Thermal Stability in Organic and Polymeric Thin Films for Organic Electroluminescent Display

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Abstract

The capacitance-temperature (C-T) measurement technique is proposed in the present work to investigate the thermal stability of organic and polymeric thin films for organic electroluminescent display (OELD). The single layer devices with the individual materials were subjected to the C-T measurement, prior to the examination of the complete OELD. The single layer devices with the small molecules destroyed below 180 °C depending on the kinds of materials. However, the device with the hole-transporting polyimide did not show any relaxation up to 200 °C. The small molecule based OELDs failed to emit light after annealing, whereas that with the hole-transporting polyimide worked well in spite of large reduction in intensity.

Introduction

To improve the stability of OELD, Tang's group reported three methods such as the insertion of stable hole-injecting layer between the hole-transporting layer and anode, use of stable hole-transporting material, and alternating current driving [1]. Alternative approach is also proposed that the ITO surface treated with the oxygen plasma improve the injection of holes into the hole-transporting layer from the anode [2]. As indicated previously [1], the material aspect is much more important than any others because the device fabricated with weak organic molecule has intrinsic instability as formed. In this sense several high molecular weight molecules including starburst or bulky aromatic group have been synthesized and applied for hole-transporting layer, but they have many limitations because of the inherent property of small molecule rather than polymer. Kim's group has reported on the first application of thermally stable polyimide with higher glass transition temperature more than 200 °C as an emissive layer and a hole-transporting layer [3,4]. However, in practice, there are many obstacles in the wet processing of angstrom scale thin film with these polyimides for the large area flat panel display.

In the present work, we have synthesized novel hole-transporting polyimide with new triarylamine moiety *via* vapor deposition polymerization (VDP). The thermal stability of the devices with this polyimide as well as several small organic molecules was examined by the capacitance-temperature (C-T) measurement.

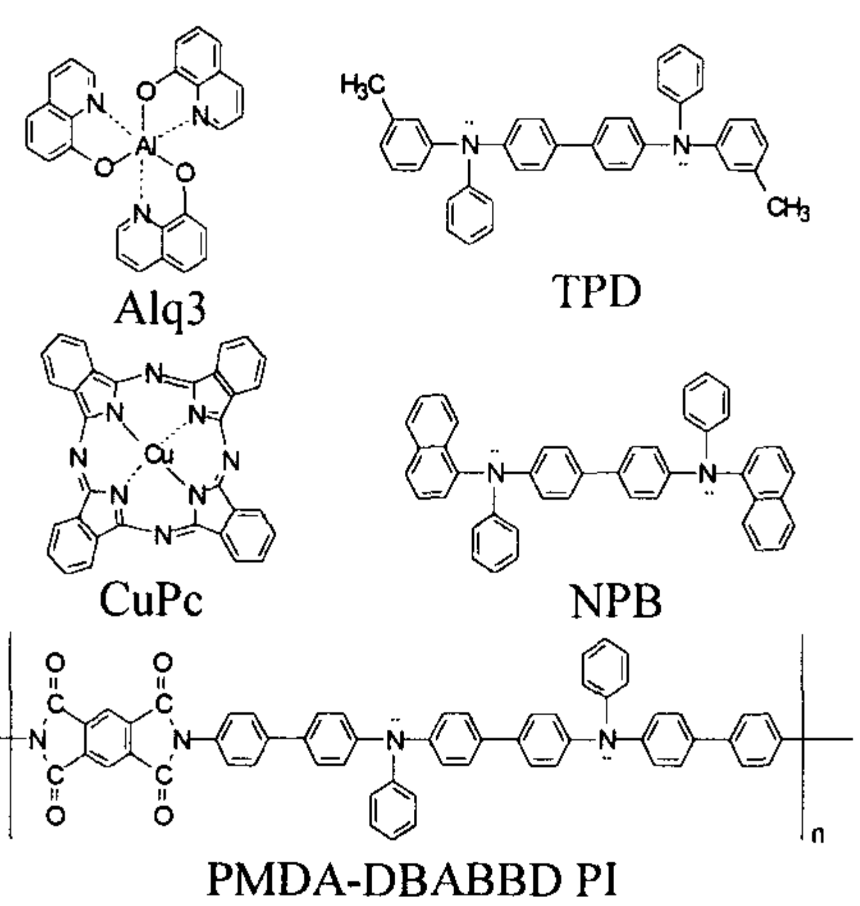

Fig. 1. Chemical structure of organic and polymeric materials

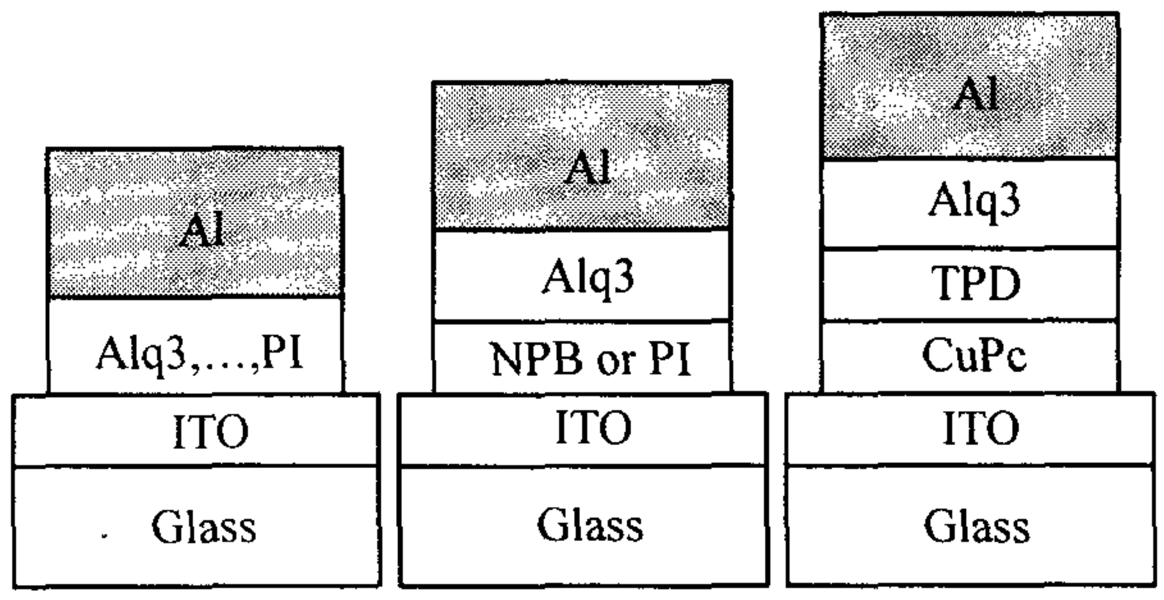

Fig. 2. Device structure fabricated in the present work.

Materials and Device Fabrication

Figure 1 shows the chemical structure of small organic molecules used in this work. Poly[*N,N'*-diphenyl-*N,N'*-bis(4-aminobiphenyl)-(1,1'-biphenyl)-4,4'-diamine pyromellitimide] (PMDA-DBABBD PI) was prepared *via* thermal imidization of the respective poly(amic acid), obtained by the VDP of *N,N'*-diphenyl-*N,N'*-bis(4-aminobiphenyl)-(1,1'-biphenyl)-4,4'-diamine (DBABBD) and pyromellitic dianhydride (PMDA), at 200 °C for 1 hr. As shown in Figure 2, several kinds of single, double, and triple layer devices were fabricated in a size of 4 mm^2 for the C-T measurement. The OELDs were annealed at 150 °C for 1 hr to investigate the luminance-current density-voltage (L-J-V) characteristics before and after annealing. All organic materials and aluminum were thermally evaporated at *ca.* 2×10^{-6} torr. The deposition rate was varied from 0.1 Å/s to 5 Å/s with respect to the material.

The C-T relationships were measured by using the IAE-C-T-SYS1 equipped with impedance analyzer (HP 4192), sample chamber, and temperature control unit. The sweep frequency was varied from 100 Hz to 1 MHz during heating the device at a heating rate of 5 °C/min. The oscillating voltage was selected from 10 mV and 100 mV considering the thickness and the property of materials. The L-J-V characteristics of the device before and after annealing at 150 °C for 1 hr were measured by using the IAE-OELD-SYS1 consisted of source-measure-unit (Keithley 237) and calibrated silicon photodiode.

Results and Discussion

Figure 3 shows the effect of temperature and sweep frequency on the capacitance of the Alq3 thin film inserted device. The capacitance of the device was marginally decreased up to 180 °C and then rapidly dropped, meaning that the film was catastrophically destroyed. It is regarded from the result that the glass transition temperature of the Alq3 thin film is *ca.* 180 °C, which is slightly different from the reported value of *ca.* 172 °C. The difference of *ca.* 8 °C is mainly owing to the practical state or shape of the samples. Because Alq3 is used in a shape of thin film, it is strongly suggested that the C-T measurement is more useful to get clear transition mode than the differential scanning calorimeter (DSC).

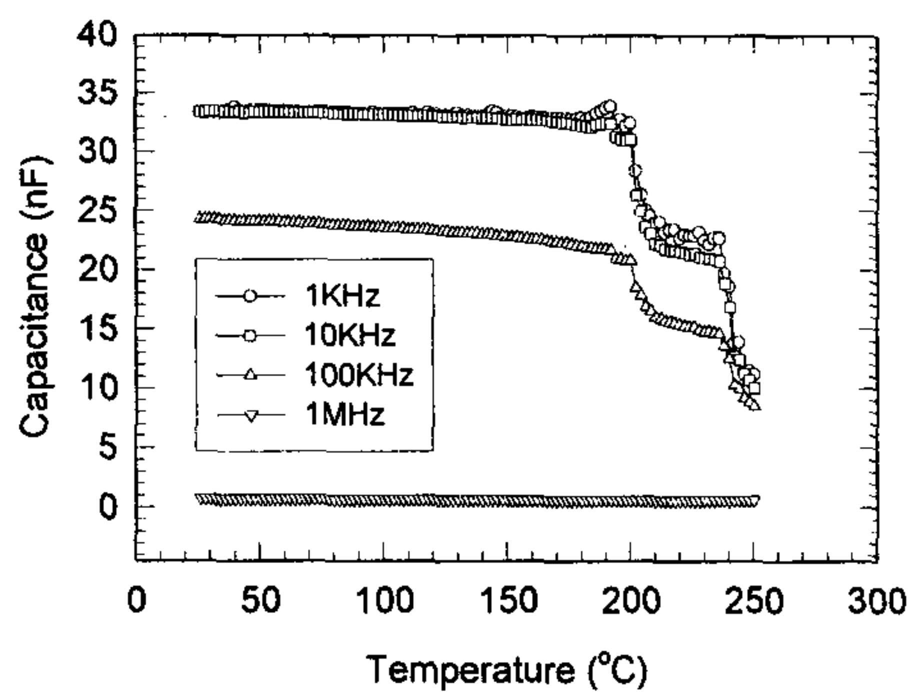

Fig. 3. C-T characteristics of ITO/Alq3/Al device with various frequencies

Figure 4 shows the C-T characteristics of the single layer devices with the fixed frequency of 1 kHz. The capacitance of the device with the CuPc thin film seems to be changed at around 125 °C as the relaxation temperature. The device with the NPB thin film was catastrophically destroyed at *ca.* 110 °C, which is higher by about 10 °C than the reported value [5]. The capacitance of the device with the TPD thin film was discretely dropped at *ca.* 76 °C and then stabilized up to *ca.* 120 °C. The initial transition temperature was also higher than that reported previously [5]. Unlike the devices with small organic molecules, the hole-transporting polyimide based device shows no catastrophic changes in the capacitance, meaning the excellent thermal stability of the polyimide thin film below 200 °C.

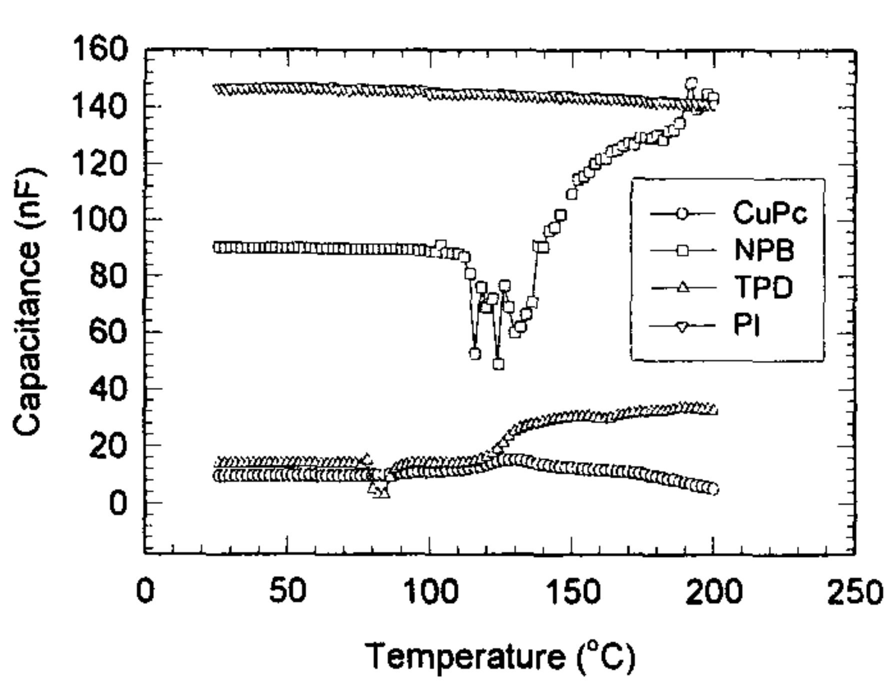

Fig. 4. C-T characteristics of the single layer devices having hole injecting or transporting materials.

The L-J-V characteristics of the OELDs before and after annealing at *ca.* 150 °C appear in Figure 5. The fresh OELD with the NPB thin film as hole-transporting layer shows the general L-J-V characteristics with the turn-on voltage of *ca.* 7 V, whereas the annealed OELD exhibits almost ohmic current and no light emission. However, the annealed OELD with the hole-transporting polyimide thin film works quite well even though there are slight decrease in the current density and the emission intensity. It is thought that the thermally induced growth of dark spots during annealing process is mainly responsible for the deterioration of the annealed device performance because the naked device without hermetic encapsulation was used for the measurement.

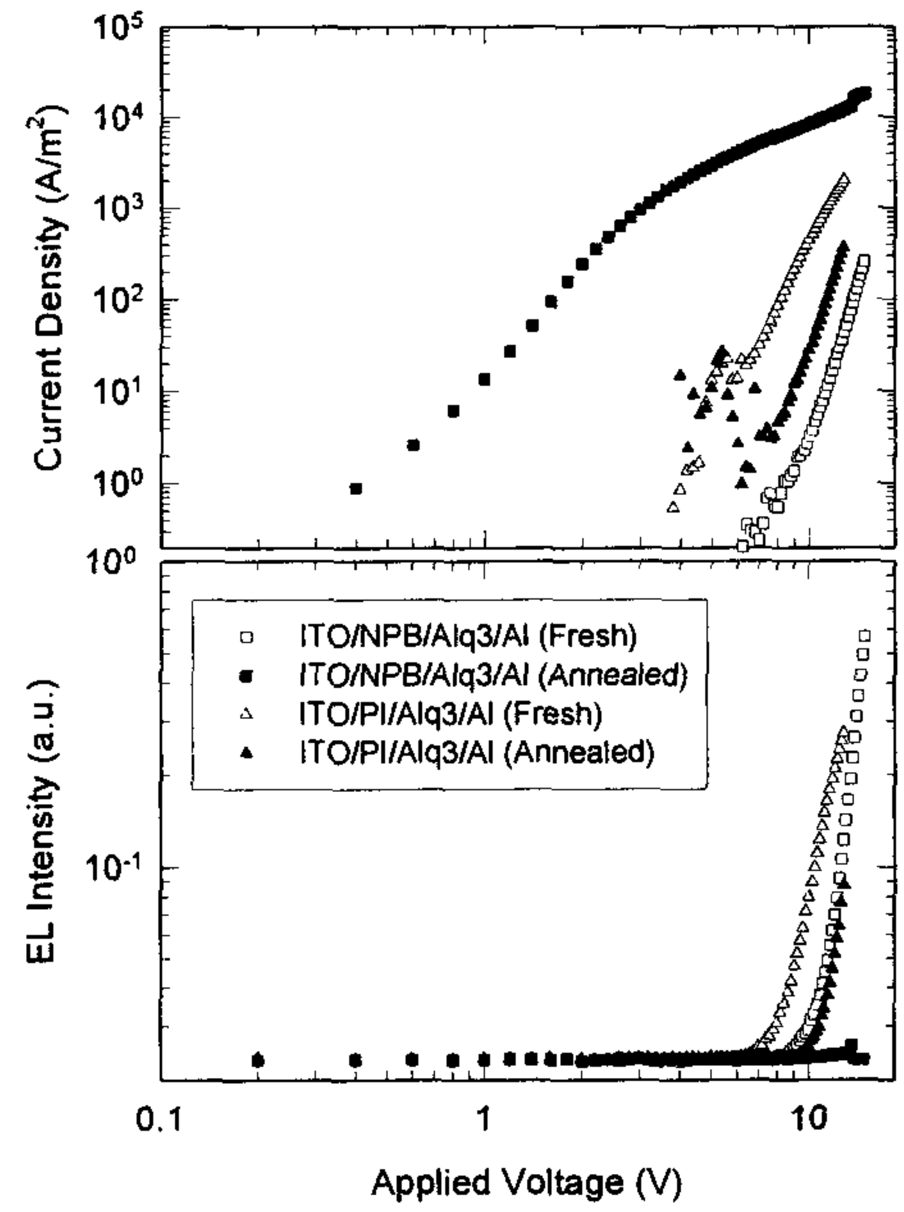

Fig. 5. L-J-V characteristics of the OELDs before and after annealing at 150 °C for 1 hr.

Conclusion

It was found that the device with the polyimide hole-transporting layer was more stable than that with the small organic hole-transporting molecules. In addition, it should be noted that the OELD maybe thermally unstable if only one is weak among the constituents. Finally the capacitance-temperature measurement is good technique to examine accurately the relaxation temperature of the organic thin film in configuration of complete device, not bulk.

References

[1] S. A. Van Slyke, C. H. Chen, and C. W. Tang, *Appl. Phys. Lett.*, vol. 69, p. 2160, 1996.

[2] C. C. Wu, C. I. Wu, J. C. Sturm, and A. Kahn, *Appl. Phys. Lett.*, vol. 70, p. 1348, 1997.

[3] J. G. Lee, Y. Kim, S. H. Jang, S. N. Kwon, and K. Jeong, *Appl. Phys. Lett.*, vol. 72, p. 1757, 1998.

[4] H. Lim, H. Park, J. G. Lee, Y. Kim, W. J. Cho, and C. S. Ha, *Proc. SPIE*, vol. 3281, p. 345, 1998., and references therein.

[5] C. H. Chen, J. Shi, and C. W. Tang, *Macromol. Symp.*, vol. 125, p. 1, 1997.