

Characterization of Parylene Deposition Process for the Passivation of Organic Light Emitting Diodes

Taejin Lee, Junho Lee and Chinho Park[†]

School of Chemical Engineering and Technology, Yeungnam University, 214-1 Dae-dong, Gyongsan 712-749, Rep. of Korea
(Received 21 March 2002 • accepted 14 May 2002)

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 dependence of deposition rate was well explained by the condensation polymerization model of the monomer on the surface. 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.

Key words: Organic Light Emitting Diodes (OLEDs), Passivation, Parylene, Chemical Vapor Condensation (CVC)

INTRODUCTION

Organic Light Emitting Diodes (OLEDs) have attracted wide attention due to their excellent device properties such as low driving voltage, high brightness, and wide viewing angle. Since Tang and VanSlyke first reported bilayer OLEDs in 1987 [Tang and VanSlyke, 1987], 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 emitters 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 [Burrows et al., 1994; Fujihira et al., 1996; Han et al., 1996; McElvain et al., 1996; Yamashita et al., 2001]. Therefore the encapsulation of an OLED is very important in commercial applications. Hermetic encapsulation techniques using a glass or a metal canister with epoxy resin in an N₂ environment have been developed to exclude water and oxygen from the active regions of the device [Burrows et al., 1994]. However, the encapsulation method has inherent drawbacks in that the thickness of the 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.

Parylene (poly-*p*-xylylene) and its derivatives are vapor-depositable polymers with many outstanding material properties applicable to OLEDs [Gorham, 1966; Göschel and Walter, 2000; Kim et al., 1998; Szwarc, 1976; Yang et al., 1996]. They can be used as

insulating or protective coating material because of their high optical transparency, low gas and H₂O permeability, low dielectric constant and high melting temperature. The materials are also known to be deposited on many different substrates without forming pinholes [Göschel and Walter, 2000; Kim et al., 1998; Yang et al., 1996].

In this study, Parylene-N films were deposited by chemical vapor condensation (CVC) technique [Gorham, 1966] 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, and ellipsometry. The deposited Parylene-N films were applied to the passivation of OLEDs, and the results are discussed.

EXPERIMENTAL

The substrates used in this study were ITO-coated glasses with the ITO film thickness of ~1,900 Å and a sheet resistance of ~8.0 Ω/□. After the substrates were chemically cleaned by TCE (trichloroethylene), acetone, and methanol in series with ultrasonification at room temperature, which removed most of the surface organic contaminants, the substrates were nitrogen blow-dried and transferred to either the Parylene deposition system or the thermal evaporator.

The Parylene deposition experiments were performed in a CVC reactor according to Gorham's method [Gorham, 1966], and the schematic of the reactor system is similar to that in literature described elsewhere [Kim et al., 1998]. 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 a 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 (99.9998%) was used as a carrier gas, and its flow rate was fixed at 50 sccm. The reactor pressure was maintained at 0.5 Torr.

[†]To whom correspondence should be addressed.

E-mail: chpark@yu.ac.kr

[‡]This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

The deposited Parylene films were characterized by FT-IR (Bio-Rad, FTS 3000FX) for structure identification, and an ellipsometer (Rudolph, AutoEL^R-II) was used to measure the refractive index. The angle of incidence was set to 70°, and an He-Ne laser (wavelength=638.8 nm) was used as the light source. Thermal properties were analyzed by TGA (CAHN, CAHN D-2), and the surface morphology and thickness were observed by SEM (HITACHI, S-4200). The surface roughness was measured by AFM (Park Scientific, Auto-probe CP).

Vacuum deposition of organic materials and metals was carried out in a thermal evaporator under a pressure of 10⁻⁶ Torr to fabricate the green OLED with a structure of ITO/TPD/Alq₃/AILi. In the OLED structure, TPD (N,N'-diphenyl-N,N'-bis(3-methyl phenyl)-1,1'-biphenyl-4,4'-diphenyl-4,4'-diamine) was used as a hole transport layer, Alq₃ (8-hydroxyquinoline-aluminum) was used as an emission and electron transport layer, and AILi alloy was used as a metal cathode.

The electrical properties and lifetime of the fabricated OLEDs were measured by semiconductor parameter analyzer (HP 4145B) and MINOLTA CS-100 chromameter, respectively.

RESULTS AND DISCUSSION

The physical properties of Parylene and its derivatives are listed in Table 1, and their molecular structures 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 characteristic 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 melt-

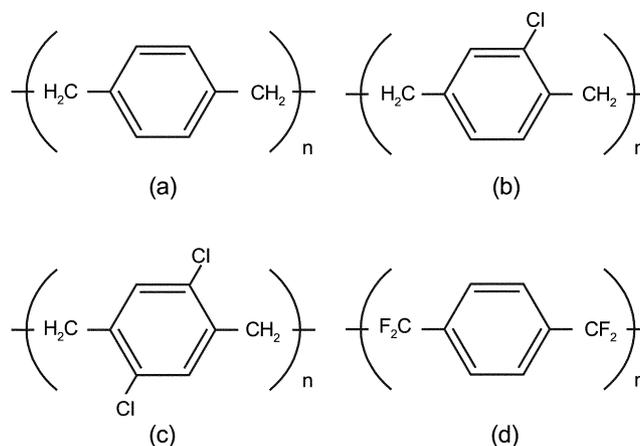


Fig. 1. Molecular structures of Parylene and its derivatives: (a) Parylene-N (poly-*p*-xylylene), (b) Parylene-C (polychloro-*p*-xylylene), (c) Parylene-D (polydichloro-*p*-xylylene), (d) Parylene-F (polytetrafluoro-*p*-xylylene).

ing 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.

The effects of precursor sublimation temperature and deposition temperature on the deposition rate and film properties were investigated. Preliminary experiments were done in a CVC reactor, and the base operating conditions were developed as follows: precursor sublimation temperature (T_s)>80 °C, precursor pyrolysis temperature (T_p)=660 °C, deposition temperature (T_d)<15 °C, the reactor pressure (P)=0.5 Torr, and carrier gas flow rate (F_{He})=50 sccm. The base operating conditions were selected by considering both the deposition rate and film quality. For example, in the case that T_s was below 80 °C or T_d was above 15 °C, the film deposition was too slow to form observable film within 1 hour. As the reactor pressure became higher than 1 Torr, hazy film was deposited due to the

Table 1. Some physical properties of Parylene and its derivatives [Alexandrova and Vera-Graziano, 1996; Gorham, 1966]

Properties	Parylene-N	Parylene-C	Parylene-D	Parylene-F	
Density (g/m ³)	1.12	1.289	1.418	-	
Index of refraction	1.661	1.639	1.669	-	
Melting temperature (°C)	420	290	380	530	
Glass transition temperature (°C)	80	80	110	-	
TGA at air (°C)	260	260	320	500	
TGA at nitrogen (°C)	490	490	460	510	
Dielectric constant (60 Hz)	2.65	3.15	2.84	2.36	
Dielectric constant (1 kHz)	2.65	3.10	2.82	2.36	
Dielectric constant (1 MHz)	2.65	2.95	2.80	2.35	
Permeability	N ₂ ^a	9	1	4.5	-
	O ₂ ^a	30	8	30	-
	CO ₂ ^a	225	21	130	-
	H ₂ O ^b	6	0.6	5	-

^aGas permeability at 25 °C; cm³ (STP)-mil/100 in.²-24 hr

^bMoisture vapor permeability at 25 °C; g-mil/atm-100 in.²-24 hr

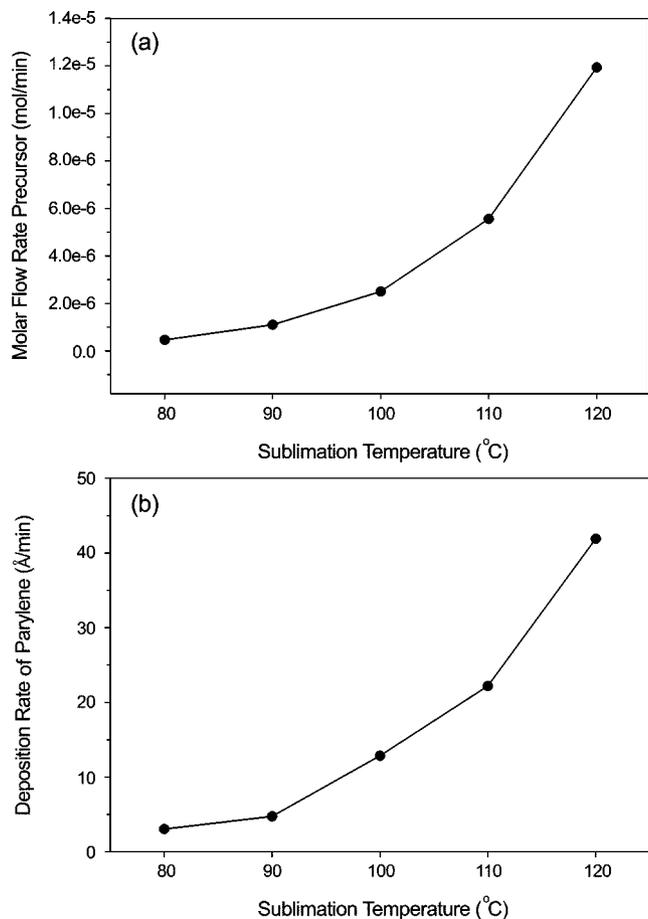


Fig. 2. Effects of precursor sublimation temperature on (a) molar flow rate of precursor; (b) deposition rate: $T_p=660$ °C, $T_d=1$ °C, $F_{He}=50$ sccm, and $P=0.5$ Torr.

particle formation in the gas phase. It was found from the preliminary experiments that the depositions with base operating conditions provide dense Parylene films without pinholes.

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 precursor increases monotonically with increasing precursor sublimation temperature from 80 °C to 120 °C. These results are in good agreement with the results of previous investigators [Göschel and Walter, 2000; Kim et al., 1998]. 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 [Göschel and Walter, 2000; Kim et al., 1998].

The molar flow rate of precursor (F_p) can be described by Eq. (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 equa-

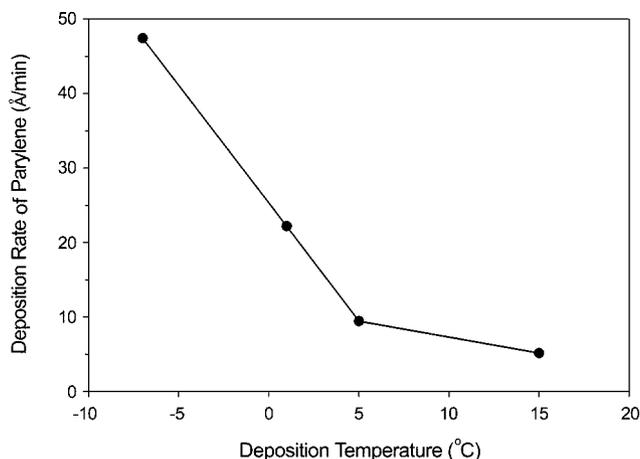


Fig. 3. Effect of deposition temperature on deposition rate: $T_s=110$ °C, $T_p=660$ °C, $F_{He}=50$ sccm, and $P=0.5$ Torr.

tion at the measured precursor sublimation temperature [Göschel and Walter, 2000]:

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

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.

The effect of deposition temperature on the deposition rate is shown in Fig. 3. As the deposition temperature is raised from -7 °C to 15 °C, the deposition rate drops rapidly from 47.4 Å/min to 5.2 Å/min. This phenomenon is contrary to the typical dependence of deposition rate on the temperature in most chemical vapor deposition processes, in which the deposition rate usually increases with the deposition temperature. The observed dependence of deposition rate on temperature can be explained by the condensation polymerization model. The polymerization process of Parylene-N progresses in three consecutive steps: initiation, propagation, and termination, and it proceeds by the free radical mechanisms [Gorham and Niegisch, 1971]. The formation rate of polymer film depends on the monomer concentration at the surface, its diffusion rate in the film, and the reaction rate of monomer with the ends of free-radical polymer chains. Accordingly, the increase in monomer concentration at the surface with decreasing substrate temperature will increase the deposition rate. This model also explains the deposition rate dependence on the precursor sublimation temperature [Fig. 2(a)], in that the increase in sublimation temperature will eventually increase the monomer concentration in the deposition chamber, which in turn increases the deposition rate. The dependence of deposition rate on the substrate temperature observed in this study agrees very

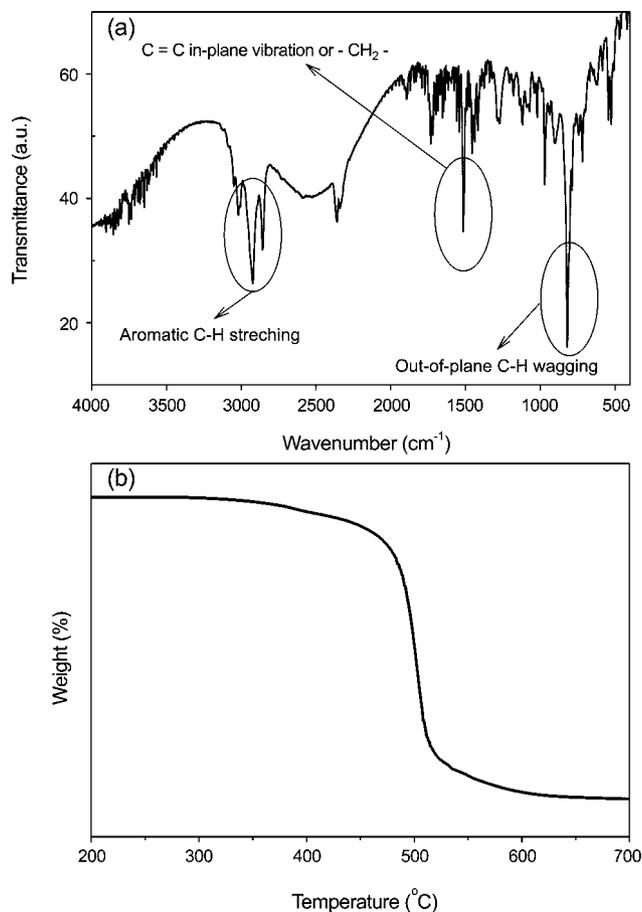


Fig. 4. Characteristics of deposited Parylene films: (a) FT-IR spectrum, (b) TGA thermogram; $T_s=110^\circ\text{C}$, $T_p=660^\circ\text{C}$, $T_d=1^\circ\text{C}$, $F_{He}=50$ sccm, and $P=0.5$ Torr.

well with the results of previous studies [Kim et al., 1998; Yang et al., 1996].

The FT-IR spectrum of the deposited Parylene-N film with typical process condition used in this study is shown in Fig. 4(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. 4(b). The sample was heated in nitrogen from 200°C to 700°C at $5^\circ\text{C}/\text{min}$. As can be seen in the figure, the weight of the sample remains constant up to 450°C but sharply decreases at around 500°C . Since the benzene rings in the Parylene film are stable at 500°C , the thermal degradation near 500°C seems to be due to the scission of chains connecting the benzene rings. The TGA analysis result matches very well the published data (Table 1).

The refractive indices of deposited Parylene-N films with varying thickness were measured by ellipsometer and shown in Fig. 5, where the thickness was varied by changing the deposition time from 30 min to 60 min at the fixed operating conditions. Silicon substrate was used for this measurement instead of the ITO-coated glass. The measured refractive indices varied between 1.62 and 1.64,

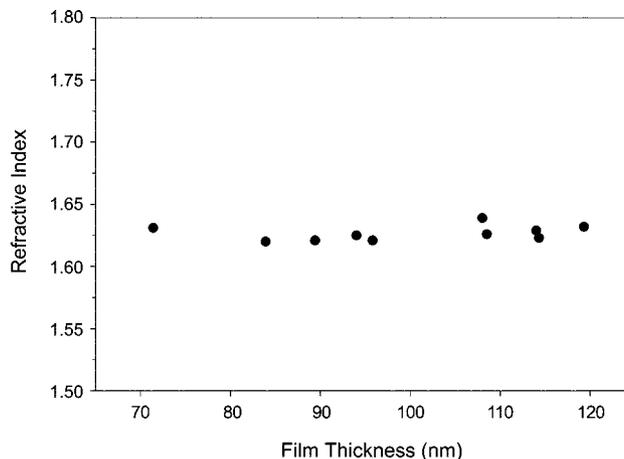


Fig. 5. Refractive index of deposited Parylene films with varying thickness: $T_s=110^\circ\text{C}$, $T_p=660^\circ\text{C}$, $T_d=1^\circ\text{C}$, $F_{He}=50$ sccm, and $P=0.5$ Torr.

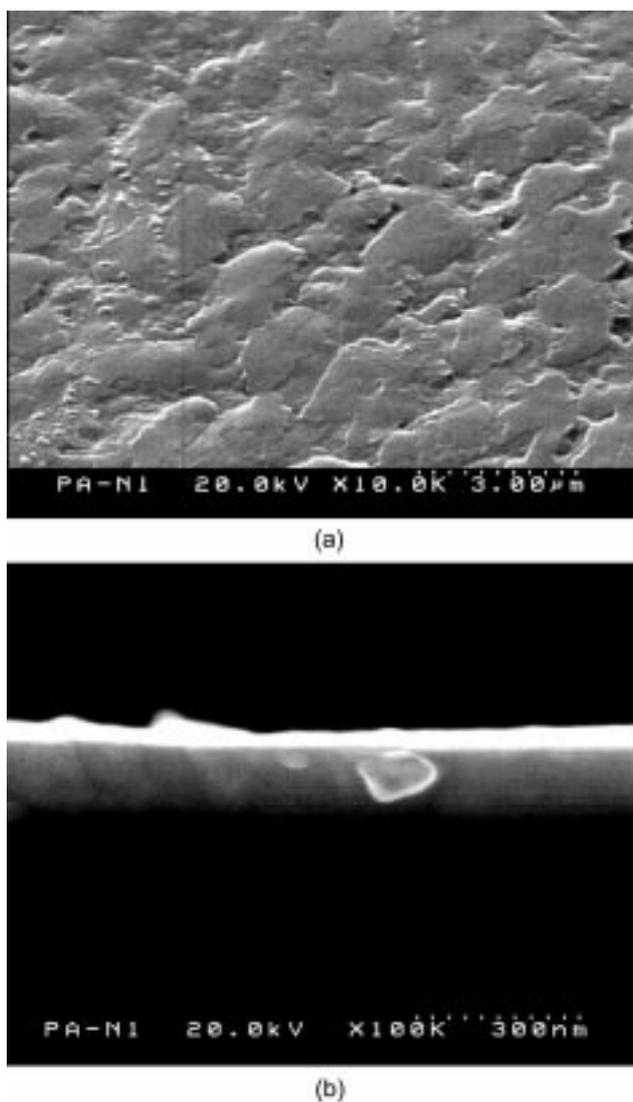


Fig. 6. SEM photographs of deposited Parylene-N films: (a) top view, (b) cross-sectional view; $T_s=110^\circ\text{C}$, $T_p=660^\circ\text{C}$, $T_d=1^\circ\text{C}$, $F_{He}=50$ sccm, and $P=0.5$ Torr.

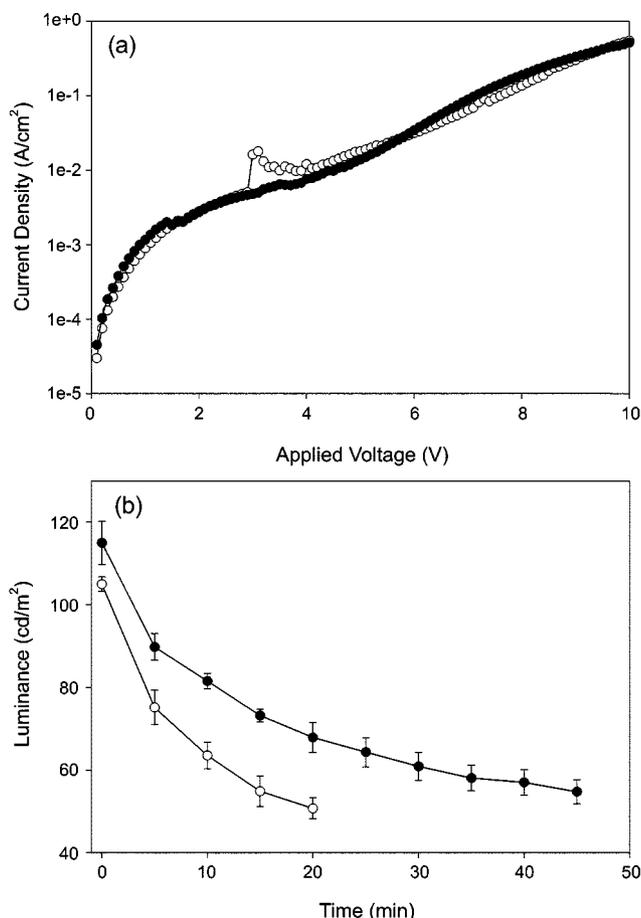


Fig. 7. Device characteristics of passivated and non-passivated OLEDs: ○: non-passivated OLED, ●: passivated OLED; $T_s=110$ °C, $T_p=660$ °C, $T_d=1$ °C, $F_{He}=50$ sccm, $P=0.5$ Torr, and film thickness= 0.5 μm ; (a) I-V characteristics, (b) lifetime at 6.0 V DC.

regardless of the thickness of film in the investigated range of this study.

The characterization results of Parylene-N films by several analysis instruments described above are reasonably consistent with those previously reported [Göschel and Walter, 2000; Kim et al., 1998], and they demonstrate that the deposited Parylene-N films have the appropriate physical properties.

Fig. 6 shows the SEM photographs of deposited Parylene-N films. The surface [Fig. 6(a)] of Parylene-N films deposited with typical process condition used in this study was relatively smooth as a passivation layer, and the measured root mean square (RMS) roughness by AFM was on the average, 705 Å. The cross-section of Parylene-N film is also shown in Fig. 6(b), which shows that the film is dense without voids or pinholes.

Fig. 7 shows the I-V characteristics [Fig. 7(a)] and lifetime measurements [Fig. 7(b)] of passivated and non-passivated OLEDs. The I-V curves for both cases showed similar behavior, and they represent typical characteristics of diodes. The electrical property of OLEDs by the Parylene-N passivation was not influenced in spite of being in contact with gaseous biradicals in the deposition chamber generated during the pyrolysis process.

The lifetime of OLEDs passivated with Parylene films was meas-

ured by monitoring the luminance intensity along with time. The lifetime of the OLEDs is defined as the time taken to reach half luminance under the application of a constant voltage (6.0 V DC) in air at room temperature. Fig. 7(b) 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.

SUMMARY

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 an increase by a factor of about 2.3 compared with that of non-passivated OLEDs.

ACKNOWLEDGEMENTS

Authors thank the Samsung Corning Co., Ltd., Gumi Plant for supplying the ITO substrates. This work was supported by grant No. 1999-1-30700-003-3 from the Basic Research Program of the Korea Science & Engineering Foundation.

NOMENCLATURE

F_{He}	: carrier gas flow rate (He) [sccm]
P	: reactor pressure [Torr]
P_b	: total pressure in the bubbler [mbar]
P^*	: saturated vapor pressure of precursor in the bubbler [mbar]
T_d	: deposition temperature [°C]
T_p	: precursor pyrolysis temperature [°C]
T_s	: precursor sublimation temperature [°C]

REFERENCES

- Alexandrova, L. and Vera-Graziano, R., "Polymeric Materials Encyclopedia," edited by Salamone, J. C., CRC Press, New York (1996).
- Burrow, P. E., Balovic, V., Forrest, S. R., Sapochak, L. S., McCarty D. M. and Thompson, M. E., "Reliability and Degradation of Organic Light Emitting Devices," *Appl. Phys. Lett.*, **65**, 2922 (1994).
- Fujihira, M., Do, L.-M., Koike, A. and Han, E.-M., "Growth of Dark Spots by Interdiffusion Across Organic Layers in Organic Electroluminescent Devices," *Appl. Phys. Lett.*, **68**, 1787 (1996).

- Gorham, W. F., "A New, General Synthetic Method for the Preparation of Linear Poly-*p*-xylylenes," *J. Polym. Eng. Sci. Part A-1*, **4**, 3027 (1966).
- Gorham, W. F. and Niegisch, W. D., "Encyclopedia of Polymer Science and Technology," edited by Mark, H. F., Gaylord, N. and Bikales, N. M., Interscience, New York (1971).
- Göschel, U. and Walter, H., "Surface Film Formation by Chemical Vapor Deposition of Di-*p*-xylylene: Ellipsometrical, Atomic Force Microscopy, and X-ray Studies," *Langmuir*, **16**, 2887 (2000).
- Han, E. M., Do, L. M., Yamamoto, N. and Fujihira, M., "Crystallization of Organic Thin Films for Electroluminescent Devices," *Thin Solid Films*, **273**, 202 (1996).
- Kim, E. J., Kim, S. K., Park, R.-H. and Kim J.-T., "Low Temperature Vapor Deposition of Parylene-N Films from [2.2]Paracyclophane," *HWAHAK KONGHAK*, **36**, 896 (1998).
- McElvain, J., Antoniadis, H., Hueschen, M. R., Miller, J. N., Roitman, D. M., Sheatts, J. R. and Moon, R. L., "Formation and Growth of Black Spots in Organic Light-Emitting Diodes," *J. Appl. Phys.*, **80**, 6022 (1996).
- Szwarc, M., "Poly-para-Xylene: Its Chemistry and Application in Coating Technology," *Polym. Eng. Sci.*, **16**, 473 (1976).
- Tang, C. W. and VanSlyke, S. A., "Organic Electroluminescent Diode," *Appl. Phys. Lett.*, **51**, 913 (1987).
- Yamashita, T., Mori, T. and Mizutani, T., "Encapsulation of Organic Light-emitting Diode using Thermal Chemical-vapour-deposition Polymer Film," *J. Phys. D: Appl. Phys.*, **34**, 740 (2001).
- Yang, G.-R., Ganguli, S., Karcz, J., Gill, W. N. and Lu, T.-M., "High Deposition Rate Parylene Films," *J. Cryst. Growth*, **183**, 385 (1998).