As can be seen, the concentrations of In, O and C are affected by the elapsed time after plasma discharge, except Sn concentration is not changed. The marked changes in the concentrations of In, O and C can be observed within 2 h after the plasma discharge. After 21 h, rather little change is found and the concentrations of In, O and C exhibit to reach the plateau values of 37.5, 43.9 and 12.7 at.%, respectively. The change in chemical composition of treated ITO surface probably results from the partial release of plasma-introduced oxygen from the ITO surface and the re-contamination of the surface by hydrocarbons in air during the elapsed time after the plasma discharge. The results indicate that the improvement in the surface stoichiometry due to the plasma discharge is not stable.

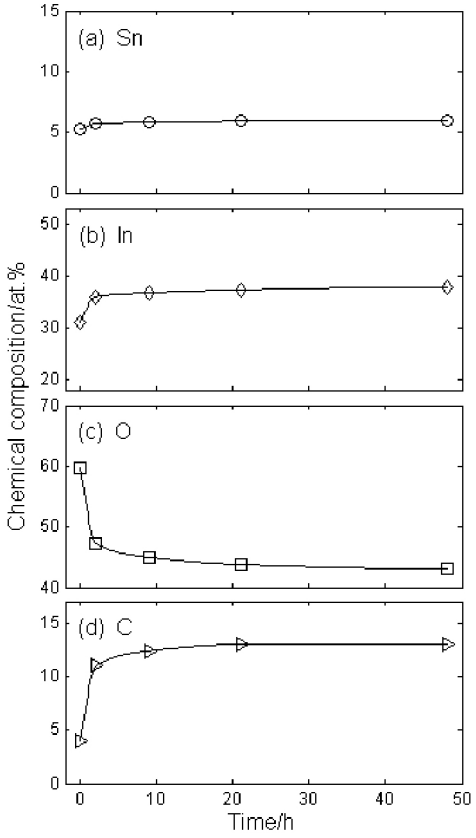

Fig.2 Chemical composition as a function of the time after plasma discharge for the treated ITO samples

图2 处理后ITO表面化学组分随时间变化的曲线

3.2 Surface wettability

Fig.3 shows the contact angle as a function of the time after plasma discharge for the treated ITO samples. As can be seen, the oxygen plasma discharge brings about a large decrease in contact angle. The H_2O contact angle θ_1 is decreased from 67.2° to 20.1°,

and the CH_2I_2 contact angle θ_2 from 51.6° to 35.5°, indicating that the treated ITO surface appears to be highly polar.

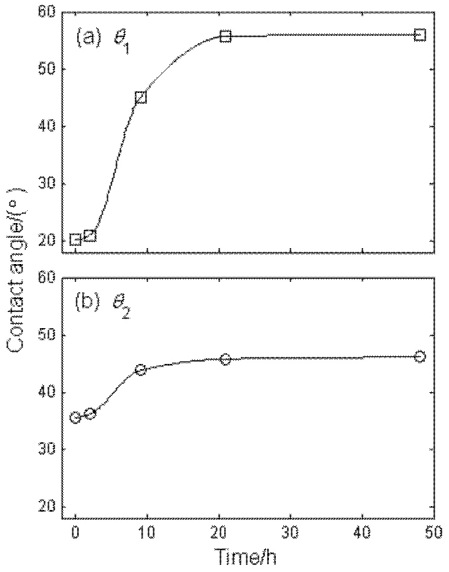

Fig.3　Contact angle as a function of the time after plasma discharge for the treated ITO samples

图 3　处理后 ITO 表面上接触角随时间变化的曲线

Fig.4 and Fig.5 present the surface energy and polarity as a function of the time after plasma discharge for the treated ITO samples. The surface energy (γ_S) and its components (γ_S^p, γ_S^d), and polarity (χ_p) can be observed to increase owing to the oxygen plasma discharge. The values of γ_S, γ_S^p, γ_S^d are increased from 42.9, 18.6, 24.3 mJ/m^2 to 70.1, 41.7, 28.4 mJ/m^2, respectively, and the χ_p value from 0.43 to 0.60. Obviously, the increased surface energy γ_S and surface polarity γ_p are mainly due to the significantly enhanced polar component γ_S^p (from 18.6 to 41.7 mJ/m^2). The high value of γ_S^p represents a strong polar interaction, which would improve adhesion. Therefore, the oxygen plasma discharge is considered as an effective method in improving ITO surface properties. We propose that the increase of the surface energy and polarity is due to several reasons [30-32]. One reason is the improvement of the surface stoichiometry, since oxygen plasma discharge introduces oxygen and increases the oxygen concentration, and meanwhile effectively removes the hydrocarbon contaminants from the ITO surface so as to reduce the carbon concentration. The second reason is the increase of water concentration that is physi- and/or chemisorbed on the surface. The third possible reason is that organic contamination may become more hydrophilic after the oxygen plasma discharge.

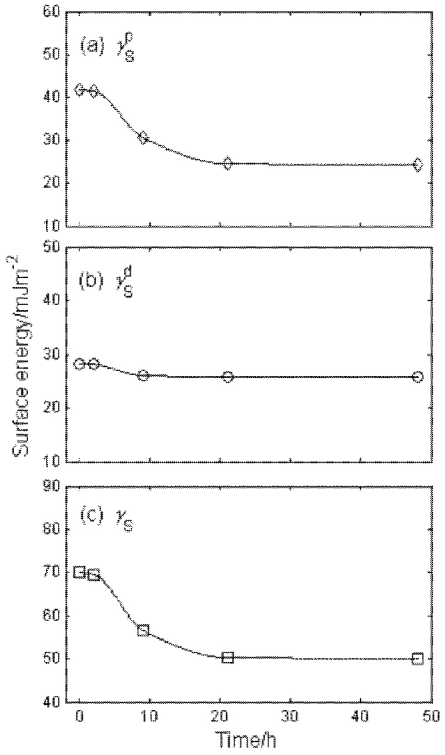

Fig.4　Surface energy as a function of the time after plasma discharge for the treated ITO samples

图 4　处理后 ITO 表面能随时间变化的曲线

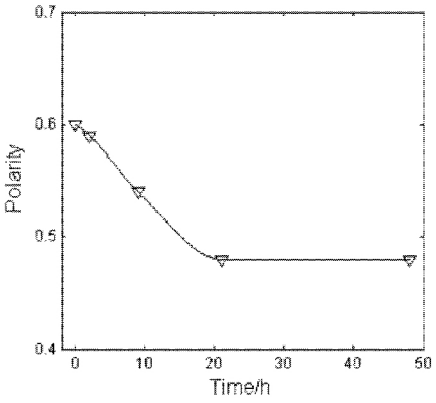

Fig.5　Polarity as a function of the time after plasma discharge for the treated ITO samples

图 5　处理后 ITO 表面极性度随时间变化的曲线

4　Conclusion

In this study, the ITO surfaces were treated by the oxygen plasma discharge. The surface properties of ITO

films were investigated through the measurements of XPS, contact angle, surface energy and polarity. Experimental results reveal that the oxygen plasma discharge improves the stoichiometry of the surface and enhances the surface wettability of ITO, so as to optimize the surface properties of ITO substrates. And the improved surface properties benefited from the oxygen plasma discharge is observed to decay with the increase of the time after plasma discharge. The difference in chemical composition, surface energy and polarity between the untreated and treated ITO surfaces appears to become smaller with the increased time after the plasma discharge. The plasma effects were re-treated 21 h after storage, indicating that re-contamination occurred on the surfaces.

References

[1] KIM D H, LEE W H, JESURAJ P J, et al. Improved charge balance in phosphorescent organic light-emitting diodes by different ultraviolet ozone treatments on indium tin oxide [J]. Org Electron, 2018, 61: 343-350.

[2] REZAIE M N, MANAVIZADEH N, NAYERI F D, et al. Effect of seed layers on low-temperature, chemical bath deposited ZnO nanorods-based near UV-OLED performance [J]. Ceram Int, 2018, 44: 4937-4945.

[3] SHEKARGOFTAR M, KRUMPOLEC R, HOMOLA T. Enhancement of electrical properties of flexible ITO/PET by atmospheric pressure roll-to-roll plasma [J]. Mater Sci Semicond Process, 2018, 75: 95-102.

[4] TANG C W, VANSLYKE S A. Organic electroluminescent diodes [J]. Appl Phys Lett, 1987, 51: 913-915.

[5] REMYA R, DEB B. Ultrathin organic spin-on layers on indium tin oxide as a prospective tool for enhanced light throughput [J]. Mater Lett, 2017, 186: 220-223.

[6] BURROUGHES H J, BRADLEY D D C, BROWN A R, et al. Light-emitting diodes based on conjugated polymers [J]. Nature, 1990, 347: 539-541.

[7] SIRRINGHAUS H, TESSLER N, FRIEND R H. Integrated optoelectronic devices based on conjugated polymer [J]. Science, 1998, 280: 1741-1744.

[8] TAHA H, JIANG Z-T, HENRY D J, et al. Improving the optoelectronic properties of titanium-doped indium tin oxide thin films [J], Semicond Sci Technol, 2017, 32: 65011-65016.

[9] JUNG S, PARK N G, KWAK M Y. Surface treatment effects of indium-tin oxide in organic light-emitting diodes [J]. Opt Mater, 2003, 21: 235-241.

[10] LIAO W, CHANG H, YANG Y, et al. Oxygen-deficient indium tin oxide thin films annealed by atmospheric pressure plasma jets with/without air-quenching [J]. Appl Surf Sci, 2014, 292: 213-218.

[11] NGUYEN T P, LE Rendu P, DINH N N, et al. Thermal and chemical treatment of ITO substrates for improvement of OLED performance [J]. Synth Met, 2003, 138: 229-232.

[12] KIM J Y, LEE D, KIM J, et al. Effects of H_2/O_2 mixed gas plasma treatment on electrical and optical property of indium tin oxide [J]. Appl Surf Sci, 2013, 265: 145-148.

[13] KIM J S, FRIEND R H, CACIALLI F. Improved operational stability of polyfluorene-based organic light-emitting diodes with plasma-treated indium-tin-oxide anodes [J]. Appl Phys Lett, 1999, 74: 3084-3086.

[14] J1IM S, GRANSTROM M, FRIEND R H, et al. Indium-tin-oxide treatments for single and double-layer polymeric light-emitting diodes: the relation between the anode physical, chemical, and morphological properties and the device performance [J]. J Appl Phys, 1998, 84: 6859-6870.

[15] FANG M, ZHANG C, CHEN Q. Tuning the ITO work function by capacitively coupled plasma and its application in inverted organic solar cells [J]. Appl Surf Sci, 2016, 385: 28-33.

[16] YAMASHITA D, ISHIZAKI A, YAMAMOTO T. In situ measurements of work function of indium tin oxide after UV/ozone treatment [J]. Appl Phys Lett, 2015, 105: 1445-1447.

[17] SO S K, CHOI W K, CHENG C H, et al. Surface preparation and characterization of indium tin oxide substrates for organic electroluminescent devices [J]. Appl Phys A, 1999, 68: 447-450.

[18] KIM M, KIM J, CHO J, et al. A study of the characteristics of indium tin oxide after chlorine electro-chemical treatment [J]. Mater Res Bull, 2016, 82: 115-121.

[19] NUESCH F, ROTHBERG L J, FORSYTHE E W, et al. A photoelectron spectroscopy study on the indium tin

oxide treatment by acids and bases [J]. Appl Phys Lett, 1999, 74: 880-882.

[20] CHOI B, YOON H, LEE H H. Surface treatment of indium tin oxide by SF_6 plasma for organic light-emitting diodes [J]. Appl Phys Lett, 2000, 76: 412-414.

[21] QIU Y, ZHANG D Q, WANG L D, et al. Performance improvement of organic light emitting diode by low energy ion beam treatment of the indium tin oxide surface [J]. Synth Met, 2002, 125: 415-418.

[22] LEE S J, KIM Y, HWANG J, et al. Flexible indium-tin oxide crystal on plastic substrates supported by graphene monolayer [J]. Scientific Reports, 2017, 5: 1-8.

[23] ZHENG H, ZHANG F, ZHOU N, et al. Self-assembled monolayer-modified ITO for efficient organic light-emitting diodes: the impact of different self-assemble monolayers on interfacial and electroluminescent properties [J]. Org Electron, 2018, 56: 89-95.

[24] WU S. Polymer Interface and Adhesion [M]. New York: Marcel Dekker, 1982.

[25] BRIGGS D, SEAH M P. Practical surface analysis by Auger and X-ray photoelectron spectroscopy [M]. New York: John Wiley & Sons Ltd, 1983.

[26] ZHONG Z Y, JIANG Y D. Surface modification and characterization of indium-tin oxide for organic light-emitting devices [J]. J Colloid Interface Sci, 2006, 302: 613-619.

[27] YOU Z Z, HUA G J. Luminescent and electrical performance of polymer light-emitting electrochemical cells with treated indium-tin-oxide electrodes [J]. Int J Electron, 2010, 97: 99-104.

[28] SONG W, SO S K, CAO L. Angular-dependent photoemission studies of indium tin oxide surfaces [J]. Appl Phys A, 2001, 72: 361-365.

[29] ZHONG Z Y, JIANG Y D. Surface treatments of indium-tin oxide substrates for polymer electroluminescent devices [J]. Phys Stat Sol A, 2006, 203: 3882-3892.

[30] KIM J S, HO P K H, THOMAS D S, et al. X-ray photoelectron spectroscopy of surface-treated indium-tin oxide thin films [J]. Chem Phys Lett, 1999, 315: 307-312.

[31] ISHII M, MORI T, FUJIKAWA H, et al. Improvement of organic electroluminescent device performance by in situ plasma treatment of indium-tin-oxide surface [J]. J Lumin, 2000, 87-89: 1165-1167.

[32] YI C H, JEONG C H, LEE Y H, et al. Oxide surface cleaning by an atmospheric pressure plasma [J]. Surf Coat, Technol, 2004, 177-178: 711-715.

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