Study on Evaluation Methods for Mechanical Properties of Organic Semiconductor Materials

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Abstract. This paper describes the evaluation method of the mechanical properties of the materials constituting organic semiconductor, and the test result of the relation between applied strain and the fracture of thin films. The final target of this work is the improvement of flexibility of organic light emitting diode (OLED), the tensile test of the thin films coated on flexible substrate is conducted, and the vulnerable parts of the constituent material of the OLED is quantitatively understood, further the guideline for designing OLED structure will be obtained. In the present paper, tensile test of an aluminium oxide thin films deposited on a poly-ethylene-tere-phtalate (PET) substrate was carried out under constant conditions, the following results were obtained: (1) Cracking of the aluminium oxide thin films was observed using an optical transparent formula microscope at more than 40 times magnification; (2) Cracking was initiated at a strain of about 3%; (3) the number of cracks increased proportional to the strain, and saturated at about 9% strain; (4) Organic thin films α-NPD caused the same cracking as oxide thin films.

1. Introduction

Since organic semiconductors can be manufactured by printing, and have higher flexibility compared to inorganic semiconductors, such as type silicon, their future is expected and the research and development of organic semiconductor including solar cells has been extensively conducted regardless of inferior electrical characteristics. In addition, organic light emitting diode (OLED) which is one of the organic semiconductors, has been practically applied as displays and lighting due to the features thin, self luminous and fast response.

It is possible to obtain flexibility by applying a polymer sheet or films, such as PEM or PET, for the substrate of organic semiconductor in stead of a conventional glass substrate. However, transparent conductive oxide (TCO) such as Indium Tin oxide (ITO) or Indium Zinc oxide (IZO) films such as SiNx should be coated on the flexible polymer sheet substrate which easily transmitted through the vapour, in order to prevent deterioration of the organic semiconductor element due to moisture. These transparent electrodes and SiNx may impair the flexibility because they are brittle inorganic materials therefore the tensile and bending tests of ITO and SiNx have been carried out to evaluate the cracking...
due to distortion. (1) Recently, it has been reported that transparent conductor organic material PEDUT:PSS (polyethylene dioxythiophene doped with polystyrene sulfonate) does not show cracking even in a tensile strain of 60% although its electric conductivity is not so low. (2) More recently, it has been also reported that the multilayer transparent electrodes having a structure of ZnS/Ag/Wo shows much higher flexibility than ITO and comparable electric properties. (3) Therefore, the improvement of flexibility of OLED can be expected.

As described above, the establishment of a method of assessing the flexibility of the thin film constituting organic semiconductor has become an important issue, however systematic consideration has not been found. Therefore, in the present work, the observation methods for the cracking of TCO and transparent organic light emitting materials were comparatively studied, and the observation results for the cracking of inorganic thin films, such as aluminium oxide and IZO, and typical organic thin film used for OLEDs were reported.

2. Experimental

2.1 Test specimens

The test specimens of inorganic thin films were the aluminium oxide with an 80 nm thickness coated on a PET substrate having a thickness of 25 μm and IZO with a 200 nm thickness coated on a PEN substrate with a 250 μm thickness. The test specimen of organic thin film was the NPD with a 200nm thickness deposited on the PEN substrate with a thickness of 250nm. The aluminium oxide thin film was vacuum deposited by a roll to roll web coater. The IZO thin film was deposited by a batch type magnetron sputtering apparatus. The deposition of the NPD thin film was carried out by a multi chamber type vacuum deposition system for organic thin films.

2.2 Tensile test

The above test pieces were cut to 4 mm in width, and the occurrence of film cracking while providing tensile strain was observed under an optical microscope. In a manner to clamp the specimen to impart tensile strain with the micromere, the gauge length was 20 mm. Therefore, assuming an error of ±5 μm in micrometer and mechanical system, and error of 0.025% was estimated at a strain of 1%, namely the relative error results in 2.5%. Moreover, in order to correspond to the transmission type optical microscope, the parts under test piece were composed of transparent acryl and opening.

2.3 Observation of crack

Digital photos were taken while specimens were observed by the optical microscope, to understand the relationship between cracking and applied strain. Thin films observed in the present study had a high light transmittance, and the substrate was transparent plastic sheet, thus it was not clearly visible by a reflection type optical microscope in which light was irradiated from the objective lens. Therefore, transmission type optical microscope where light was introduced from blow the transparent specimen to the objective lens was employed. In addition, since the cracking of the organic thin films...
was too fine to observe clearly even with the transmission type optical microscope, a laser microscope (manufactured by JOEL, JSM 6700F) were used in combination for observing the occurrence and the configuration of the cracking. In the observation of organic film, gold was deposited in a thickness of 3nm on the specimen for the prevention of charge up because of the high electrical resistance materials.

3. Result and Discussion

3.1. Inorganic thin films
Firstly, Fig3 shows an example of the cracking occurred in the aluminium oxide film. Cracking was easily observed by the transmission type optical microscope. The relation between the tensile strain and the number of cracks per unit length in the direction of the tensile is show in Fig.4. The number of cracks increased with the increase of strain, then strain of about 8% or more, number of cracks was saturated to a constant value. Next, Fig.5 shows an example of the cracking in the IZO film. As with the aluminium oxide film, cracking occurred in approximately 3% applied strain, the number of cracks increased with the increasing strain, and it showed a constant value.

![Fig.3 An example of the cracking in aluminium oxide film](image)

![Fig.4 Relation between strain the number of cracks per unit area in aluminium oxide film on PET substrate](image)
3.2. Organic film

3.2.1 Observation result using optical microscope

Figure 6(a) shows a transmission type optical micrograph of $\alpha$-NPD film. Cracking could not be recognized in 40 times magnification which was different from the cracking of aluminum oxide and IZO films, and fine cracking in $\alpha$-NPD film was confirmed in 400 times magnification. The cracks narrow spacing and unclear in the magnification.

As shown in Fig.7, the cracking of the test piece applied around 8% strain was clearly observed at 400 times magnification with the optical microscope.
3.2.2 Observation result using laser microscope

In order to confirm the presence or absence of cracking in the specimens applied low strain, specimens were observed after tensile test using laser microscope and a field emission type scanning electron microscope (FE-SEM). First, Fig.8 shows the result observed specimen shown in Fig.6 with the laser microscope. The optical microscope images were taken with a reflection type optical microscope. It was found that the recognition of cracks, which was not possible at 400 magnifications with transmission type microscope, was possible at 4500 times magnification even with reflection type optical microscope, although the image was not so clear. On the other hand, crack was clearly recognized by the reflection of the laser light image. In addition, it was confirmed by the height measurement that something that looks like points were the projections of about 2 μm in height, thus it has been suggested that the projections are the adhesion of splash or foreign material on the substrate. Since cracks did not pass through the toe of the projection, it has been suggested that the projections are not the origin or the passage.

![Laser + Colour](image1)

![Colour](image2)

![Laser](image3)

![Height](image4)

Fig.8 Images of the specimen shown in Fig.6 observed by a laser microscope at 4500 times magnification

Secondly, Fig.9 shows the result observed the specimen shown in Fig.7. In addition to the vertical line-shaped cracks, granular or short horizontal stripes were observed. From the result of height measurement by laser, the longitudinal line and the granular or lateral stripes had a convex height of around more than 9 μm, which was different from the concave line indicating crack that was expected. Therefore, further observation was conducted using the FE-SEM at higher magnification to investigate the configuration, as the following section.
3.2.3 Observation result using laser microscope

Figure 10 shows the image of the specimen, shown in Fig. 8 (b), by FESEM. From observation at a magnification of 10000, it was estimated that the vertical stripes were cracks and they were concave. The protrusion having a height of 6 \( \mu m \) in Fig. 8 (b) was assumed that the end of the crack in the film is peeled from the substrate and curled. It was also estimated that the convex shape, which was recognized as a short horizontal lines or granular, unlike the vertical protrusion, was an overlapping or bridged shape which was created by buckling lifted the coating film to peel resulted from the compressive stress. The compressive stress was produced by the shrinkage in the longitudinal direction due to the tensile strain in the horizontal direction. For reference, the specimen in Fig. 6 (a) was observed by FESEM, the crack was not recognized. It was considered that this was because the crack had not opened almost no irregularities were formed.
3.2.4 Summary of observation method

- Regarding transparent films and substrate, transmission type optical microscope was suitable for observing crack in coated film, and crack was observed at a magnification of 40 times or more.
- When the interval of crack was narrow and crack was unclear, the magnification of the optical microscope needed to be changed to 400 times, or laser reflection microscope was recommended.
- Less information was obtained by using SEM for small cracks in the low strain condition where convex-concave was not created.

4. Conclusion

(1) Cracking of the aluminium oxide thin films was observed using an optical transparent formula microscope at more than 40 times magnification.
(2) Cracking was initiated at a strain of about 3%.
(3) The number of cracks increased proportional to the strain and saturated at about 9%.
(4) Organic thin film $\alpha$-NPD caused same cracking as oxide thin films.

References

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