Improving the Performance of ITO Thin Films by Coating PEDOT:PSS

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This work studies the effect of PEDOT:PSS on electrical, optical and mechanical properties of ITO glass. Various thickness PEDOT:PSS films are deposited on ITO glass by spin coating. The sheet resistance, transmittance, surface roughness, residual stress, friction, and critical load of the coated specimens are tested in sequence. We find that PEDOT:PSS films not only improve the electric performance but also increase the adhesion of ITO glass. The experimental results show that the PEDOT:PSS film improves the surface roughness and then results in a lower electric resistance. It also increases the adhesion and reduces the residual stress of the ITO films. Furthermore, only 1% transmittance is lost due to the PEDOT:PSS film, showing the potential in the applications of organic photovoltaic cells and light-emitting diodes.

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1. Introduction

With high optical transmittance and low electric resistance, indium tin oxide (ITO) thin films on glass substrates have been broadly applied as conductive electrodes for various displays and photovoltaic devices.^{1,2} While ITO is the most popular transparent conducting film (TCF) in inorganic materials, PEDOT:PSS is the most promising candidate in organic TCFs.³⁻⁵ In the applications of organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs), PEDOT:PSS is often coated on the ITO, where the ITO is utilized as an anode and the PEDOT:PSS is as hole conducting layer.^{6,7} OPVs or OLEDs with a PEDOT:PSS layer on top of an ITO anode have longer lifetime and higher photovoltaic performance than those using ITO anode alone.⁸ The improvement in device stability can be attributed to the ability of the polymer coating to clean the anode surface that substantially slows down device degradation. The photovoltaic performance improved because the conducting polymer may produce a smaller energy barrier that lowers the turn-on voltage of the electronic device.⁹

The structure, morphology and electro-optical characteristics of the transparent anode hole conducting layers play an important role on the final device performance.¹⁰⁻¹² Except electrical and optical properties, mechanical properties also play an important role in thin film devices. Large deformation and debonding of thin films will affect the performance and stability of electronic devices. The elastic modulus

and hardness of the transparent anode and hole conducting layers provide basic mechanical support in the layer stack.¹³ However, residual stresses appearing in the deposited thin films are unavoidable. The mismatch of lattice and thermal expansion between the thin film and substrate induces certain amount of stresses.¹⁴ Heat accumulates during the usage of OPVs and OLEDs resulting in thermal stresses. Stresses in thin films can be either beneficial or detrimental to the performance, which may improve the film stiffness or distort its structures, resulting in cracking in the case of tensile stresses or buckling in compressive stresses. Moreover, delamination reduces the lifetime and reliability of deposited films. The adhesion between inorganic and organic films is a crucial factor that needs to improve in component fabrication.¹⁵ However, study of the mechanical properties of organic electronic devices is still rare in literature.

To improve the performance of the organic electronic devices, it is important to get a better understanding of the interaction between PEDOT:PSS and ITO films. Therefore, this work focuses on characterizing the properties of PEDOT:PSS coated on ITO glass. The influence of various thickness PEDOT:PSS on the structure, morphology and electro-optical characteristics of ITO glasses has been analyzed. Furthermore, the mechanical properties of the thin film/substrate structures, including elastic modulus, hardness, residual stress, and critical load, are first reported. All test results are compared with those of the bare ITO glass.

2. Experimental Details

Various thickness PEDOT:PSS (Clevios AI4083) films are deposited on a 20*30 mm ITO glass by spin coating. All the ITO glass substrates are cleaned in an ultrasonic bath and treated by O₂ plasma. Three thicknesses of the PEDOT:PSS films are considered, including 30, 40, and 50 nm. The thickness of each layer are controlled by the spin speed and confirmed by a Kosaka ET4000 surface profiler.

A grazing-incidence X-ray diffraction (XRD) machine (PANalytical X'Pert PRO MPD) with a copper anode ($\lambda = 0.154$ nm) is utilized in the microstructure analysis. Residual stresses of thin films are measured by using the $\sin^2\psi$ method of XRD in this work. The basic concept of the XRD analysis is that the lattice spacing varies with the orientation of the lattice planes with respect to the loading direction.^{16,17} In XRD analysis, Bragg's law gives¹⁶

$$n\lambda = 2d\sin\theta \quad (1)$$

where $n = 1, 2, 3, \dots$, λ is the wavelength, d denotes the lattice spacing, and θ is the diffraction angle. According to the variation of the lattice spacing, the elastic strain can be defined as

$$\varepsilon = (d - d_0)/d_0 \quad (2)$$

where d_0 is the strain-free lattice spacing. Note that the lattice spacing is measured in the direction of the scattering vector, which decreases as the lattice spacing planes parallel to a tensile stress and increases as its planes are normal to a the tensile loading direction. For elastically isotropic crystallites, Hooke's law relating the mechanical strain tensor ε_{ij} to the mechanical stress tensor σ_{kl} is given as¹⁷

$$\varepsilon_{ij} = S_{ijkl}\sigma_{kl} = \left[S_1\delta_{ij}\delta_{kl} + \frac{1}{4}S_2(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \right] \sigma_{kl} \quad (3)$$

where S_{ijkl} is the compliance tensor. Summation convention over the dummy indices is adopted throughout the paper. The only two independent components S_1 and S_2 are defined as

$$S_1 = -\nu/E, \quad S_2 = 2(1 + \nu)/2 \quad (4)$$

which relate to the elastic modulus E and Poisson's ratio ν . Consequently, the strain tensor in the diffraction direction can be expressed as

$$\begin{aligned} \varepsilon_{\varphi\psi} = & \frac{1}{2}S_2\sin^2\psi[\sigma_{11}\cos^2\varphi + \sigma_{12}\sin 2\varphi + \sigma_{22}\sin^2\varphi] \\ & + \frac{1}{2}S_2[\sigma_{13}\cos\varphi\sin 2\psi + \sigma_{23}\sin\varphi\sin 2\psi + \sigma_{33}\cos^2\psi] \\ & + S_1(\sigma_{11} + \sigma_{22} + \sigma_{33}) \end{aligned} \quad (5)$$

For a rotationally symmetric biaxial stress state, it gives

$$\sigma_{11} = \sigma_{22} = \sigma, \quad \sigma_{12} = \sigma_{13} = \sigma_{23} = \sigma_{33} = 0, \quad \varphi = 0$$

Then, the strain can be reduced to

$$\varepsilon_{\psi} = \left(2S_1 + \frac{1}{2}S_2\sin^2\psi \right) \sigma \quad (6)$$

Therefore, the biaxial stress or the residual stress σ can be obtained from the slope of the straight line in the plot of ε_{ψ} versus $\sin^2\psi$.¹⁷ This method is also called the $\sin^2\psi$ method and will be used in the following discussion.

Typical nanoindentation experiments are performed by using a Hysitron Triboindenter fitted with a standard Berkovich indenter. The loading time, holding time, and unloading time of the indentation tests are all 5 sec. The peak load is controlled at 250 μ N. A standard analysis to determine the hardness and elastic modulus from the unloading load-depth curve is conducted according to the Oliver and Pharr method.¹⁸ The hardness H can be defined as

$$H = P_{max}/A \quad (7)$$

where P_{max} represents the peak load and A is the projected contact area. The hardness is the mean pressure that a material can support under load. The relation between the load (P) and the depth (h) can be represented as¹⁸

$$P = \alpha(h - h_f)^m \quad (8)$$

where α is an indent constant, m depends on the geometry of the indenter, and h_f indicates the final depth. The elastic modulus of the indented sample can be inferred from the initial unloading contact stiffness, $S = dP/dh$, i.e., the slope of the initial portion of the unloading curve. Based on the indentation analysis developed by Snedden,¹⁹ the relation between the contact stiffness, contact area, and elastic modulus can be derived as

$$S = 2\beta\sqrt{\frac{A}{\pi}}E_r \quad (9)$$

where β is a constant that depends on the geometry of the indenter, $\beta = 1.034$ for Berkovich indenter, and E_r is the reduced elastic modulus, which accounts for the elastic deformation occurs in both the sample and the indenter. Hence, E_r is given by

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad (10)$$

where E_i and ν_i are the elastic modulus and Poisson's ratio of the indenter. The elastic modulus E of the sample can be determined by Eq. (10) with assuming a proper Poisson's ratio ν . The standard analysis of nanoindentation is called Oliver and Pharr method.¹⁸ Then, following the Oliver and Pharr method, the hardness and elastic modulus can be determined by Eqs. (7) and (10).

Electrical sheet resistance of the thin films was examined by using a four-point probe (QUATEK 5610Y/QT-50). Optical transmittance of the specimens was measured by using an UV/VIS/NIR spectrophotometer (BWTEK BTC112) with normal incidence in the visible wavelength ranged from 400 to 800 nm, taking the air as reference. In addition, the surface roughness was tested by a white light interferometer (BMT WLI LAB).

The critical load of micro scratch testing can be used to represent the adhesion of thin films. In this work, the micro scratch is conducted by a Rhesca CSR-02F thin film scratch tester. A 5 μ m diameter stylus is utilized, and the stage angle is tilt 1° with speed 10 μ m/s. In the

micro scratch, the specimen is mounted on the tilt stage which moves horizontally to push up the stylus on the top end of the sensor. A load, as a consequence, is applied to the surface of the specimen by the stiffness and strain of the cantilever stylus. The cartridge of the micro scratch tester oscillates parallel to specimen surface at fixed amplitude acted by the build-in actuator. The friction between the specimen and the stylus causes relative movement and then generates electric output signals. As long as the specimen surface is not damaged, the sensor can generate output signals proportional to the stylus velocity. As the load reaches the critical value, some scratch noises are generated due to the destruction or rough surface of the sample film, which are reflected and observed as output signals.²⁰

3. Results and Discussion

In order to confirm the crystal phase of ITO, XRD analysis is performed. Fig. 1 shows the XRD patterns of ITO glass with various thickness PEDOT:PSS films. Five XRD peaks, (211), (222), (400), (441), and (622), of ITO are positively identified,¹⁴ showing the preferred orientation (222) texture at $2\theta = 30.0^\circ$ for all cases.²¹ The detail values of 2θ , intensity, and Full width at half maximum (FWHM) of the preferred orientation (222) are listed in Tables . No significant changes of the micro structures have been found after adding the PEDOT:PSS films, meaning no chemical reaction occurs between PEDOT and ITO.

The optical transmittance of ITO glass with various thickness PEDOT:PSS films is shown in Fig. 2. It shows the average transmittance of the ITO glass without PEDOT:PSS film is 91.86%, and then decreases to 91.20, 91.09, and 90.49% as adding 30, 40, and

50 nm thick PEDOT:PSS films, respectively. The visible transmittance of the ITO glass is 95% at 500 nm.²¹ It shifts to 550 nm after adding the PEDOT:PSS films. The transmittance of ITO glass with 30 and 40 nm thick PEDOT:PSS films are even higher than the bare ITO glass. The transmittance shift may be the thickness effect because the thickness of ITO is 120 nm and the PEDOT:PSS arrives to 30-50 nm. However, The PEDOT:PSS film slightly decreases 1% transmittance of the ITO glasses, illustrating PEDOT:PSS has good transparent performance.

Fig. 3 shows the residual stress of ITO glasses with various thickness PEDOT:PSS films. Based on the biaxial stress model shown in Eq. (6), the residual stress of the ITO thin film can be determined from the XRD results. Fig. 3 shows all the residual stresses for all cases are compressive. The residual stress of the ITO glass without PEDOT:PSS film is 2147.7 MPa, and then decreases to 1792.6, 1770.8, and 1757.3 MPa as adding 30, 40, and 50 nm thick PEDOT:PSS films, respectively. It illustrates the PEDOT:PSS film deposited by spin coating provides a tensile stress which reduces the compressive

Fig. 1 XRD patterns of ITO glass with various thickness PEDOT:PSS films

Table 1 XRD results of peak (222) of ITO/Glass with various thickness PEDOT:PSS films

	Without PEDOT:PSS	30 nm	40 nm	50 nm
2θ (deg)	30.31	30.32	30.32	30.32
Intensity (cps)	18755	19867	18648	18376
FWHM (deg)	0.43	0.43	0.43	0.43

Fig. 2 Transmittance of ITO glass with various thickness PEDOT:PSS films

Fig. 3 Residual stresses of ITO glass with various thickness PEDOT:PSS films

residual stress of the ITO film. Consequently, the residual stress decreases as the PEDOT:PSS thickness increases. In average, the PEDOT:PSS film decreases 17% residual stress of the ITO glass.

The load-depth curves of ITO glasses with various PEDOT:PSS thicknesses measured by nanoindentation are shown in Fig. 4, where the maximum load $250 \mu\text{N}$ is applied. It illustrates the load-depth curves shift to right as the PEDOT:PSS films add, meaning the indentation probe is easier to press into the specimen's surface. The residual indentation depth of the ITO glass without PEDOT:PSS film is 5 nm, and then increases to 40, 55, 65 nm as adding 30, 40, and 50 nm thick PEDOT:PSS films, respectively. The elastic reduced modulus and hardness of ITO glasses with various thickness PEDOT:PSS films measured by nanoindentation are listed in Table 2. The results show that the reduced modulus of the ITO glass without PEDOT:PSS film is 153.2 GPa, and then largely decreases to 77.23, 76.60, and 79.33 GPa as adding 30, 40, and 50 nm thick PEDOT:PSS films, respectively. The hardness is 20.30 GPa, and decreases to 2.12, 2.88, and 1.58 GPa, similarly. It indicates that the PEDOT:PSS coating reduces the elastic modulus and hardness of the ITO film, because the mechanical properties of the polymeric coating are much smaller than the oxide conductive films. No discontinuities are found in the loading or unloading segment, showing neither twinning nor pressure-induced phase transformation is involved in the indentation process.

Fig. 5 and 6 show the micro scratch results of ITO glasses with

Fig. 4 Load-depth curve of ITO glass with various thickness PEDOT:PSS films

Table 2 Experimental results of ITO/Glass with various thickness PEDOT:PSS films

	Without PEDOT:PSS	30 nm	40 nm	50 nm
Transmittance (%)	91.86	91.2	91.09	90.49
Residual stress (MPa)	-2147.7	-1792.6	-1770.8	-1757.3
Reduced modulus, Er (GPa)	153.2	77.23	76.60	79.33
Hardness, H (GPa)	20.30	2.12	2.88	1.58
Critical load (mN)	166.0	172.3	182.3	192.3
Surface roughness, Ra (nm)	11.0	8.62	6.26	5.36
Sheet resistance ($\Omega/\square$)	13.77	5.28	4.78	4.35

various thickness PEDOT:PSS films. The scratch distance of the ITO glasses is illustrated in Fig. 5, showing the scratch distance of the ITO glass without PEDOT:PSS film is 2.15 mm and increases to 2.26, 2.30, 2.32 mm as adding 30, 40, 50 nm thick PEDOT:PSS films. Similarly, the scratch distance of the ITO glasses is illustrated in Fig. 6 which shows the scratch distance of the ITO glass without PEDOT:PSS film is 166.0 mN and then increases to 172.3, 182.3, 192.3 mN as adding 30, 40, 50 nm thick PEDOT:PSS films, respectively. It reveals that the critical load of the ITO glass with PEDOT:PSS is higher than that without PEDOT:PSS. In average, the PEDOT:PSS increases 10% critical load of the ITO film. The scratch results indicate that the PEDOT:PSS film can improve the adhesion between the ITO thin film and the glass substrate.

Furthermore, all experimental results are listed in Table 2, including the surface roughness and electrical resistance. It indicates the surface roughness of the ITO glass without PEDOT:PSS film is 11.0 nm, and decreases to 8.62, 6.26, and 5.36 nm as adding 30, 40, and 50 nm thick PEDOT:PSS films, respectively. It also indicates the sheet resistance of the ITO glass without PEDOT:PSS film is $13.77 \Omega/\square$, and decreases

Fig. 5 Scratch distance of ITO glass with various thickness PEDOT:PSS films

Fig. 6 Scratch force of ITO glass with various thickness PEDOT:PSS films

to 5.28, 4.78, and 4.35 $\Omega/\square$ as adding 30, 40, and 50 nm thick PEDOT:PSS films, respectively. In average, the surface roughness decreases 39% and the sheet resistance decreases 65% by adding the PEDOT:PSS film. It emphasizes the PEDOT:PSS film effectively improves the surface roughness and results in a lower electrical resistance of ITO glasses. In organic electronic devices, the sheet resistance of the ITO anode should be as low as possible. Kim et al.²² reported that the electric properties of ITO can be significantly modified by smooth surface. They also indicated that the presence of a PEDOT:PSS hole-transport layer inserted between the ITO anode and the emissive polymer layer is beneficial for the devices such as organic photovoltaic cells and light-emitting diodes. It is consistent with the results of this work.

4. Conclusions

The effects of various thickness PEDOT:PSS films on the performance of ITO glasses are discussed. Three thicknesses PEDOT:PSS are deposited on the ITO glass substrate by spin coating. The microstructure, mechanical properties, optical transmittance, and electric resistance of the PEDOT:PSS coated ITO glasses are tested in sequence. The results show that, comparing to the bare ITO glass, the PEDOT:PSS coated ITO glass improve 17% residual stress, 10% adhesion, 39% roughness, and 65% electric resistance of the ITO glass. However, 1% transmittance, 49% modulus, and 89% hardness of the ITO glass are lost by adding the PEDOT:PSS films. In conclusion, the high conductivity and good adhesion indicate the compound of PEDOT:PSS and ITO will continue to play an important role in the applications of organic photovoltaic cells and light-emitting diodes.

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