Cracking of Aluminum and Silver Alloy Thin Films on Polymer Thin Films

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Abstract: Critical cracking strain of transparent conductive polymer thin films, aluminum and silver alloy thin films on polymer thin films prepared on a flexible polyethylene naphthalate (PEN) substrate was investigated by applying tensile strain to the specimens with monitoring the electric resistance of the thin films. The final target of the present research is the improvement of flexibility of organic devices, flexible displays and flexible organic light emitting diodes (OLEDs). As a result, it was found that transparent conductive polymer PEDOT: PSS films do not cause cracking and the electric resistance increased theoretically by around 10% of strain. Regarding the two layer thin films, cracking initiated at a strain of around 4% then the electric resistance started increasing. The reason has suggested that cracking was caused by the strain resulting in cracking with forming network shape. Furthermore it was found that the aspect of the cracking depends on the under-layers suggesting the effect of ductility and adhesion of the films.

Keywords: Organic semiconductor, Light emitting diode, Flexibility, Aluminum, Magnesium-silver alloy, PEN

1. Introduction

Although organic semiconductors have inferior electrical characteristics compared with inorganic semiconductors such as Si based, they can be produced by printing and are excellent in flexibility and the like, and therefore future is expected and research and development has been conducted intensively [1]. For organic light emitting devices (OLED: Organic LED) which is one type of organic semiconductors, it has already been put to practical use as display and lighting [2], taking advantage of features such as thinness, self-luminous property and high speed response. With respect to flexibility, it can be realized by using a polymer sheet or film such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN) as a substrate instead of an ordinary glass substrate [3]. For OLEDs, a transparent conductive oxide (TCO) such as indium tin oxide (ITO) or indium zinc oxide (IZO) is used as an anode, and in order to prevent the deterioration of the organic devices due to moisture, a plastic barrier layer such as silicon nitride (SiNx) is formed on the substrate [4–8]. These transparent electrodes and SiNx are inorganic materials, which are fragile thus may lose flexibility, therefore some crack generation tests applying tensile or bending strain to ITO or SiNx thin films have been carried out [4, 9, 10]. In addition, although polyethylene dioxythiophene (PEDOT: PSS) which is an organic conductive material has low conductivity, it has been reported that cracking does not occur even when applied strain is more than 60%. Furthermore, it has been reported that the ductility and electrical characteristics of multi-layer structure such as ZnS/Ag/WO3 are superior to those of ITO, therefore the improvement of flexibility can be expected [3]. More recently, it has been reported that carbon nanotubes and silver nanofibers are dispersed in an organic transparent electrode to significantly improve the conductivity of the organic film [11].

Therefore, in the previous paper, we established a method to evaluate the flexibility of the thin films for organic semiconductors, then identified and improved the brittle constituent layers in the light emitting devices. As a result it was confirmed that the ductility of the mixed layer of Alq3 and α-NPD is better than that of α-NPD. Furthermore, it was confirmed that the light emission was normally obtained by using the mixed layer, although the current/voltage characteristics slightly shifted to the high voltage side [12].

However, a test method for applying strain to OLED device while emitting light has not been established, and further, a method for improving the damage of the metal electrode and the damage of the transparent conductive film has not completely been established. In addition, although there are reports on metal electrode single layers [13, 14], since actual devices are composed of multiple layers, there are no reports that examined the effects of the
under layer. Furthermore, no reports have been found on the damage of high conductivity polymer transparent films with improved conductivity. Therefore, as a preliminary step for fabricating an improved flexible OLED structure, in this study, (1) the influence of the under layer on the damage of the metal electrode, and (2) the damage of the transparent polymer film with high conductivity were investigated experimentally, more concretely the mechanical properties and electrical characteristics of the latest PEDOT: PSS thin films assuming the anode side of OLED, and two layered thin films assuming the cathode side, were investigated.

2. Experimental

2.1 Specimens
Organic thin films were prepared on a PEN substrate with a dimension of 30 mm x 30 mm, which is widely used for OLEDs, as shown in Fig.1.

PEDOT: PSS thin films were coated in a wet process using a spin coater on a PEN substrate, then dried the solvent in an oven filled with the dry nitrogen. The thickness was from 60 nm to 100 nm by keeping the viscosity of the solution and rotational speed of the spin coater. PEDOT: PSS is mainly assumed to be used for transparent anode electrode as shown in Fig.2.

The two layered thin films assuming the cathode side, were the combination of aluminum (Al) or magnesium-silver alloy (MgAg) and small molecular organic materials Tris(8-hydroxyquinolinato) aluminum (Alq3) or 4,4′ -Bis(N-carbazolyl)-1,1′ -biphenyl (CBP) as shown in Fig.2. Organic thin film Alq3 or CBP with a thickness of 40 nm was deposited on the PEN substrate having a thickness of 0.2 μm then Al or MgAg was deposited by a multi chamber vacuum deposition system for OLED which equipped with cryogenic pumps to evacuate water vapor under a vacuum pressure less than 2 x 10⁻⁶ Pa. Organic materials and metals were evaporated from aluminum nitride (AlN) crucibles heated by electric heaters with controlling the film thickness by a crystal thickness monitor at a deposition rate of 0.1-0.2 nm/s. MgAg layer was deposited by the co-deposition method by controlling the arrival ratio of Mg to Ag as 1/10. The purities of the evaporation materials were 99.99% for metals and 99.9% for organic materials.

After the deposition, the coated samples were deserved in a package filled with dry nitrogen which has a purity more than 99.9995% and a dew point of -80 °C. The tensile specimens were cut the coated specimen into 4 mm in width.

Fig.1 Coated specimens. (Left: Specimen by vacuum deposition. Right: Specimen by wet process)
3. Result and Discussion

3.1 PEDOT: PSS
A first series of results is shown in Fig.4-Fig.6. With regard to the conventional PEDOT-PSS, which are “Empirical A” and “Empirical C” shown in Fig.4, electric resistances increase with increasing the tensile strain up to more than 20%. The experimental result (dot lines) is consistent well with theoretical resistance by 10%. Then the empirical electric resistance value shows higher than theoretical values probably due to the increase of the distance among each PEDOT molecular or cluster. Here, theoretical values were calculated using equation (1).

\[ R' = R \left( \frac{L + \Delta L}{L} \right) \left( \frac{S - \Delta S}{S} \right) \]  

Where \( R \) is an original electric resistance, \( R' \) is the electric resistance after applying strain, \( L \) and \( S \) are length and cross-sectional area of specimen respectively, \( \Delta L \) and \( \Delta R \) are the change from original values.

Generally PEDOT molecules or clusters which contribute to electric conductivity are adhered on the surface of PSS molecules, thus it is suggested that the interaction among each molecules was dramatically changed by the applied strain in the range of more than 10%. In Fig.5, the result of the latest PEDOT: PSS which has high conductivity is shown as “Empirical B”. The electric resistance is lower in two magnitude of orders than the conventional shown in Fig.4. The empirical resistance are well consistent with the theoretical in the strain range from zero to 20%, which is different from the conventional PEDOT: PSS. It would be explained that the amount of PEDOT molecules structure is greater than that of the conventional PEDOT: PSS, then the distance among each the end of molecules do not change or the interaction of each PEDOT molecules are not ruptured. Fig.6 shows images obtained by an optical digital microscope. No cracks were observed in the both conventional and the latest PEDOT: PSS even after being applied 20% of strain or more.

![Fig.4 Relation between applied strain and electric resistance of PEDOT: PSS (Conventional)](image)

![Fig.5 Relation between applied strain and electric resistance of PEDOT: PSS (High conductive type)](image)

![Fig.6 Optical microscope images of PEDOT: PSS thin films after applying a strain of 20%](image)

3.2 Aluminum top layer on polymer thin films
Fig.7 and Fig.8 show the relation between applied strain and electric resistance for the specimens with Al top layer. The electric resistances start increasing at around 3.25-4.25% and 3.25-4.85% for the specimens with Alq3 under layer (Al/Alq3/PEN) and with CBP under layer respectively, then they reach a resistance level of 7.5-70 kΩ and 1-4 kΩ respectively at an applied strain of 10%. Fig.9 and Fig.10 shows SEM images corresponding to Fig.7 and Fig.8. It is observed that the direction of cracks is perpendicular to the tensile direction. However the cracks do not pass through completely (see solid arrows), that is aluminum film still has network circuit to conduct current, which is the reason why the electric circuit has conductivity without causing rupture. The increase of the electric resistance means the increase of the length of pass due to the increase of cracks.

![Fig.7 Relation between applied strain and electric resistance of Al/Alq3/PEN](image)
3.3 MgAg top layer on polymer thin films

The other hand, in the case of MgAg, the drastic increase of electric resistance was not observed as shown in Fig.11 and Fig.12, especially MgAg/CBP/PEN specimen does not show any increase of electric resistance even at a strain of 20% or more. Regarding MgAg/Alq3/PEN structure, although the increase in electric resistance was observed from an applied strain of 8-10%, the electric resistance was only 40Ω, that is around 0.003% of Al top layers. Consequently, it was found that MgAg films shows much higher electric conductivity than that of Al thin that of Al thin films.

In terms of Mg-Ag top layer, the electric resistance of MgAg/Alq3/PET started increasing with increasing the applied strain. However, the electric resistance of MgAg/CBP/PET did not start increasing. Observing the SEM images of the MgAg top layer as shown in Fig.13 and Fig.14, the MgAg/Alq3/PET specimen has straight cracks passed through and a few network like cracks. The other hand, MgAg/CBP/PET structure shows no straight cracks. This implies that MgAg top layer caused cracking after the under layer Alq3 had caused cracking, however, in the case of MgAg top layer, it is suggested that the effect of under layer CBP had not been emerged at the applied strain due to the excellent ductility of MgAg top layer. It may be suggested that the aluminum film had been oxidized to be brittle as the tensile test was conducted in the air. However, specimens had been kept in dry nitrogen with package double shielded by aluminum/polymer layered gas barrio sheets after the preparation in a UHV vacuum chamber then taken out to a grove box filled with the high purity dried nitrogen without taking out to air. Therefore oxidation in the aluminum thin layer with a thickness of 2000 nm does not occur.
3.4 Influence of under layer

With regards to the influence of the under layers, the critical cracking strain of Alq3 and CBP monolayers on PEN substrate is 5.0 % and 7.3 % respectively, indicating that CBP has a little higher ductility than Alq3 [15]. As mentioned in Fig.7-Fig.8, the critical cracking strain of Al/Alq3/PEN and Al/CBP/PEN structures were 3.25-4.25 % and 3.25-4.85 %, thus it have been suggested that the influence of under layer was emerged on the cracking phenomena of Al top layer. However another possibility is not denied, namely the critical cracking strains of the Al/Alq3/PEN and Al/CBP/PEN were smaller than those of monolayers, indicating the aluminum layers started cracking at smaller strain than organic under layers of Alq3 and CBP.

3.5 Delamination mechanism in the direction perpendicular to the tensile direction

Since the test piece of this experiment is thin, it can be assumed that it is in a plane stress state at the time of tensile test. The strain component in the plane stress state is expressed by the following equations.

\[ \varepsilon_x = \frac{1}{E} (\sigma_x - \nu \sigma_y) \]  \hspace{1cm} (2)

\[ \varepsilon_y = \frac{1}{E} (\sigma_y - \nu \sigma_x) \]  \hspace{1cm} (3)

Therefore, when pulling in the x direction, distortion of the following equation occurs also in the y direction, as shown in Fig.15.

\[ \varepsilon_x = \frac{V \sigma_y}{E} \]  \hspace{1cm} (4)

It has been therefore suggested that the compressive strain in the y direction causes the delamination (Buckling), as shown in Fig.9, Fig.10 (see dot arrows) and Fig.16, which probability depends on the adhesion force to the substrate.

The delamination phenomena was examined by using numerical simulation with a finite element method (FEM) where compressive stress was applied in the direction parallel to the surface of aluminum thin film on PEN substrate. In this case, a thin interface layer was inserted in order to simulate the adhesion. One of the calculated results are shown in Fig. 17. It was found that the stress to cause delamination in the direction perpendicular to the aluminum surface is created by the compressive stress, resulting in buckling.
4. Conclusions

It was found that the PEDOT: PSS films do not cause cracking and the electric resistance increased theoretically by around 10% of strain. Regarding the two layer thin films, cracking initiated at a strain of around 4% then the electric resistance started increasing. The reason has suggested that cracking was caused by the strain resulting in cracking with forming network shape. Furthermore it was found that the aspect of the cracking depends on the under-layers suggesting the effect of ductility and adhesion of the films.

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