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Influence of electrochemical treatment of ITO surface on nucleation and growth of OLED hole transport layer

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ABSTRACT

Indium–tin–oxide (ITO) surfaces were electrochemically treated with voltages from 0 to +2.8 V in 0.1 M $K_4P_2O_7$ electrolyte. The initial growth mode of hole transport layer (HTL) was investigated by atomic force microscope (AFM) observation of thermally deposited 2 nm N,N-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) on the electrochemically treated ITO surfaces. The results showed that the morphology of NPB thin film was significantly influenced by the treating voltage via the change in surface energy, especially the polar component. The treatments with +2.0 and +2.4 V were found to be most effective for more uniform and denser nucleation of NPB. The influence of the electrochemical treatments on the nucleation and growth mode of HTL and therefore the device performance were discussed.

1. Introduction

Indium–tin–oxide (ITO) is commonly used as an anode in organic light emitting diodes (OLEDs) due to its high conductivity, transparency in visible wavelength range, wide energy band gap and relatively high work function. The devices fabricated from pristine ITO, however, were found to have problems as a hole injection anode, such as shorting, unstable I-V characteristics and indium diffusion into the organic layers after device operation. These problems can cause degradation in device performance [1]. To mitigate these problems, various surface treatment processes have been adopted to modify the ITO surface properties, such as UV ozone [2,3], gas plasma [4–6], acids [7,8], hydrogen peroxide [9], and electrochemistry [10]. Among these methods, the oxidative treatments were found to be most effective in improving OLED device performance in terms of driving voltage, efficiency, and stability.

The work function hypothesis was often used to explain the mechanisms behind the surface treatments, in particular to explain the reduced device driving voltage [11–15]. Besides the work function, other surface properties have also been found to play an important role in controlling the device performance [5–17]. It was reported that the increased surface energy would provide a better adhesion of the polymer layer and reduce the interfacial tension between polymer and substrate [6]. This would lead to an improved charge carrier injection through the interface, and thereby the OLED performance due to the better electronic contact between the two materials. Other experimental results [18,19] showed that the devices fabricated on ITO substrates with similar work functions but different surface morphologies (e.g. roughness) exhibited markedly different performance. Chen et al. [19] recently reported their experimental results using different hole injection layers (HILs) with different levels of highly occupied molecular orbital (HOMO), and concluded that the energy barrier difference between the ITO/HIL interface was not the main factor in determining the hole injection efficiency from the ITO anode to HIL. Instead, they proposed that the morphology of HIL and therefore the contact between HIL and hole transport layer (HTL) would play a decisive role in the device performance. Therefore, more experimental work is needed to further understand the mechanisms behind the improved device performance by surface treatments.

Our previous work [20] shows that plasma treatment of ITO surface imposes an influence on OLED performance through changing surface energy that controls the nucleation and growth of the HTL. In this study, ITO surface was electrochemically treated with varied voltages from 0 to +2.8 V in $K_4P_2O_7$ electrolyte. The initial growth mode of HTLs was investigated by atomic force microscope (AFM) observation of thermally deposited 2 nm thick N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) layers on the electrochemically treated ITO surfaces. The results reveal that the morphology of NPB on the ITO surface is highly correlated to the treating voltage via the change of surface energy, especially the polar component. A more uniform NPB thin film was obtained on the ITO surfaces electrochemically treated at +2.0 V and +2.4 V, which is corresponding to the improved device performance. The findings suggest that the performance enhancement is a consequence of the high quality interface between ITO surface and HTL.

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2. Experiment

ITO-coated glass substrates (Präzisions Glas & Optik GmbH) with an initial sheet resistance of 20Ω/ were used for surface treatment and analysis. After the routine cleaning process, involving a sequence of sonication in detergent solution, ethanol and de-ionized (DI) water, the ITO glass samples were electrochemically treated in 0.1 M $K_4P_2O_7$ (97%, Aldrich Chem. Co.) electrolyte [10]. In this process, a platinum plate was used as the cathode and the ITO substrate as the anode. Voltages of 0, + 1.2, + 1.6, + 2.0, + 2.4, and + 2.8 V were applied to the respective ITO substrates in the electrolyte for 30 s. For comparison, an ITO sample was immersed in the same electrolyte albeit in the absence of an applied voltage, which was referred to as the 0 V sample. All the treated samples were thoroughly rinsed, via sonication in DI water, to remove the residual electrolyte, before being dried with a nitrogen stream.

Surface energy values of the treated and untreated ITO surfaces, as a sum of dispersion and polar components, were calculated by using geometric-mean method from the contact angles measured with water and glycerol [10,20]. 2 nm thick NPB ultra thin films were deposited on both treated and untreated ITO surfaces by thermal evaporation at a deposition rate of 0.2 nm/s and a pressure of 1×10^{-4} Pa in one vacuum run. The surface morphology of the ultra thin NPB films on ITO surfaces was studied using a Digital Instruments Nanoscope IIIA AFM. The images for the morphological studies had a scan size of $1\times1\ \mu m^2$. Non-contact AFM with tapping mode was used, as the contact mode could result in physical distortion of the organic films due to its constant force applied. All AFM results were shown in phase mode to provide a clearer picture of the organic film morphology.

3. Results and discussion

Table 1 summarizes the surface energies of ITO samples electrochemically treated at different voltages, including energy components, total surface energy, and polarity that is defined as the ratio of the polar component to total surface energy [6]. The results show that the more hydrophilic surfaces (with lower water contact angles) are corresponding to the higher surface polarities, and that the total surface energy of ITO surface is remarkably increased from 52.9 mJ/m^2 of the untreated sample to 72.9 and 72.1 mJ/m^2 of the samples treated at + 2.0 and + 2.4 V, respectively.

As-deposited ITO film by DC magnetron sputtering features with a so called "grain–subgrain" surface morphology and polycrystalline structure, as shown in Fig. 1(a) (height mode) or 1(b) (phase mode). Each "grain" (200–600 nm in size) consists of a cluster of 10–40 nm sized subgrains, which are highly aligned in crystalline orientation. More discussions on their crystallinity features were reported in literature [21].

Fig. 2 shows the phase AFM images of 2 nm NPB thin film deposited on the ITO surfaces treated by 0 V (a), + 1.2 V (b), + 1.6 V (c), + 2.0 V (d), + 2.4 V (e), and + 2.8 V (f), respectively. It can be seen that the surface coverage with 2 nm thick NPB highly depends on the treating voltage. The + 2.0 V treated sample has the highest coverage, followed by + 2.4 V, + 1.6 V, 0 V, + 1.2 V, and + 2.8 V.

Table 1
Surface energies and polarities of ITO samples pre-treated at different voltages, based on contact angle measurement and calculation by geometric-mean method.

Sample	Contact angle (°)		γ_s^p (mJ/m)^2	γ_s^d (mJ/m)^2	$\gamma_s=\gamma_s^p+\gamma_s^d$ (mJ/m)^2	$\chi_P=\gamma_s^p/\gamma_s$
	Water	Glycerol				
0.0 V	49.4	35.2	24.1	28.8	52.9	0.46
1.2 V	51.5	36.8	22.2	29.6	51.8	0.43
1.6 V	23.8	18.9	47.8	18.9	66.8	0.72
2.0 V	16.9	29.7	63.6	9.4	72.9	0.87
2.4 V	13.8	21.9	59.1	13.0	72.1	0.82
2.8 V	50.2	34.4	22.3	30.9	53.2	0.42

The total surface energy γ_s is the sum of the polar (γ_s^p) and dispersion (γ_s^d) components ($\gamma_s=\gamma_s^p+\gamma_s^d$) and the polarity χ_P is the ratio of the polar component to the total surface energy ($\chi_P=\gamma_s^p/\gamma_s$) [6].

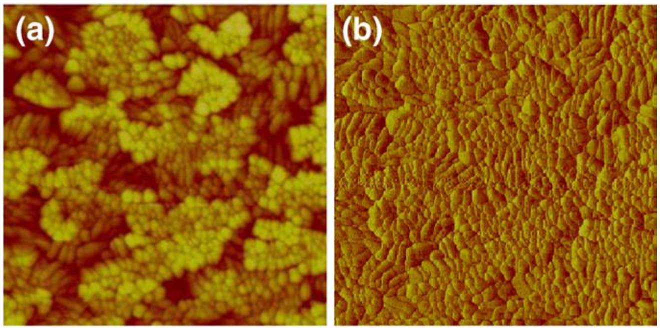

Fig. 1. AFM image of as-clean ITO thin film deposited by dc magnetron sputtering: (a) height mode and (b) phase mode.

Island-like morphology is observed for all the electrochemically treated ITO surfaces, although there are differences in shape and distribution. Basically, the NPB islands discontinuously distribute along grain and/or subgrain boundaries, but the surfaces are clearly differentiated by the fraction of surface coverage, in an order of + 2.0 V > + 2.4 V > + 1.6 V > 0 V > + 1.2 V > + 2.8 V. It is obvious that + 2.0 V and + 2.4 V treatments lead to more uniform NPB thin film coverage on the ITO surface without significant conglomeration. In comparison, the + 2.0 V treatment is preferred due to the resulted higher subgrain coverage. Considering the fact that deposition rate and substrate temperature strongly influence the surface morphology of organic films [22,23], the deposition of NPB on all the ITO samples was carried out in the same batch, and thus the morphological difference can be attributed to the different treating voltages.

The surface morphology of thin films grown from vapour phase is affected by the surface energy of substrate and film, as well as the interfacial energy between them. In general, a higher surface energy of the substrate is beneficial to a smooth growth of the film (i.e. layer growth mode) and a strong bonding of the film to the substrate, whereas an island growth mode is corresponding to a relatively low surface energy of the substrate. In most thin film deposition processes, nucleation of the product phase occurs heterogeneously at some preferential sites on the substrate, such as grain boundaries [24], subgrain boundaries [25], dislocations [26], or other surface defects [27–29], where the surface energy is remarkably higher than the rest of the surface. When the substrate is not uniform in surface energy, the adsorbed molecules are locked or irreversibly trapped on to the surface defects and grow into stable nuclei [30,31], because the energy barrier for nucleation is significantly lower at high surface energy areas. On the other hand, the arrived species on the lower surface energy sites tend to migrate towards the active sites and finally add onto the stable nuclei. In this case, the bonding energy between two deposited atoms is greater than the average bonding energy between a deposited atom and a substrate atom [32], leading to thin film growth in island mode [33,34]. As a consequence, the coverage of lower energy areas will mainly rely on the lateral growth or spreading of islands instead of dense nucleation. This is the case when 2 nm NPB is deposited onto, for example, the 0 V, + 1.2 V and 2.8 V treated ITO surfaces, as shown in Fig. 2(a), (b), and (f).

As the DC sputtered polycrystalline ITO is characterized with a nano-scaled grain–subgrain structure, surface energy over ITO surface should accordingly vary from place to place from micro point of view. Therefore, the NPB film normally grows on the ITO surface in island growth mode, as previously reported [35]. More importantly, the number of initial nucleation sites seems to be more related to the surface polarity. For example, the lowest polarity of + 2.8 V treated ITO surface, $\chi_P = 0.42$ as shown in Table 1, is corresponding to the least nucleation sites, which produces the coarsest islands.