

Utilization of Parylene Thin Film for Passivation of Organic Light Emitting Diodes

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Abstract

The chemical vapor condensation process of Parylene-N thin films was investigated and applied to the passivation of the organic light emitting diodes (OLEDs). The effects of process variables on the deposition rate were studied, and it was found that the deposition rate of Parylene increases with increasing precursor sublimation temperature but decreases with increasing substrate temperature. The Parylene film was used as a passivation layer for OLEDs, and as a result, the lifetime of the passivated OLEDs was increased by a factor of about 2.3 compared with that of non-passivated OLEDs.

Introduction

Organic Light Emitting Diodes (OLEDs) have attracted broad attention due to their excellent device properties such as low driving voltage, high brightness, wide viewing angle, etc. Since Tang and VanSlyke first reported bilayer OLEDs in 1987[1], many researchers have made considerable efforts to improve the emission efficiency and prolong the lifetime of the devices. Since most of the organic materials currently available for OLED emitter are moisture sensitive, it is still a critical issue in developing commercial OLEDs to provide practical sealing method in order to sustain the initial device performance for sufficiently long lifetime.

It is well known that OLEDs have a limited lifetime because of a decrease in EL efficiency under atmospheric condition. The OLED lifetime is severely limited in the presence of humidity and oxygen[2]. Therefore the encapsulation of an OLED is very important in commercial applications. However, Hermetic encapsulation techniques using a glass or a metal canister with epoxy resin in a N₂ environment have inherent drawbacks in that the thickness of encapsulation layer is greater than the OLED itself and the method cannot be applied for flexible OLEDs. Thus it is necessary to develop a thinner and low-cost encapsulation technique for commercial OLEDs

In this study, Parylene-N films were deposited by chemical vapor condensation (CVC)[3] technique

using [2.2]paracyclophane dimer as a precursor. The effects of process variables on the deposition rate were investigated, and the properties of deposited films were characterized by various characterization techniques such as FT-IR, TGA, etc. The deposited Parylene-N films were applied to the passivation of OLEDs, and the results are discussed.

Experiment

The Parylene deposition experiments were carried out in a CVC reactor according to the Gorham's method. After the precursor ([2.2]paracyclophane, >97%) was sublimated in a bubbler above 80 °C, the precursor was transferred by the carrier gas to the tube furnace, where it was pyrolyzed into p-xylylene monomers at the temperature of 660 °C. The product monomers then enter into the deposition chamber, in which they are condensed on the substrate surface and subsequently polymerized. Helium was used as a carrier gas, and its flow rate was fixed at 50 sccm. The reactor pressure was maintained at 0.5 Torr.

The deposited Parylene films were characterized by FT-IR (Bio-Rad, FTS 3000FX) for structure identification. Thermal properties were analyzed by TGA (CAHN, CAHN D-2). The film thickness and surface roughness were measured by surface profiler system (VEECO, Dektak3).

The OLEDs with the structure of ITO/TPD/Alq₃/AlLi were fabricated, and the lifetime was measured.

Results and discussion

Molecular structures of parylene are shown in Fig.1. In the Parylene family, Parylene-N (poly-p-xylylene) is commercially easily available, and it has the highest melting temperature and lowest dielectric constant among the unfluorinated Parylenes. The dielectric constant of Parylene-N does not vary with changes in frequency, which is the desired characteristics for interlayer dielectrics in ULSI devices. Parylene-C (polychloro-p-xylylene) provides an excellent combination of

electrical properties and a very low permeability to moisture and gases, but it has relatively low melting temperature. Parylene-D (polydichloro-*p*-xylylene) has similar physical properties to Parylene-C with added ability to endure higher temperatures, but it has relatively higher gas and moisture permeability. Parylene-F (polytetrafluoro-*p*-xylylene) has the highest melting temperature and lowest dielectric constant among the whole Parylene family, however it is the most expensive material. Therefore, based on the consideration of the material properties and cost, Parylene-N was selected as a test material for OLED passivation in this study.

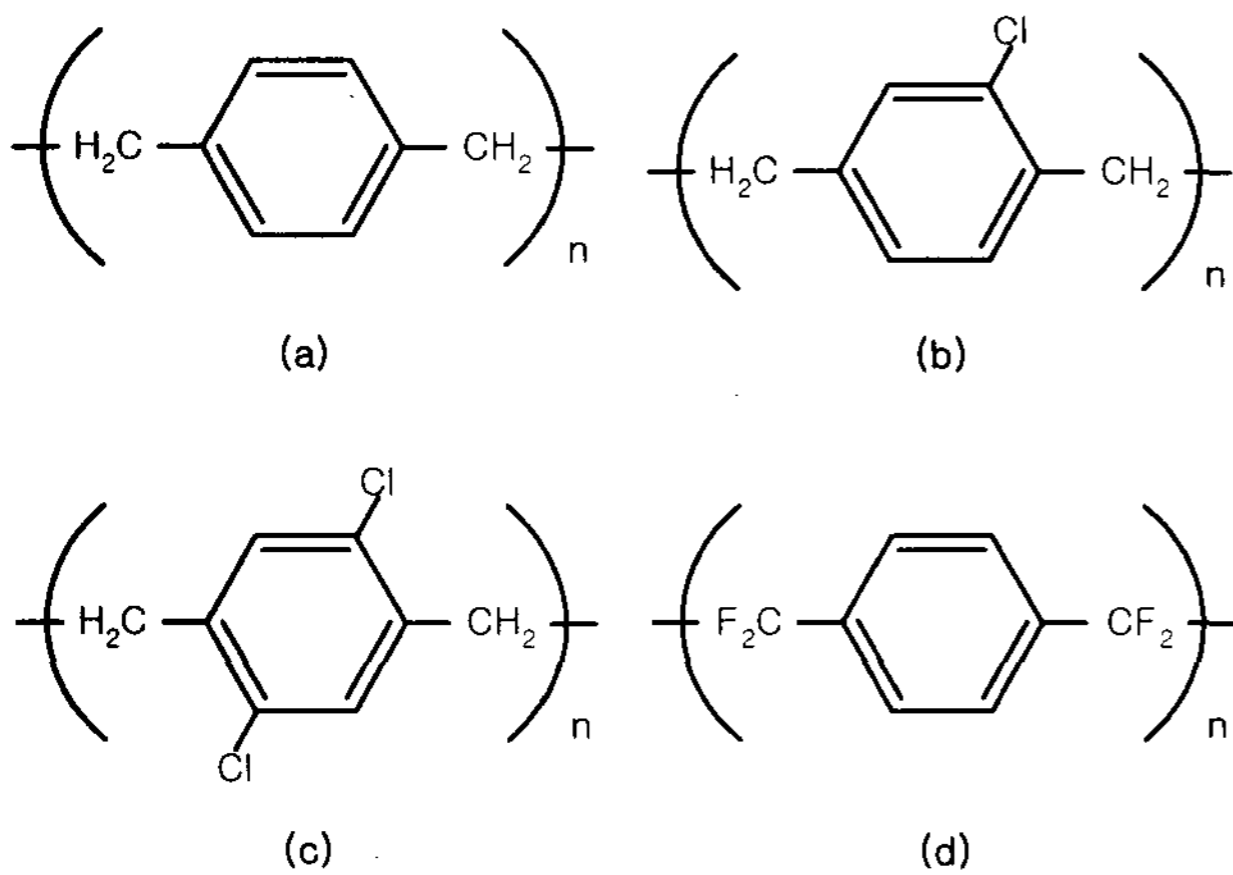
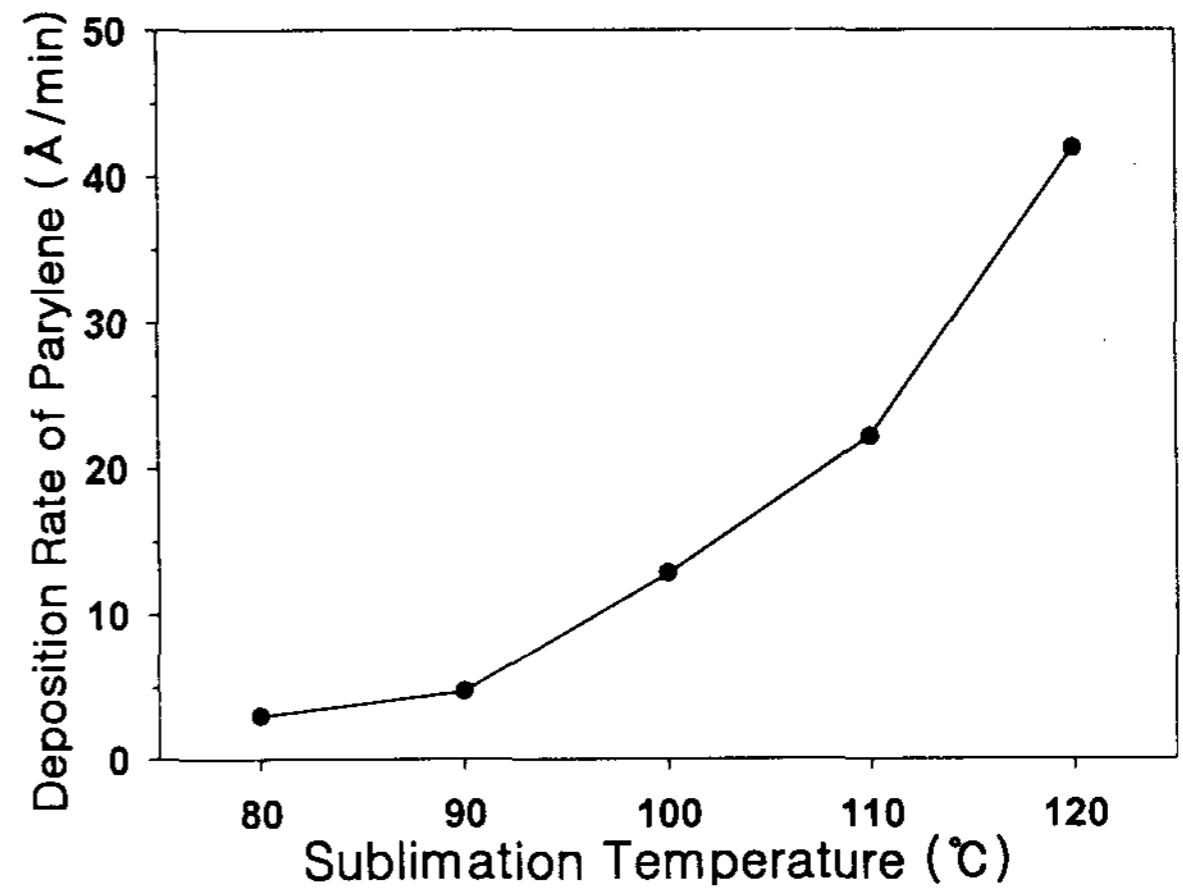
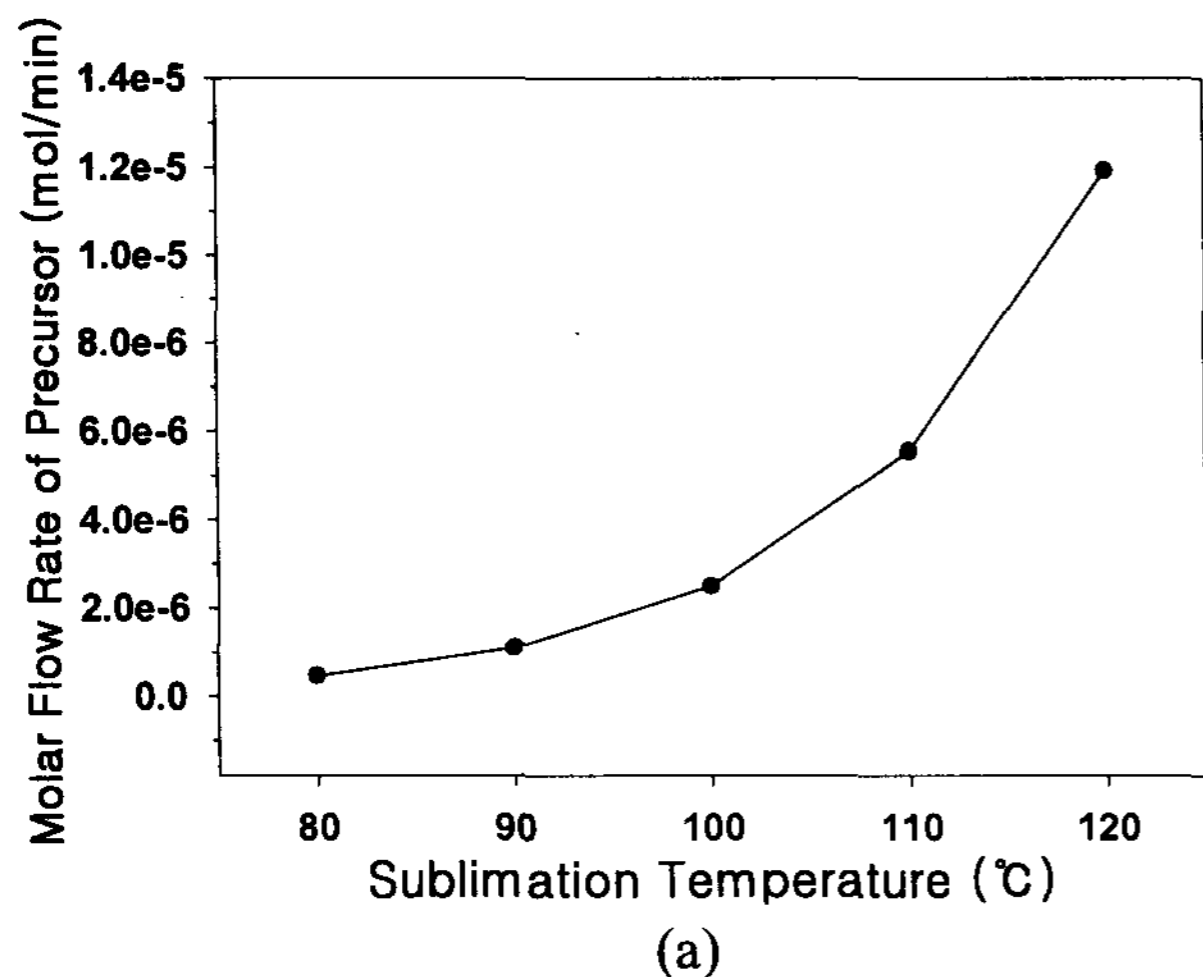


Fig. 1. Molecular structures of Parylene and its derivatives: (a) Parylene-N (poly-*p*-xylylene), (b) Parylene-C (polychloro-*p*-xylylene), (c) Parylene-D (polydichloro-*p*-xylylene), (d) Parylene-F (polytetrafluoro-*p*-xylylene).

Fig. 2 shows the dependence of molar flow rate of precursor (Fig. 2(a)) and deposition rate (Fig. 2(b)) on the precursor sublimation temperature at otherwise fixed operating conditions.

As shown in the figure, the molar flow rate of



(b)

Fig. 2. Effects of precursor sublimation temperature on (a) molar flow rate of precursor, (b) deposition rate: $T_p = 660$ °C, $T_d = 1$ °C, $F_{He} = 50$ sccm, and $P = 0.5$ Torr.

precursor increases monotonously with increasing precursor sublimation temperature from 80 °C to 120 °C. The molar flow rate of precursor entering into the pyrolysis furnace to produce monomers is known to depend on the carrier gas flow rate, bubbler pressure, and precursor sublimation temperature[4].

The molar flow rate of precursor (F_p) can be described by equation (1):

$$F_p = \frac{F_{He} P^*}{(P_b - P^*)} \quad (1)$$

where P_b is the total pressure, and P^* is the saturated vapor pressure of precursor, in the bubbler. The F_{He} and P_b were measured and controlled by the mass flow controller and the pressure gauge, respectively. The P^* was calculated from the reported vapor pressure equation at the measured precursor sublimation temperature[5]:

$$\log P^* = 11.504 - 5.038 \times \frac{1000}{T_s} \quad (2)$$

where T_s is in K, and P^* is in mbar. The dependence of precursor molar flow rate on the sublimation temperature can then be easily understood by the increase in vapor pressure with increasing sublimation temperature. The effect of precursor sublimation temperature on the deposition rate is also shown in Fig. 2(b). The deposition rate increased exponentially with increasing precursor sublimation temperature, and it is believed to be due to the increased concentration of precursor in the pyrolysis furnace which enhances the pyrolysis reactions to produce more monomers, and

consequently increases the monomer concentration in the deposition chamber. The increased monomer concentration in the deposition chamber will increase the deposition rate.

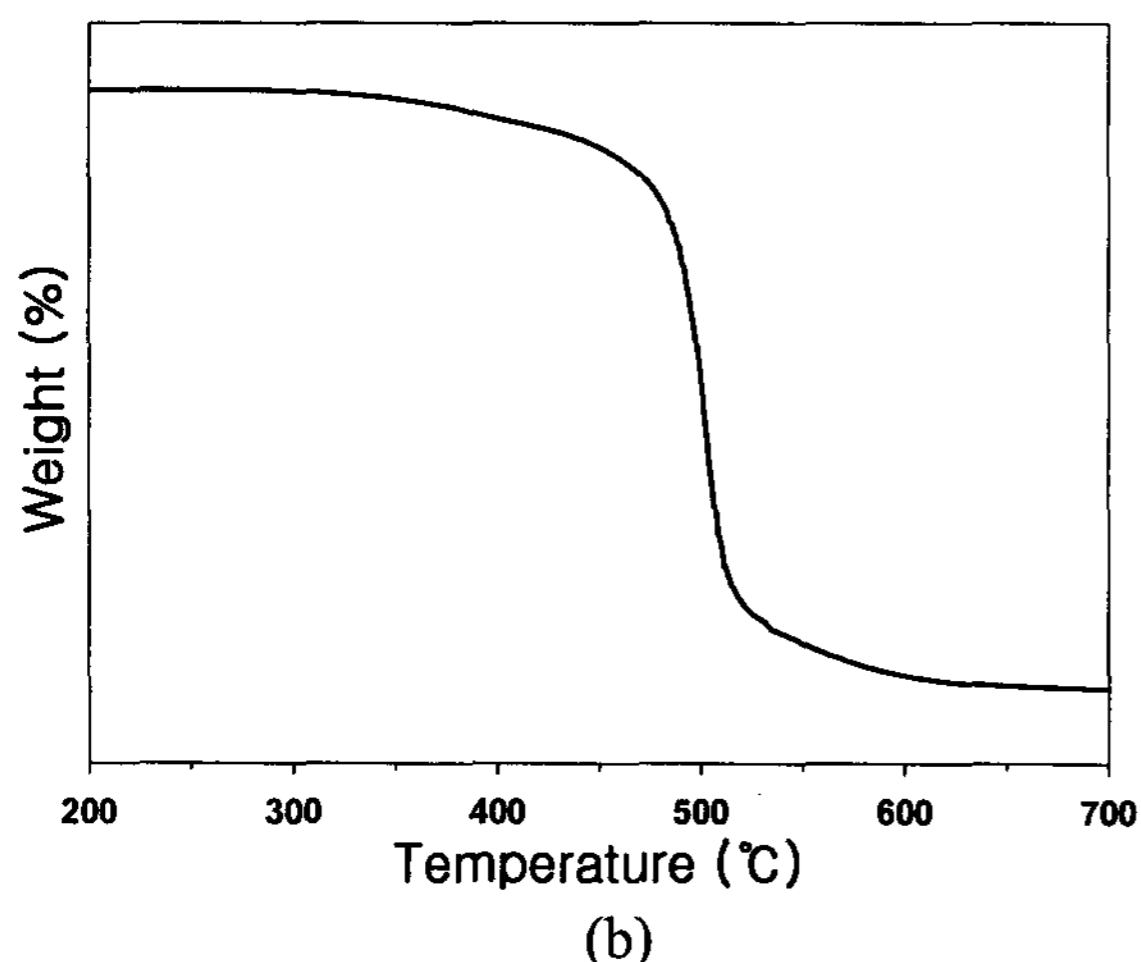
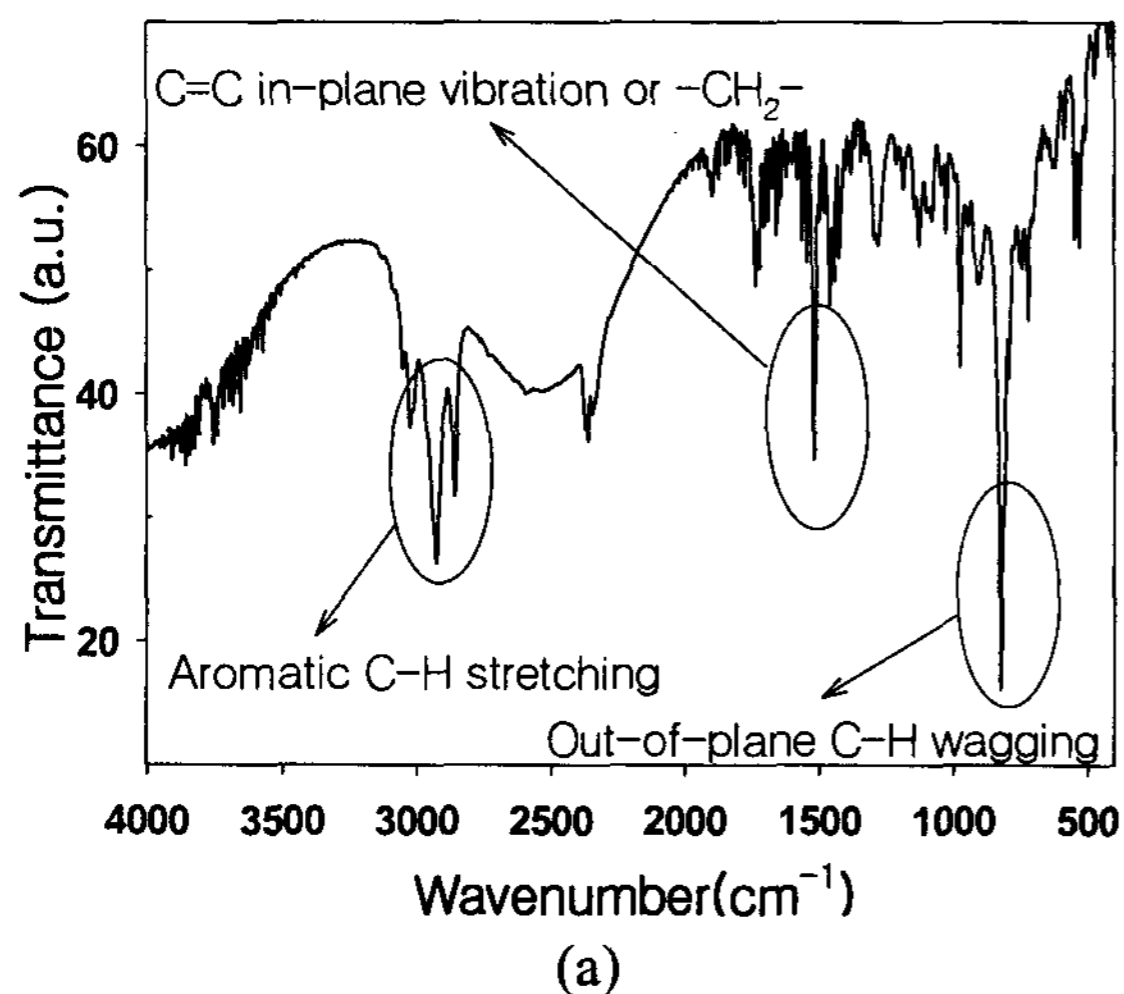


Fig. 3. Characteristics of deposited Parylene films: (a) FT-IR spectrum, (b) TGA thermogram; $T_s = 110\text{ }^\circ\text{C}$, $T_p = 660\text{ }^\circ\text{C}$, $T_d = 1\text{ }^\circ\text{C}$, $F_{\text{He}} = 50\text{ sccm}$, and $P = 0.5\text{ Torr}$.

The FT-IR spectrum of the deposited Parylene-N film with typical process condition used in this study is shown in Fig. 3(a). The aromatic C-H stretching vibration band near $3,000\text{ cm}^{-1}$, C=C in-plane vibration or $-\text{CH}_2-$ bending vibration band near $1,500\text{ cm}^{-1}$, and out-of-plane C-H wagging vibration band at 800 cm^{-1} are apparent in the spectrum, which clearly identifies the chemical groups expected in the Parylene-N structure. The thermal behavior of the deposited Parylene-N film is illustrated in Fig. 3(b). The sample was heated in nitrogen from $200\text{ }^\circ\text{C}$ to $700\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C}/\text{min}$. As can be seen in the figure, the weight of the sample remains constant up to $450\text{ }^\circ\text{C}$ but sharply

decreases at around $500\text{ }^\circ\text{C}$. Since the benzene rings in the Parylene film are stable at $500\text{ }^\circ\text{C}$, the thermal degradation near $500\text{ }^\circ\text{C}$ seems to be due to the scission of chains connecting the benzene rings.

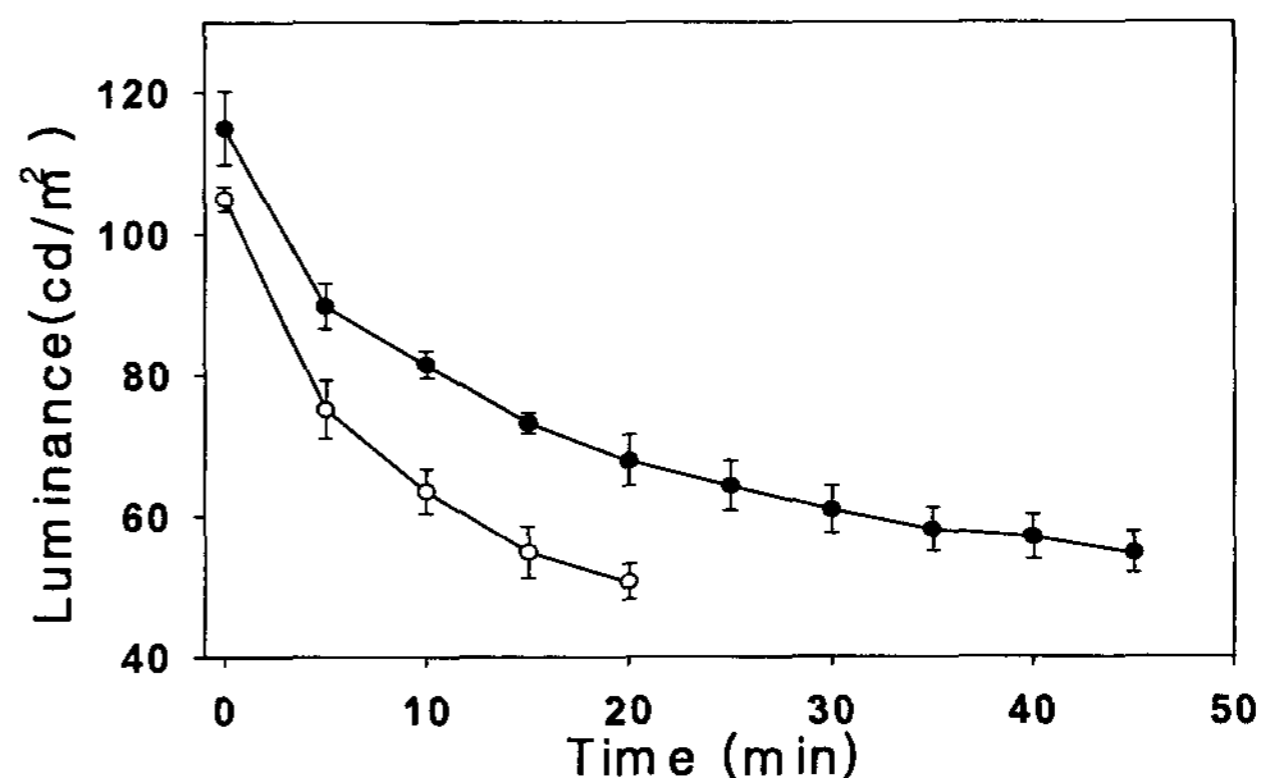


Fig. 3. Lifetime measurements of passivated and non-passivated OLEDs: \circ : non-passivated OLED, \bullet : passivated OLED, $T_s = 110\text{ }^\circ\text{C}$, $T_p = 660\text{ }^\circ\text{C}$, $T_d = 1\text{ }^\circ\text{C}$, $F_{\text{He}} = 50\text{ sccm}$, $P = 0.5\text{ Torr}$, and Parylene-N thickness = $0.5\text{ }\mu\text{m}$.

Fig. 4 shows the time dependence of luminance of the passivated and non-passivated OLEDs, and it is shown that the lifetime of non-passivated OLEDs in air is about 20 min, while that of passivated OLEDs is about 45 min which is about 2.3 times longer than that of the non-passivated case. It is well known that the degradation of the OLED luminescence is due to the oxidation of active layers by moisture or oxygen in the atmosphere. The Parylene-N passivation seems to enhance the stability and lifetime of OLEDs significantly, and it is believed to be due to the protection of devices from oxygen and moisture in the air.

Conclusion

The CVC technique using [2.2]paracyclophane as a precursor molecule was used to deposit Parylene-N films on various surfaces, and it was found that the technique is well suited for the passivation process for OLED fabrication. The deposition rate was investigated as a function of process conditions and the properties of Parylene-N films were characterized. It was found from the results that the deposition rate of Parylene-N films increases with increasing precursor sublimation temperature and decreases with substrate temperature. The deposited Parylene-N films showed appropriate physical properties without voids or pinholes. Finally the Parylene-N deposition was utilized as a passivation of OLEDs,

and the lifetime of passivation OLEDs showed increase by a factor of about 2.3 compared with that of non-passivated OLEDs.

Acknowledgement

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Reference

- [1] C. W. Tang and S. A. Van Slyke, *Appl. Phys. Lett.* **51** (1987) 913.
- [2] P.E. Burrow, V. Balovic S.R. Forrest, L.S. Sapochak, D.M. Mcarty and M.E. Thompson, *Appl. Phys. Lett.*, (1994) 2922.
- [3] Gorham, W.F., *J. Polym. Eng. Sci. Part A-1*, **4** (1966) 3027.
- [4] Kim, E.J., Kim, S.K., Park, R.-H. and Kim J.-T., *HWAHAK KONGHAK*, **36** (1998) 896.
- [5] Göschel, U. and Walter, H., *Langmuir*, **16** (2000) 2887.