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Effects of annealing temperature on mechanical durability of indium-tin oxide film on polyethylene terephthalate substrate

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ABSTRACT

Effects of the annealing temperature on mechanical durability of indium-tin oxide (ITO) thin films deposited on polyethylene terephthalate (PET) substrates were investigated. The ITO films were annealed at the range from 150 °C to 195 °C after the DC sputtering deposition for the production of polycrystalline ITO layers on the substrates. The onset strains of cracking in the annealed ITO films were evaluated by the uniaxial stretching tests with electrical resistance measurements during film stretching. The results indicate that the onset strain of cracking in the ITO film is clearly increased by increasing the annealing temperature. The in-situ measurements of the inter-planer spacing of the (222) plane in the crystalline ITO films during film stretching by using synchrotron radiation strongly suggest that the large compressive stress in the ITO film increases the onset strain of cracking in the film. X-ray stress analyses of the annealed ITO films and thermal mechanical analyses of the PET substrates also clarifies that the residual compressive stress in the ITO film is enhanced with increasing the annealing temperature due to the considerably larger shrinkage of the PET substrate.

1. Introduction

Indium-tin oxide (ITO) has been widely used as transparent electrodes in optoelectronic devices due to high transparency and high conductivity. In recent years, ITO films deposited on flexible plastic substrates have been also applied to flexible optoelectronic devices, such as touch screens and organic light-emitting diodes, due to their additional advantages in terms of flexibility and lightweight. On the other hand, the electrical failure of the ITO film occurs easily with the initiation of tensile cracks by bending and stretching deformation, when the ITO layer is deposited on a plastic substrate. Therefore, it is crucial for the growth of the products of this type of ITO films to increase the onset strain of cracking against bending and tensile stretching.

Many researchers have tried to produce ITO films with good mechanical durability. However, it is difficult to obtain ITO films with good mechanical durability without special treatments, such as the insertion of additional buffer layers with a low elastic modulus as proposed by Park et al. [4].

It is important to understand the fracturing mechanism in order to improve mechanical durability of the ITO films on plastic film substrates. The fracturing mechanism of ITO layers on plastic substrates during bending and stretching tests was investigated with optical microscopy, scanning electron microscopy (SEM), electrical resistance measurement and residual stress analysis [1–7]. It was found that the evolution of the cracks is substantially affected with external tensile forces as well as temperature and humidity conditions for flexibility of polymer substrates [7]. However, microscopic behaviors of strain and stress in the ITO film during the deformation still have not been well understood because of the limitation of resolution of observation methods. Furthermore, from an industrial viewpoint, quantification of the onset strain and stress of cracking during bending and tensile stretching is so important for expanding their application.

In this paper, the effects of the annealing temperature on mechanical durability of the ITO layers on plastic film substrate were investigated. The onset strains of cracking in the ITO layers deposited on polyethylene terephthalate (PET) substrates were actually evaluated by the stretching test after annealing at the range from 150 °C to 195 °C in temperature. Results show that the onset strain of cracking in the ITO film is increased by the high temperature annealing. The in-situ measurements of the inter-planer distances (d-spacings) of the ITO crystalline plane during film stretching by using synchrotron radiation X-ray were carried out to investigate the fracturing mechanism. The results of the residual stress analysis and thermal mechanical analysis will be also reported for the ITO films and the PET substrates, respectively.

2. Experimental details

The thin ITO films were deposited on the biaxially stretched PET substrate with a thickness of 23 μm by using a roll to roll DC magnetron sputtering system using an ITO ceramic target (90 wt.% In_2O_3 and 10 wt.% SnO_2). The base pressure was 1×10^{-4} Pa and the working pressure was 0.4 Pa in a gas mixture of Ar and 0.5 at.% O_2. The deposition rate was 80 nm/min and the thickness of ITO layer on the substrate was 25 nm. For the production of the polycrystalline ITO films, as-deposited ITO films were annealed at 150 °C, 180 °C and 195 °C for

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1 h, respectively. The onset strains of cracking of the ITO films were evaluated by the uniaxial stretching test. In the stretching tests, the electrical resistances of the ITO film samples with a gauge length of 15 mm and a gauge width of 7 mm were measured during film stretching up to 5% strain in the machine direction of the PET substrate by using a film tensile stretch machine (Linkam 10073A, Japan High Tech Co.) and a digital ohmmeter. The resistance ratios (R/R_0) at each film strain were calculated by dividing the electrical resistances (R) by the initial one (R_0).

In order to clarify the mechanism of the increase in the onset strain of cracking, the in-situ measurements of the d-spacings of the (222) plane in the ITO crystallites during the film stretching process were carried out by using synchrotron radiation at the beamline BL03XU of SPring-8 [8]. Fig. 1 shows a schematic diagram of the experimental setup. This system consists of the same stretch machine used in the uniaxial stretching tests and a 2-dimensional complementary metal-oxide-semiconductor (CMOS) detector (Hamamatsu Photonics, Flat panel sensor). The wavelength of synchrotron radiation was 0.1 nm and the beam size at the specimen position was approximately 0.3 mm × 0.5 mm. The X-ray was irradiated on the films from the direction normal to the film surface direction. Therefore, the incident X-ray proves the crystalline planes aligned in the direction perpendicular to the film surface direction. The camera length between the specimen and the CMOS detector was 85 mm. All the ITO film samples were prepared with a gauge length of 75 mm and a gauge width of 7 mm and the initial distance between two chucks of the stretching apparatus was 15 mm. In the stretching test, the ITO film samples were stretched up to 5% strain with 2 μm/s (0.8%/min) symmetrically with respect to the center position which assured that the X-ray beam always illuminated the same position of the sample during stretching. 2-Dimensional X-ray diffraction data were converted to 1-dimensional diffraction profiles with a homemade data processing program. The calibration of the diffraction angle was carried out by using the diffraction data of the Si powder purchased from the National Institute of Standards and Technology. For each strain, the d-spacings of the (222) plane were deduced from the peak positions of the (222) diffractions with Bragg's law, $2d\sin\Theta = \lambda$, where λ is the wavelength and Θ is a half of the scattering angle.

Residual stresses in the annealed ITO films were evaluated by X-ray diffractometry with $\sin^2\Psi$ method [9]. In this method, X-ray diffraction measurements were performed at 5 different Ψ angles between 45° to 90° (Ψ is the angle between the normal of the film and the normal of the diffraction plane). The strains of the d-spacing of the (222) plane were linearly plotted as a function of $\sin^2\Psi$ and the in-plane stress in the ITO layer was calculated with the slope of the plots and the elastic modulus of ITO.

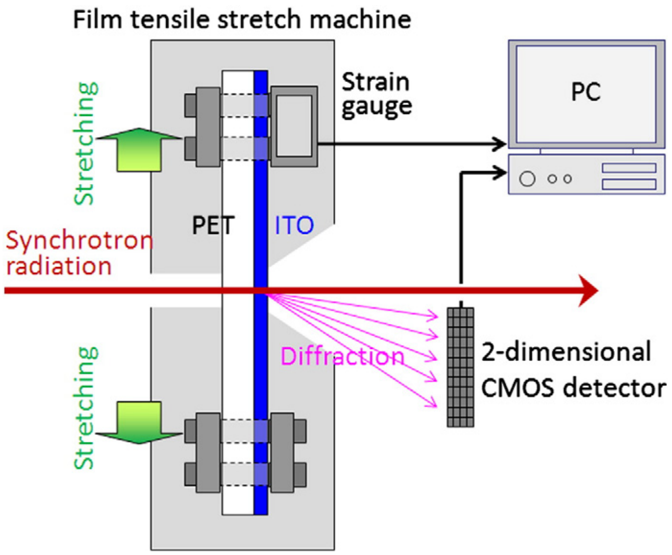

Fig. 1. Schematic diagram of the in-situ measurement system of the d-spacings of the (222) plane in the ITO crystallite during film stretching. This system consists of a film tensile stretching machine and a 2-dimensional CMOS detector.

In order to evaluate the dimensional changes of PET substrates during the annealing process, thermal mechanical analysis (TMA) was carried out with TMA/SS6100 (Seiko Instruments Inc.). The dimensional changes of the PET substrate were measured during the sequential heating – isothermal annealing – cooling processes with a 19.6 mN load. The heating and cooling rate were approximately 5 °C/min and the isothermal annealing was programmed for 1 h.

3. Results and discussion

Fig. 2 shows the electrical resistance ratios (R/R_0) as a function of the strain in the stretching tests of the ITO films, which were annealed at 150 °C, 180 °C and 195 °C, respectively. In all samples, R/R_0 increases rapidly between 2.8% and 4.4% film strain due to the initiation of cracks in the film. R/R_0 increases more lately with increasing the annealing temperature. As a result, the onset strain of cracking in the ITO film strongly depends on the annealing temperature, that is, the onset strain of cracking can be increased as the annealing temperature rises.

Fig. 3 shows the 1-dimensional X-ray diffraction profiles around the diffraction peak originated from the (222) plane in the ITO film, which was annealed at 150 °C as a function of the macroscopic film strain from 0% to 5.0%. It is clarified that the diffraction peak shifts to a smaller angle by the film stretching. That is to say, the d-spacing of ITO crystallite increases with increasing the macroscopic strain of the samples.

Fig. 4 shows the d-spacing in the stretching direction as a function of macroscopic film strain for the samples annealed at 150 °C, 180 °C and 195 °C. The initial d-spacing prior to the stretching decreases with increasing the annealing temperature and the d-spacing during film stretching increases in proportion to the strain up to the same value of about 0.2937 nm. It seems that the d-spacing of the (222) plane is elastically extended with strain up to 0.2937 nm, subsequently constant at the value during the following stretching. The constant d-spacing of 0.2937 nm must be attributed to the initiation of the cracks in the ITO layer, because the cracks prevent the crystalline planes from further stretching with strain. Therefore, the decrease in the initial d-spacing leads to a later occurrence of the cracks. Consequently, the film has a higher onset strain of cracking after annealing at a higher temperature.

It is considered that the film with a lower initial d-spacing is subjected to a larger compressive stress after annealing at a higher temperature compared to the case of the film annealed at a lower one. The compressive internal stress in the ITO layer may be ascribed to the substantial shrinkage of the PET substrates in the annealing process. In general, commercial grade PET films are biaxially stretched for the

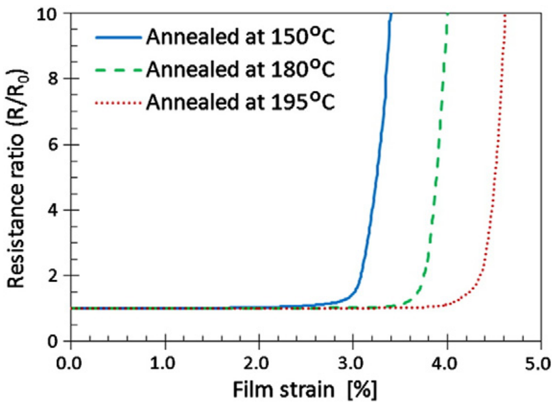

Fig. 2. Resistance ratios as a function of the strain of the ITO films annealed at 150 °C, 180 °C and 195 °C.