

Electrochemical Corrosion Failure of ITO-Coated PET Film for Display Application

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Purpose: The electrochemical corrosion behavior of tin oxide film coated on PET substrates has been studied under varying concentrations of acrylic acid to investigate possible corrosion in contact with the acidic environment.

Method: Potentiodynamic test was performed for a commercial ITO/PET film in 0.1, 0.3, and 0.5 M of acrylic acid. The surface morphology was analyzed by scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS).

Results: Potentiodynamic test results showed an increase in I_{corr} and decrease in E_{corr} value with increasing concentration of acid. Microscopic evaluation suggested the presence of certain deep cracks on the surface of the film in addition with a severe acidic attack.

Conclusion: Exposure of ITO to acrylic acid resulted in the stress corrosion cracking of ITO film due to the mechanical mismatch between brittle inorganic ITO film and a compliant organic PET substrate leading to the subsequent failure of the film.

Keywords: Indium tin Oxide, Flexible Displays, Corrosion, Stress Corrosion Cracking

1. Introduction

The manufacturing of a flat panel display constructed of thin flexible substrates that can be bent, flexed, conformed, or rolled to a radius of curvature of a few centimeters without losing its functionality has received a great interest in the recent years by the researchers [1]. Therefore, Indium tin oxide films (ITO) coated on various kind of organic substrates such as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) have been widely used in flexible displays such smart phones touch screen systems, LCD's and flexible OLED's due to their excellent optical transmittance and light conducting properties as well as their light weight and ease

of bendability [1, 2].

ITO is an oxide film composed of mainly 90 wt. % In_2O_3 and 10 wt. % SnO_2 . The resistivity of ITO on various kinds of organic and inorganic substrates can be as low as $1 \times 10^{-4} \Omega \text{ cm}$ to $3 \times 10^{-4} \Omega \text{ cm}$ depending on the thickness of ITO film [3]. And the optical transmittance can be as high as 89~90% at 550 nm. Tin-doping in In_2O_3 contributes towards the conductivity of ITO film [4].

The fabrication of flexible optoelectronic devices involves the deposition of a barrier layer and ITO layer on PET substrate [5]. Pressure sensitive acrylate based glues are sandwiched between these barrier layers and ITO film to provide firm bonding and improve the mechanical properties. However, these acrylate based adhesives

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and glues can affect the electrochemical stability of ITO films because of the sensitivity of ITO to acidic environment. Hence, prolonged interaction of ITO with these adhesives can lead to the corrosion. Moreover, a mechanical mismatch between brittle ITO and a flexible substrate can give rise to various kinds of stress raisers. Thus, a combine action of corrosion and stresses can lead to the stress corrosion cracking of ITO film; which indirectly affects the reliability of flexible displays [6].

Up to now, various interesting results on the study of electrochemical and electromechanical behavior of ITO film sputtered on organic substrates have been presented [5, 6]. Sierros *et al.* reported that when ITO anodes become exposed to voltage differences in the presence of moisture and contamination, their resistance to corrosion is decreased. Moreover the components of the flexible display device can come into contact with acidic solutions from either harsh environment conditions or epoxy resins, these acidic solutions can corrode the brittle ITO layer and any applied or residual stresses can result in stress corrosion cracking, resulting in crack formation, propagation and/or delamination [6].

Kyle Burrows studied the effect of acrylic acid on the electro-mechanical behavior of ITO films sputtered on organic PET and PEN substrates and reported that exposure of ITO to acrylic acid prior to induced uniaxial strain results in a significant reduction of the samples ability to resist strain due to weakening of the ITO film as a result of stress corrosion cracking [1]. Bejital *et al.* studied the effect of acrylic acid on electrochemical stability of ITO as a function of immersion time and found out that the corrosion of ITO increases significantly as a function of time along with an increase in electrical resistivity [5].

Until now, a lot of researches have been carried out to study the effect of acrylic acid on electromechanical stability of ITO coated PET substrates. Few researches have been presented which correlate the electrochemical stability of ITO under acrylic acid environment as a function of immersion time and applied stress. However, the detailed influence on corrosion, stress corrosion cracking and in turn the electrical properties of ITO as a function

of acrylic acid concentration has not been reported in detail.

Therefore, the aim of this study is to investigate the corrosion and stress corrosion cracking behavior of ITO films on PET substrates in acrylic acid environment as a function of applied potential and to evaluate the overall damage caused by acidic environment on the electrochemical and electrical resistance of ITO.

2. Experimental Procedure

ITO films used in this work were commercial products, which were deposited on polyethylene terephthalate (PET) substrate by DC magnetron sputtering. The thickness of the ITO film is about 140 nm with a sheet resistance of approximately $15 \Omega / \text{cm}^2$. The as-received ITO was prepared from DC-diode sputtering system, and the source target composed of 90% wt.% In_2O_3 and 10 wt.% SnO_2 . A schematic illustration of ITO specimen used for experimental work is shown in <Fig. 1>. ITO coated PET specimens were cut in the rectangular shape with $75\text{mm} \times 20\text{mm} \times 0.7\text{mm}$ dimensions. The specimens were then rinsed with de-ionized water, acetone and dried in a stream of cold air. Surface area of about $1 \times 1 \text{cm}^2$ controlled by mounting with fast curing epoxy (Araldite Rapid, Huntsman Advanced Materials (Switzerland) GmbH), and corrosion resistant tape was exposed to electrolyte. Acrylic acid ($\text{C}_3\text{H}_4\text{O}_2$) was used to corrode the ITO layer of the films. It has a molecular mass of 72.06g/mol and a relative density of 1.05g/ml at 25°C . The acid was supplied by Sigma Aldrich. A stock solution was produced with a concentration of 1M. From this stock solution, varying concentrations of 0.1M to 0.5M were produced.

The corrosion process was controlled at room temperature by applying cathodic and anodic polarization using the potentiodynamic method. The potential was measured versus a reference saturated $\text{Ag}/\text{AgCl}/\text{NaCl}$ (3M) electrode (RE-5B, Bioanalytical Systems Inc., USA). A potentiostat/galvanostat system (WonaTech Co., Ltd., Korea) was used with a coiled platinum wire counter electrode

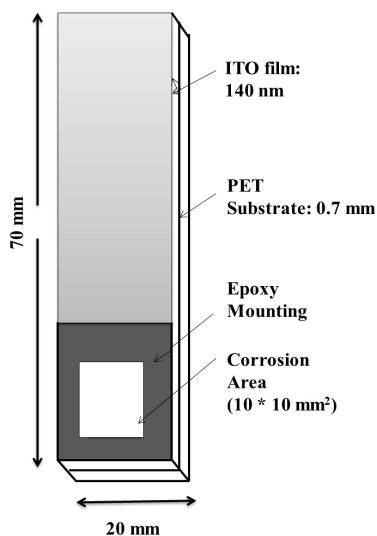


Fig.1 A schematic diagram of specimen geometry

(MW-1033, Bioanalytical Systems Inc., USA). The corrosion test was implemented in varying concentrations of acrylic acid solution at -1,500V to 2,500V potential range. The specimen was polarized positively by open circuit potential (EOCP) with a scan rate of 1mV/s, until the EOCP became stable after immersion in acrylic acid solution.

The microstructure of corroded ITO specimens were compared with the as-received specimen by optical microscopy, scanning electron microscopy (SEM), EDS (energy dispersive spectroscopy). 4-point probe test was used to measure the sheet resistance values.

3. Results and Discussion

<Fig. 2> correlates the polarization behavior of ITO film coated on PET substrates as a function of varying acrylic acid concentration. As depicted in the figure, the corrosion potential (E_{corr}) shifts towards low values with an increase in concentration of acrylic acid along with a forward shift in the anodic and cathodic polarization curves; thus increasing the overall corrosion rate. The corrosion of ITO increases sharply at anodic polarization region resulting in the increase in electro-chemical activity of ITO film. When the ITO electrode is cathodi-

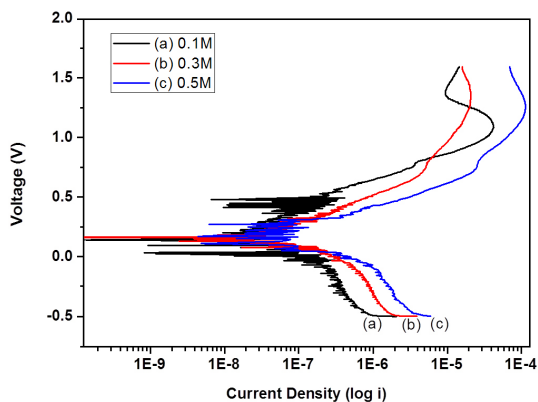


Fig. 2 Potentiodynamic polarization curves of ITO-coated PET substrate at (a) 0.1M, (b) 0.3M and (c) 0.5M acrylic acid

cally polarized in acrylic acid, ITO may reduce to metallic indium. The anodic polarization curves are assumed to represent the oxygen evolution reaction through oxidation reaction. Produced oxygen ions are supposed to be removed from ITO resulting in the formation of metallic indium.

Moreover, a transpassive region is shown by all the polarization curves under 1~1.5V potential range which implies that electro-chemical activity of ITO film decreases significantly after reaching a high potential value due to the formation of surface layer of dissolved In^{3+} and Sn^{2+} cations; thus hindering further corrosion. Increase in concentration of acrylic acid decreases the transpassive region implying that increased acid concentration. Lowers the passivity of ITO film by increasing the electrical activity and subsequent removal of adsorbed surface cations in the form of byproducts of corrosion. E_{corr} decreases whereas i_{corr} increases as a function of acrylic acid concentration, thus resulting in an accelerated corrosion attack.

<Table 1> depicts the potentiodynamic polarization parameters and correlates the E_{corr} and i_{corr} values of ITO showing an increase in E_{corr} and a decrease in i_{corr} with a decrease in acrylic acid concentration.

<Fig. 3> shows the optical micrographs of corroded ITO film as a function of increasing molar concentration of acrylic acid. The OM images show the extent of corrosion of ITO film and are in close agreement with the potentiodynamic polarization data which suggest a con-

Table 1 Potentiodynamic polarization parameters for ITO films immersed in varying concentration of acrylic acid solution

Acrylic Acid Concentration(M)	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)
0.1	205	2.48×10^{-2}
0.3	167	6.53×10^{-2}
0.5	157	9.97×10^{-2}

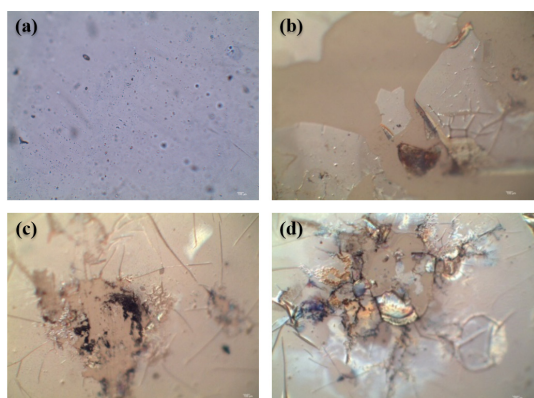


Fig. 3 Optical micrographs showing corrosion and stress corrosion cracking of ITO films; (a) before exposure to acrylic acid, (b) under 0.1M acrylic acid, (c) under 0.3M acrylic acid, (a) and (d) under 0.5M acrylic acid solution

tinuous dissolution of ITO with increasing acrylic acid concentration (<Fig. 3(a)> and <Fig. 3(b)>). Moreover, the presence of deep cracks is clearly obvious in the microstructures and the concentration of cracks increases significantly as a function of acrylic acid concentration. The combined effect of the mechanical stresses and the corrosion lead to stress corrosion cracking of film. This stress corrosion cracking phenomenon in the specimens did not initiate due to some external stresses. However, the internal stresses between the brittle ITO film and the ductile polymeric PET substrate acted as stress raisers and caused micro level internal cracking of ITO film which when exposed to acidic environment accelerated the corrosion attack; thus responsible for the stress corrosion cracking of specimen. Presence of stresses accelerates the corrosive attack, make the film porous and hence, causing an easy and sudden failure of ITO films.

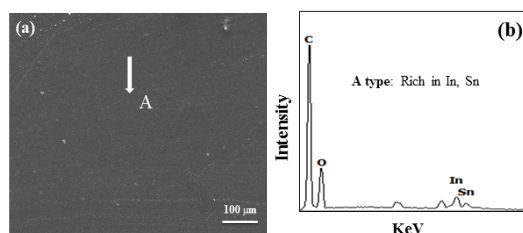


Fig. 4 (a) SEM image and (b) EDS spectra of the as-received ITO coated PET substrate

By studying the SEM images of ITO surfaces immersed in 0.1 to 0.5M acrylic acid, a corrosion dominated ITO cracking process is revealed. <Fig. 4> shows the morphology and EDS spectra of commercial ITO before corrosion. ITO film evenly covered the PET substrate with no dissolved surface. However after exposure to 0.1M acrylic acid (as shown in <Fig. 5>), a significant dissolution of ITO film took place along with the presence of deep surface cracks which shows the initiation of stress corrosion cracking attack. EDS spectra reveals an In deficient matrix phase and a dissolved phase containing In and Sn peaks along with traces of Cl absorbed from the moisture. Similarly, with an increase in acrylic acid concentration (as shown in <Fig. 6> and <Fig. 7>), the stress corrosion cracking attack becomes more significant and obvious; thus causing the removal of almost entire ITO film from the substrate surface in the form of adsorbed surface by products of corrosion.

Sheet Resistance was measured in order to reveal the effect of corrosion and stress corrosion cracking on electrical properties of ITO (as shown in <Fig. 8>). The resistance of the film increased significantly with the increase in acrylic acid concentration. This is due to the fact that the electrical conductivity is directly related to the number of free charge carriers in the ITO film which in turn is related to the area fraction of ITO film left on the PET substrate after the corrosive attack. With the increase in concentration of acrylic acid, corrosion rate increases which accelerates the dissolution of ITO film; thus reducing its sheet resistance. Moreover, increase in the number of stress corrosion cracks increases the hindrance to the flow of free charge carriers; thus affecting its electrical activity.

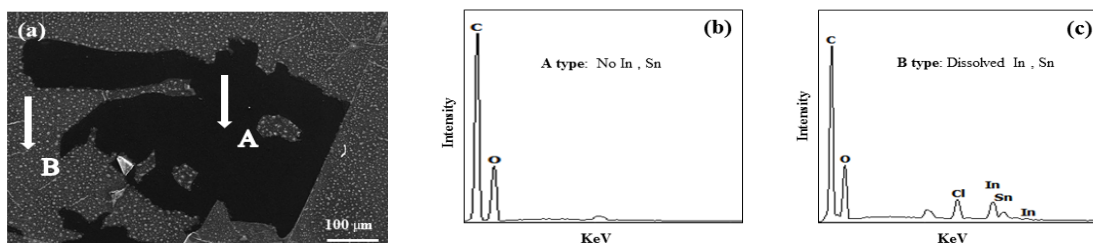


Fig. 5 SEM image of (a) ITO after polarization in 0.1M acrylic acid, (b) EDS spectra of matrix phase 'A' in (a), and (c) EDS spectra of dissolved phase 'B' in (a).

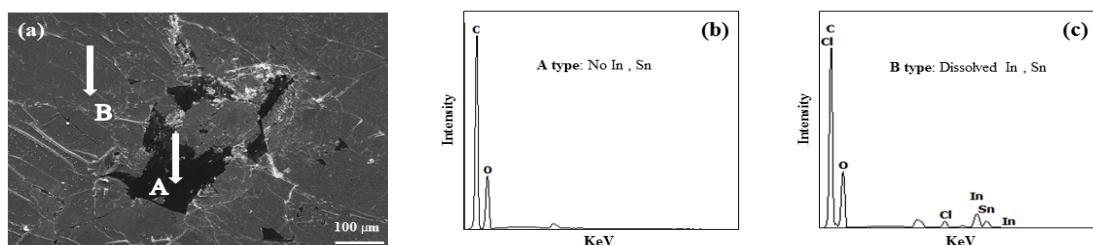


Fig. 6 SEM image of (a) ITO after polarization in 0.3M acrylic acid, (b) EDS spectra of matrix phase 'A' in (a), and (c) EDS spectra of dissolved phase 'B' in (a).

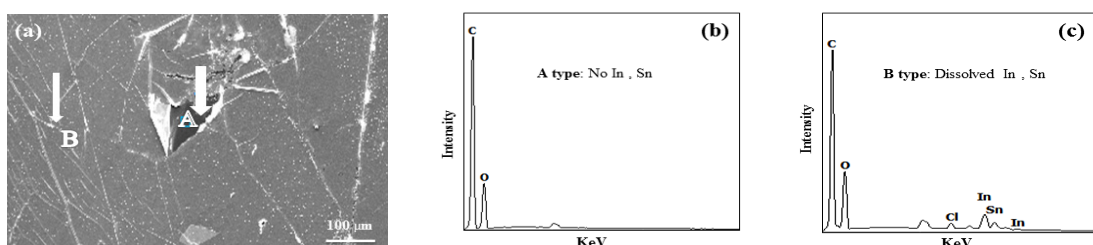


Fig. 7 SEM image of (a) ITO after polarization in 0.5 M acrylic acid, (b) EDS spectra of matrix phase 'A' in (a), and (c) EDS spectra of dissolved phase 'B' in (a).

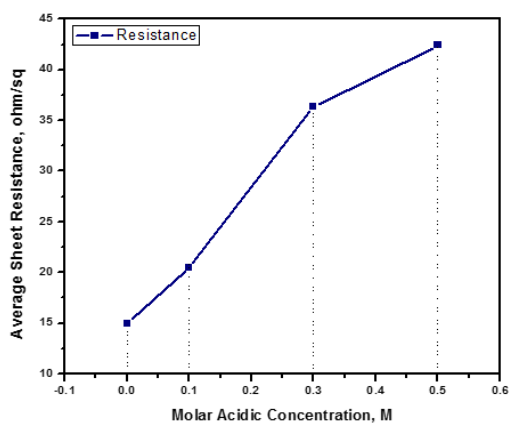


Fig. 8 Correlation between varying molar concentration of acrylic acid and corresponding Sheet Resistance values

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4. Conclusion

The current study investigated the corrosion and stress corrosion cracking behavior of ITO film coated on PET substrates in 0.1~0.5M acrylic acid solutions. Combination of stress and corrosion accelerated the dissolution of ITO along with a sharp stress corrosion cracking attack. Potentiodynamic polarization data revealed a decrease in E_{corr} and increase in i_{corr} values with an increase in acrylic acid concentration. Sheet resistance measurements depicted a significant decrease in electrical conductivity as a function of molar concentration of acid; thus lowering the reliability of flexible displays.

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