Fracture of Conductive Ceramic Thin Film on Polymer Substrate in Opto-electric Devices

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Keywords: Thin film, Ceramic, Polymer, Ultra-violet ray, Indentation, Channeling crack

Abstract. The aim of this paper is to investigate the effect of ultra-violet (UV) ray irradiation on the crack formation of brittle ceramic coating on polymer substrate. It is well known that ultra-violet ray irradiation degrades the mechanical properties of polymer and polymer-based coating films. We carried out the tensile tests of PET/ITO film specimen after UV irradiation under the microscope and observed the crack formation on ITO surface. Also, we carried out nano-indentation tests of PET substrate after removing ITO layer to characterize the change of the mechanical properties near the interface between PET and ITO. The results show that the number of cracks vertical to loading direction and the rate of vertical crack formation decreased after UV irradiation. Hardness and Young's modulus of PET substrate increase due to the oxidation of PET after UV irradiation. To explain the relationship between the crack formation and mechanical property change, the energy release rates of the thin film channeling cracks are considered.

Introduction

Attention has been directed to an electric conductive ceramic film, which is deposited on a polymeric substrate[1,2]. The applications of those conductive films are the display of mobile computers, cellular phones or flexible paper like display. Those conductive films have the advantage of low power consumption or flexibility to deformation. The popular components of those films especially for display usage are ITO (Indium Tin Oxide) and PET (Polyethylene Terephthalate). It is well known that the mechanical properties of polymers, such as tensile strength or rupture strain, are degraded by the irradiation of ultra-violet(UV) ray[3]. When the polymer based conductive films are used in the open air, it is necessary to consider the degradation of the mechanical properties in design of products. When UV ray irradiates polymeric materials, the principal chains are cut and oxidized. Those reactions may affect the bonding strength between ceramics and polymers.

The aim of this paper is to investigate the effect of ultra-violet (UV) ray irradiation on the crack formation of ceramic coating on polymer substrate. We carried out the tensile tests of PET/ITO film specimen after UV irradiation under the microscope and observed the crack formation on ITO surface. Also, we carried out nano-indentation tests of PET substrate after removing ITO layer to characterize the change of the mechanical properties near the interface between PET and ITO. The relationships between the crack formation and mechanical property change are discussed.

Experimental Procedure

Cracks easily formed on ITO layer under tensile loading since ITO is a brittle ceramic. Once the surface crack is formed, the functionality of the complex film will be lost. Our interest is how the interfacial strength affects the crack formation on ITO layer. The specimen is composed of ITO and PET. All specimens were fabricated by spattering ITO on PET substrate. The thickness of each layer was 108 nm for ITO and 100 μm for PET substrate. To investigate the effects of UV irradiation, half of specimens were kept in a fade meter for 12 to 120 hours. The specimen was irradiated by the UV ray from ITO face and the intensity of UV ray was about 30 W/m^2. The small tensile testing machine was used under a video microscope to observe the crack formation. The rectangular specimens with 1 mm in width and 50 mm in length were prepared. During the tensile tests, load and displacement were recorded by a personal computer and the microscopic images were recorded by a digital video recorder. The stress-strain relation of the complex film is shown in Fig.1. It is noted that the strain is measured from the cross head displacement divided by the initial length between cramps. The stress-strain behavior in elastic and plastic regions is independent of irradiation periods. Only the rupture strain depends on the irradiation periods. Figure 2 shows the peel energies of PET/ITO interface obtained by Multi-stages peel tests[4]. Peel energy corresponds to the interfacial adhesion strength between PET and ITO. The interfacial adhesion strength decreased with UV irradiation periods.

To characterize the change of the mechanical properties near the interface between PET and ITO, we used a nano-indentaiton equipment (Hysitron Triboscope®). Some specimens were soaked in hydrochloric acid (1 mol/l) to remove ITO layer. Then, appeared PET surfaces were indented and the indentation hardness and Young's modulus were measured.

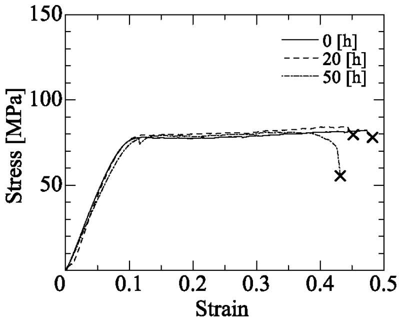


Figure 1 Stress-strain relations of PET/ITO film after several UV-irradiation periods.

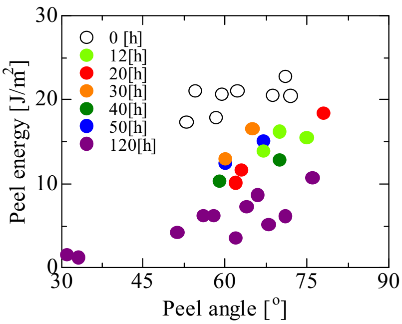
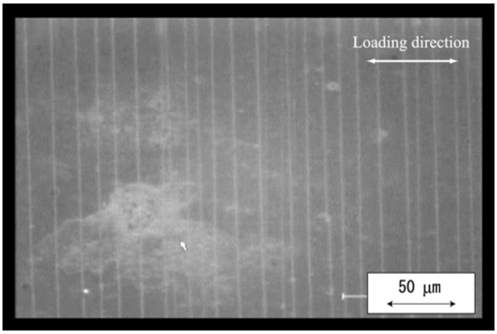


Figure 2 Peel energy of PET/ITO interface after several UV-irradiation periods.

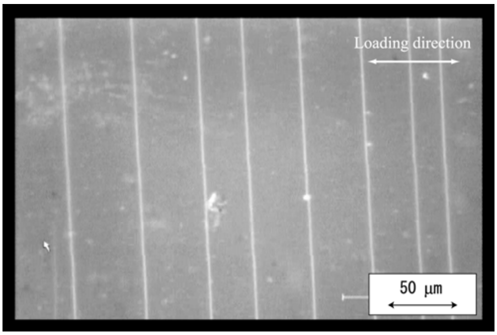
Experimental Results

The in-situ observation of surface crack formation at 14 % strain is shown in Fig.3. The distance between cracks depends on UV irradiation periods. On as-received specimen, the distance between cracks is about 5 μm. The distance between cracks is about 30 μm for 20 hours UV irradiation and 50 μm for 50 hours UV irradiation, respectively. The density of vertical cracks increased with applied strain. The driving force for surface crack formation is shear force between ITO and PET layers (Yanaka et al.[5], Chen et al.[6]). When the interfacial strength is large, the interfacial shear rigidity is stiff and the same strain within PET film will be induced in ITO layer. That brings about high tensile stress in ITO layer and cracks are easily formed even in small strain range.

Figures 4 and 5 show the results of nano-indentation tests. Figure 4 shows the relationships between indentation hardness and indentation depth. The indentation hardness decrease as the indentation depth increases. After UV irradiation, PET surfaces become harder than that of as-received specimen. Figure 5 shows the relationships between Young's modulus and indentation depth. Similarly, Young's modulus decreases as the indentation depth increases. Young's modulus measured by tensile tests for the same PET film is about 1.8-2.0 GPa. Therefore, it is considered that the stiffer layers were formed on PET surface due to the chemical reactions by UV irradiation.



(a) As-received specimen



(b) UV irradiation for 50 hours

Figure 3 Formation of surface crack on ITO layer under about 14% strain.

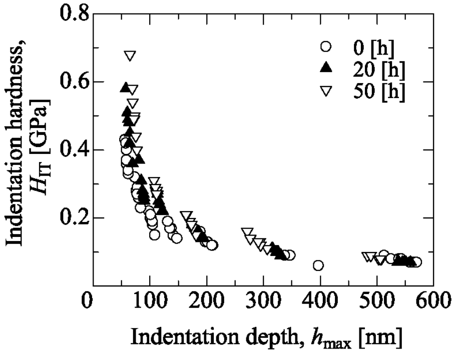


Figure 4 Indentation hardness vs. indentation depth.

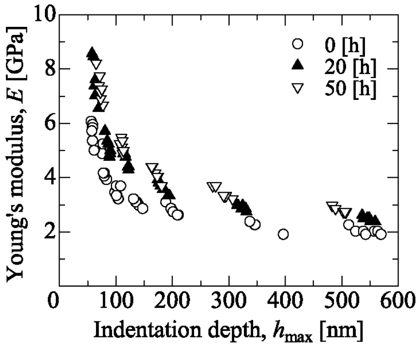


Figure 5 Young's modulus vs. indentation depth.

The surface crack shown in Fig.3 are well known as a channeling crack. The channeling crack formations are closely related to the substrate Young's modulus. The steady-state energy release rate for channeling crack has been proposed by Beuth[7] as,

$$G_{ss} = \frac{1}{2}\frac{\sigma_f^2 h_f}{\overline{E}_f}\pi g(\alpha, \beta) \tag{1}$$

where, σ_f is the stress in the film, h_f the thickness of the film. $\overline{E}_f = E_f / (1 - \nu_f^2)$, where E_f, ν_f are Young's modulus and Poisson's ration of the film. $g(\alpha, \beta)$ is a non-dimensional energy release rate which is a function of Dundurs's parameters[8]. To estimate the stress induced in the film, shear-lag model with inter-layer is used[9]. When the thickness of the substrate is assumed to be too thick compared to the film thickness and inter-layer thickness (i.e. $h_s >> h_f, h_{\text{int}}$), the stress induced in the film can be written as,

$$\sigma_f\left(\frac{x}{L}\right) = \sigma_0 \frac{E_f}{E_{\text{int}}}\left(1 - \frac{\cosh \gamma (x/L)}{\cosh \gamma}\right) \tag{2}$$

$$\gamma = \sqrt{\frac{L^2}{2(1+\nu_{\text{int}})h_f h_{\text{int}}} \frac{E_{\text{int}}}{E_f}} \tag{3}$$

where, σ_0 is the applied stress, E_f, h_f is the Young's modulus and thickness of the film, $E_{\text{int}}, \nu_{\text{int}}$ is the Young's modulus and Poisson's ratio of the inter-layer. h_{int} is the thickness of the inter-layer. L is the segmantation length. The maximum stress induced in the film is,

$$\sigma_f(0) = \sigma_0 \frac{E_f}{E_{\text{int}}}\left(1 - \frac{1}{\cosh \gamma}\right) \tag{4}$$

For simple approximation, the stress induced in the film is assumed to be constant and calculated from Eq.(4). The thickness of the inter-layer is assumed to be 100 nm and the segmentation length is 10 μm from Fig.3 (a). The steady-state energy release rate can be calculated from Eq.(1) and the ratio of the steady-state energy release rate between before and after UV irradiation can be estimated as,

$$\frac{G_{ss}^{20h}}{G_{ss}^{0h}} = 0.397, \quad \frac{G_{ss}^{50h}}{G_{ss}^{0h}} = 0.249 \tag{5}$$

After UV irradiation, the steady-state energy release rates drastically decrease and the channeling cracks are difficult to form. Therefore, the distance between cracks becomes wider after UV irradiation as shown in Fig.3.

Conclusion

The effect of ultra-violet (UV) ray irradiation on the crack formation of brittle ceramic coating on polymer substrate is studied and the relationships between the crack formation and mechanical property change of PET substrate are discussed. The distance between cracks becomes wider after UV irradiation. These phenomena can be explained by the steady-state energy release rates of channeling cracks.

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