Retardation and Imidization Study of Polyimide in OLED

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The degree of imidization of polyimide used in VIA and PDL materials is important characteristic because of relationship with life cycles in OLED. During the curing process, a polyimide film optically changes to a negative C-plate like sheet structure. The more polyimide chains packed closely, the higher out-of-plane retardation (Rth) is. In other words, for analyzing retardation properties of polyimide except for imidization ratio, Rth could be a useful analyzing method. In this study, using polyimide formed from different curing temperature and various chemical compositions, relation between Rth and properties of polyimide film was investigated.

1. Background

Flexible Organic Light Emitting Diodes (OLED) technology has been adopted in smart phone display. Polyimide (PI) has been used widely as the material in flexible display because of high temperature stability and good mechanical properties. Polyimide is not only used as substrate but also as planarization organic material and pixel defined layer. In OLED display, the preventing out gas such as lots of unreacted chemical chains and solvents in PI curing process is very important, which damages OLED and reduces the luminance. So the minimization of out gas in organic material is the key to make good reliable OLED display.

Poly imidization is a condensation reaction due to heat in Fig. 1. Amic acid functional group is changed imide and the ring or sheet-like structure is made.

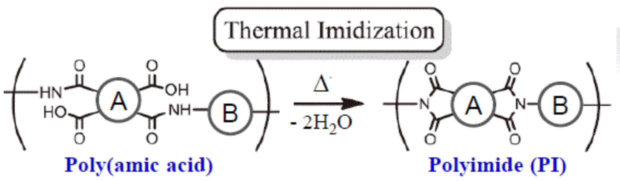

Fig. 1. Poly imidization reaction from poly amic acid

Fourier transform infrared spectroscopy (FT-IR) was used to know the degree of imidization of PI in curing process. [1-3]. It is a simple tool and easily quantify from imide peak. In Fig. 2., the degree of imidization is saturated over 250℃. Generally the curing temperature of planarization PI in OLED fab process is about 250℃. So the degree of poly imidization from FT-IR is over 90%. But when there is the thickness variation of PI or the processing temperature of the equipment fluctuates, pixel shrinkage failure frequently happens and the source of the problem is guessed because of out-gas from PI. But from FT-IR measurement, the difference between abnormal and normal panel could not be distinguished. So many engineers and scientists have tried to find another tool to evaluate the property of organic material.

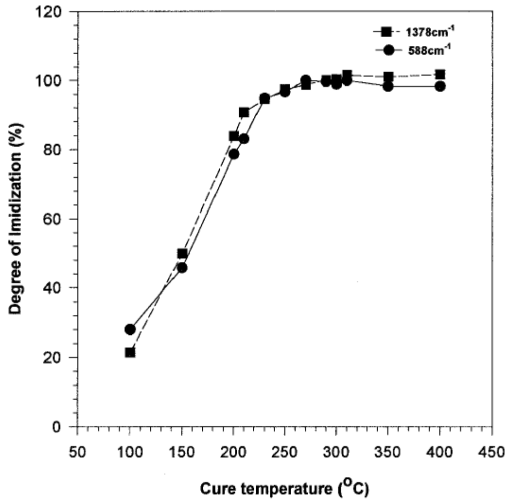

Fig. 2. W.S. LI, et. al., showed the degree of poly imidization from FT-IR according to temperature. [3]

In this paper, we measured out of plane retardation (Rth) of PI according to curing temperatures and found the correlation of packing density of PI and reliable properties of OLED panel. The ides was gotten measurement. After polymerization of PI from poly amic acid (PAA), the structure is changed to negative C-plate optically. Polyimides may stack like in Fig. 3 allowing the carbonyls of the acceptor on one chain to interact with the nitrogen of the donor on adjacent chains. This characteristic gives the high temperature stability. The degree of stacking order can be measured as out of plane retardation (Rth). In this case, Rth value is negative because in-plane refractive indexes (nx, ny) smaller than out of plane refractive index (nz) and Rth definition is like equation (2)

$$\mathrm{Re} = (n_x - n_y) \times d \quad (1)$$

$$R_{th} = \left(n_z - \frac{n_x + n_y}{2} \right) \times d \quad (2)$$

where Re, Rth, nx, ny, nz, and d represent in-plane retardation, out of plane retardation, x,y,z axis refractive index, and thickness, respectively

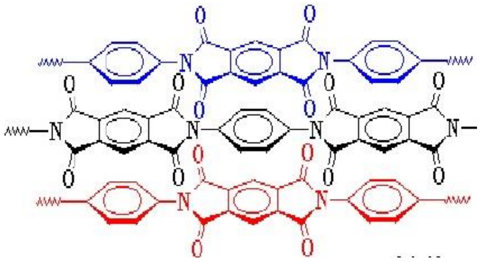

Fig. 3. The stacking structure of polyimides

Re value is almost zero because there is no ordering in x-y plane, that is to say random arrangement.

The Rth value is assumed to be decided by two factors. One is the degree of poly imidization. Because it becomes the ring structure as the more imide groups are made, to be stabilized with the energy, it is aligned in the sheet-like structure. The other is residual solvent ingredients and small –size molecule such as additives. These obstruct the sheet-like structure and make bent structure. In this case, the absolute value of the Rth becomes small. As shown in Fig. 2, when the curing temperature comes to over 250℃, amic acid groups get to be mostly changed to imide. Therefore, we can think that residual solvent ingredients or additives get to decrease as the absolute Rth value becomes larger.

2. Experiment and Result

To know the retardation according to curing temperature of PI, the planarization PI materials were coated on glass as 3.0 ㎛ thickness. These PI are two kinds of type. One has photoactive compound (PAC) as an additive in poly amic acid. And it can be patterned during photo lithography. If this additive doesn't react all and remains after photo lithography processes, it can become the cause for the out gas and obstruct sheet-like structure of PI. Then we cured the coated glasses with PI in oven with the various curing temperatures from 230℃ to 300℃ for 1 hour. The other type is PI without PAC as a control group. This glass was cured in 250℃ for 1 hour. Retardation measurement machine is Axo-scan 40H. It had been made by Axometrics Company. The measurement condition is as below.

Wavelength [nm]	Tilt angle	Azimuthal angle	Number of measurement
550nm	-20°~ 20°	0° ~180° 90°~270°	10 times

Table. 1. Retardation measurement condition.

3. Discussion

Retardation data according to incident angles in Axo-scan40H is shown in Fig. 4. Red and blue lines indicate the two retardation data in azimuthal scan directions. Y value means absolute retardation and we can get the Rth in 90° incident angle from extrapolation curve.

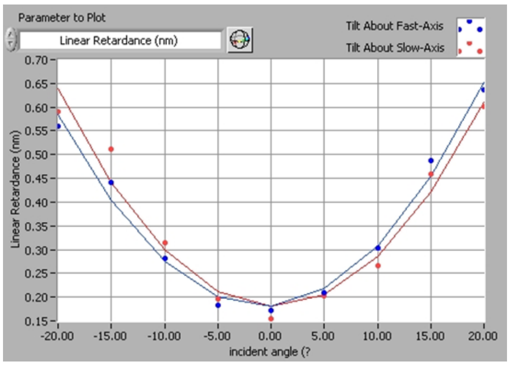

Fig. 4. The stacking structure of polyimides

In Fig. 5, we could know that Rth values increase gradually from curing temperature 230℃ to 300℃. It means the sample in 300℃ has higher packing density than the sample in 230℃. Because as curing temperature goes up even after for the enough imidization over 250℃, the residual solvent ingredients or additives were decreased. So at 300℃ curing temperature, PI chains become a good sheet-like structures. The other proof of this condensation reaction is the comparison Rth data of PIs with PAC and without PAC. PAC ingredient is one of the obstacle factors to form sheet-like structure and when the Rth of PI without PAC is higher than the Rth of PI without PAC.

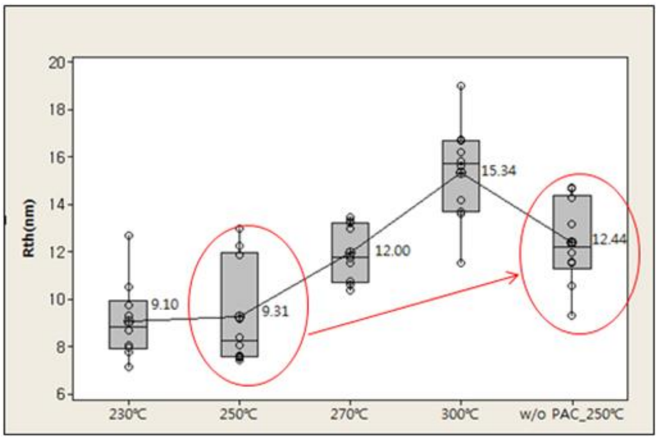

Fig. 5. Absolute Rth measurement data in various curing temperatures and Rth of PI without PAC

4. Impact

We evaluated the Rth of PIs in the various curing temperatures and revealed the correlation. The retardation analysis could be good estimation tool in reliability test of PI. In the future, we are planning to make sure whether the high Rth samples has long life cycles in OLED in PI curing test.

5. Reference

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