Characterization of Chemical Vapor Condensation Reactor for Parylene-N Thin Film Deposition

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Abstract

Chemical vapor condensation (CVC) reactor was investigated for the deposition of Parylene-N thin films as the passivation layer for organic light emitting diodes (OLEDs). Several gas inlet manifold designs were tested to improve the deposition rate and its uniformity, and it was found that proper inlet design is crucial to get the desired film properties. Process characterization was also performed with the modified inlets to optimize the process variables.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted broad attention due to their appealing device properties such as high brightness, low driving voltage, wide viewing angle, etc. Since Tang and VanSlyke[1] first reported OLED using organic thin films in 1987, tremendous research efforts have been made to improve emission efficiency and lifetime of the OLED.

The lifetime of OLED is usually limited under atmospheric condition because of the presence of humidity and oxygen in the air[2]. Thus it is critical in developing commercial OLEDs to provide practical sealing method in order to achieve sufficiently long device lifetime. Hermetic encapsulation technique using a glass with epoxy resin in N_2 atmosphere was recently proposed, and various modifications and improvements have been being made. But this method has inherent drawbacks, in that the thickness of encapsulation layer is thicker than the OLED itself and in addition it is difficult to be utilized in making flexible OLEDs. Also there is a continuing thrust for a thinner and low-cost encapsulation technique for commercial OLED production.

Parylene-N thin film was proposed as a transparent encapsulation layer for OLEDs due to its excellent material properties (e.g. low H_2O and O_2 permeability) and process characteristics (e.g. dense film with relatively high deposition rate). It is also suitable for flexible OLEDs. Preliminary deposition studies have recently been done by chemical vapor condensation (CVC) technique[3] using [2.2]paracyclophane dimer as precursor, and the results showed that the lifetime of OLEDs could be increased by a factor of 2.3 compared with that of non-passivated OLEDs[4]. One of the problems encountered in Parylene-N deposition, however, was the appreciable loss of reactant precursors at the gas inlet, causing deposition rate degradation and particle impingement onto the substrate. Deposition rate uniformity also needed further improvement.

Therefore, in this study, modifications are made in the CVC reactor geometry, and the modified reactor is tested to deposit Parylene-N films with better film properties. The gas inlet design was particularly investigated in the reactor modification, and the process characterization was made to improve the deposition rate and its uniformity.

2. Experimental

The Parylene-N deposition experiments were carried out in a custom-made CVC reactor system, which has similar design and hardware features with the reactor system developed by Kim, et al[5]. The system is composed of four units: precursor sublimation bubbler unit, dimer-cracking furnace, deposition chamber and

vacuum and exhaust gas facilities. Pressure controlled and particle filtered He was used as a carrier gas, and the flow rate was controlled by mass flow controllers (MFCs). Substrate temperature was controlled by the recirculating coolant bath located underneath the deposition chamber. Details of the reactor system are described elsewhere[5].

Substrates used in this study were indium-tin-oxide (ITO)-coated glasses. After the substrates were chemically cleaned in series by TCE (trichloroethylene), acetone and methanol with ultrasonification at room temperature, which removed most of the surface particles and organic contaminants, the substrates were nitrogen blow-dried and transferred to the CVC system.

First, the precursor ([2.2]paracyclophane, >97%) was sublimed at above 90 ℃ in a bubbler contained in the heat bath, and the vapor species were then transferred by the carrier gas to the dimer-cracking furnace, where they were pyrolyzed into p-xylylene monomers at the temperature of 660 ℃. The product monomers then enter into the deposition chamber and condense on the substrate surface, which subsequently polymerize on the surface.

Modifications are made in this study to improve the reactor performance, and the major design changes were made in the gas inlets. Fig. 1 shows the design changes made from the original one (Fig. 1(a)) to improve the deposition rate of parylene-N film and its uniformity. The first design change (Fig. 1(b)) was made to shorten the distance between the outlet of dimer-cracking furnace and the substrate in the deposition chamber. It is expected that by shortening the distance, the unwanted wall depositions inside the inlet tubing could be minimized with subsequent heating, and thus more reactants could reach the substrate surface, which would increase the deposition rate. Susceptor was tilted to achieve deposition rate uniformity in this case. The second design change (Fig. 1(c)) was made mainly to improve the deposition rate uniformity, in which a straight and capped stainless steel tube was used instead of straight tube with single outlet (Fig. 1(b)). The new tube had many small holes opened toward the substrate.

Carrier gas stream was divided into two, and the flow rates of each stream were independently controlled to vary the residence time of reactants, keeping the dimer supply rate constant.

Thickness of deposited film was measured by Dektak surface profiler, and surface morphology and roughness were examined by SEM and AFM, respectively.

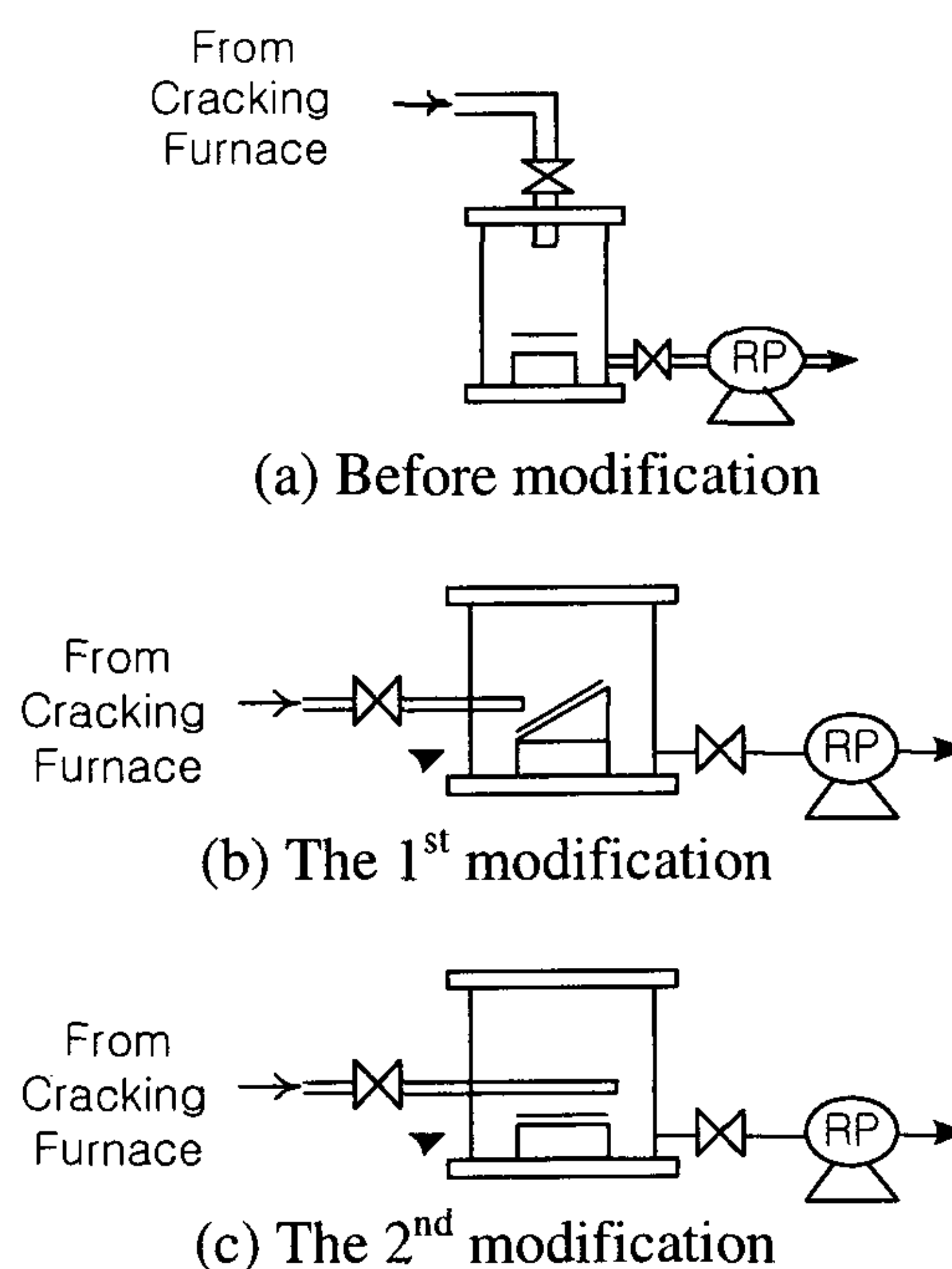

Fig. 1. Design changes made in the gas inlet

3. Results and discussion

Process characterizations were made after each reactor modification, and the deposition rate was measured and compared. The base operating conditions were developed from the previous study[4], and they were as follows: flow rate of carrier gas to the precursor sublimation bubbler (F_{He}) at 50 sccm, precursor decomposition temperature (T_p) at 660 ℃ and reactor pressure (P) at 0.5 Torr. The precursor sublimation temperature (T_s) and the deposition temperature

(T_d) were varied in the range of 90 ℃ $\leq T_s \leq$ 110 ℃ and −7 ℃ $\leq T_d \leq$ 15 ℃, respectively. Figs. 2 and 3 show the results.

After the 1st design change, the deposition rate was increased by a maximum of about 3 fold, and this was presumably because the shortened distance between the outlet of the dimer-cracking furnace and the substrate reduces the residence time of reactants in the inlet tubing, thus reducing the unwanted wall depositions. The film uniformity, however, was quite bad.

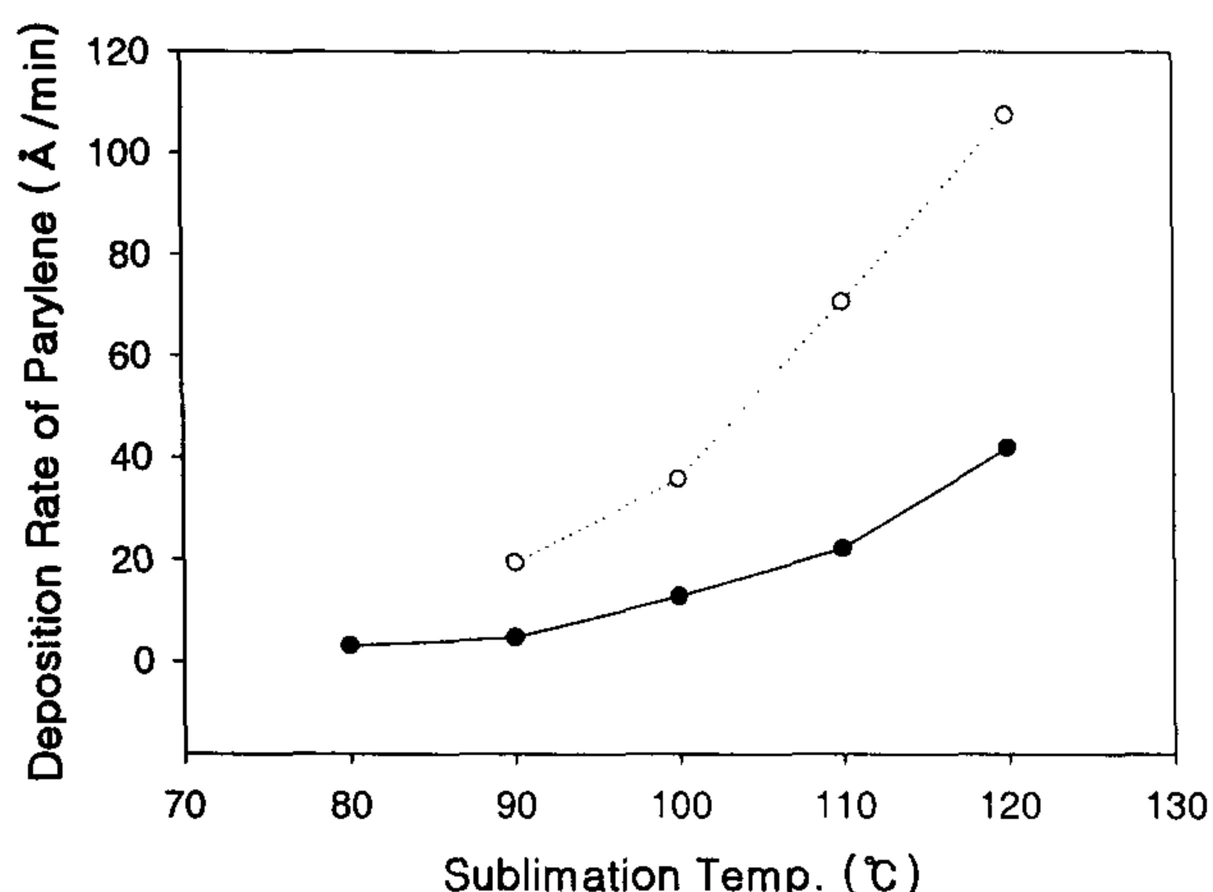

Fig. 2. Effect of precursor sublimation temperature on deposition rate: T_p = 660 ℃, T_d = 1 ℃, F_{He} = 50 sccm, and P = 0.5 Torr (dark circles: before 1st design change, open circles: after 1st design change).

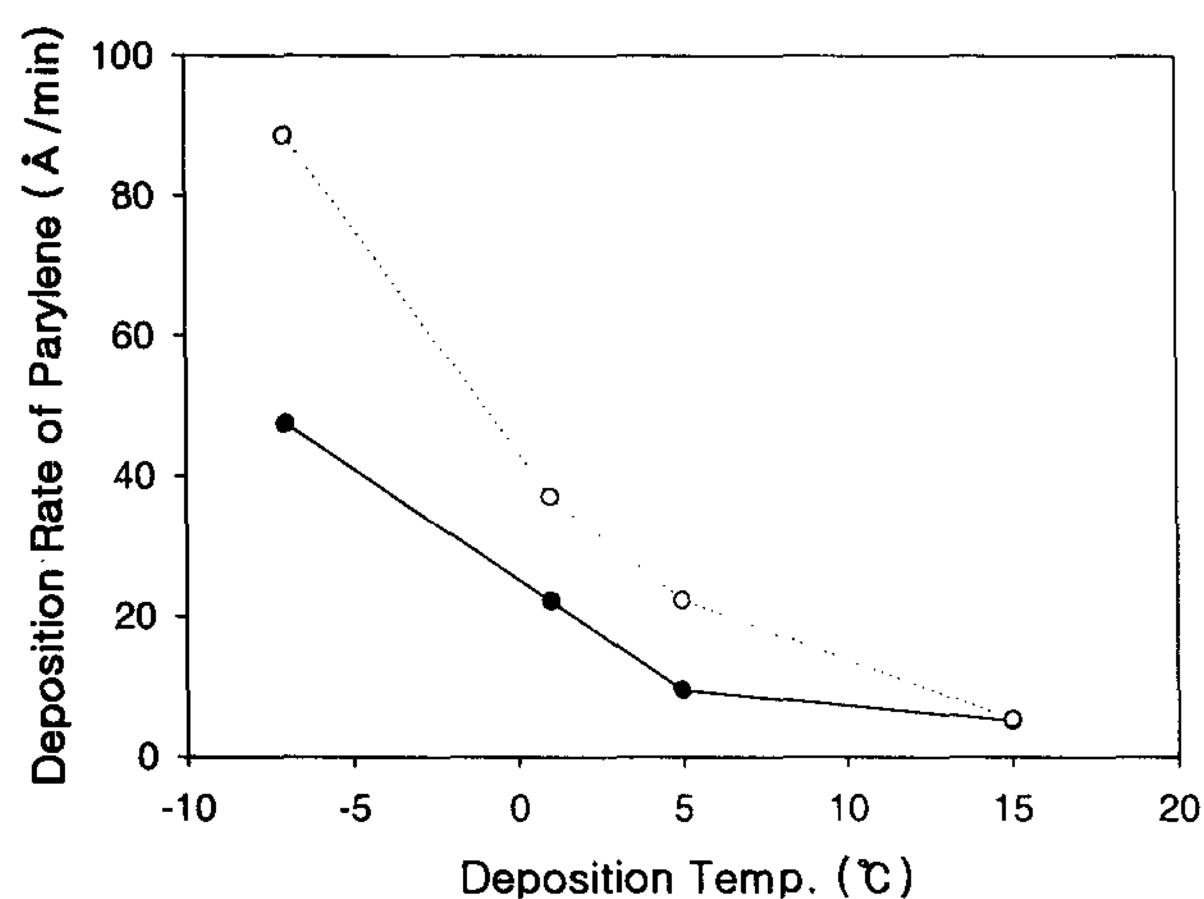

Fig. 3. Effect of deposition temperature on deposition rate: T_p = 660 ℃, T_s = 110 ℃, F_{He} = 50 sccm, and P = 0.5 Torr (dark circles: before 1st design change, open circles: after 1st design change).

The second reactor modification was made to further improve the deposition rate and its uniformity. After the modification, the reactor pressure (P) and the total gas flow rate (F_T) were varied to find the optimum deposition condition. Reactor pressure and total gas flow rate were varied in the range of 0.5 Torr $\leq$ P $\leq$ 2 Torr, and 75 sccm $\leq F_T \leq$ 200 sccm, respectively. Figs. 4 and 5 show the results.

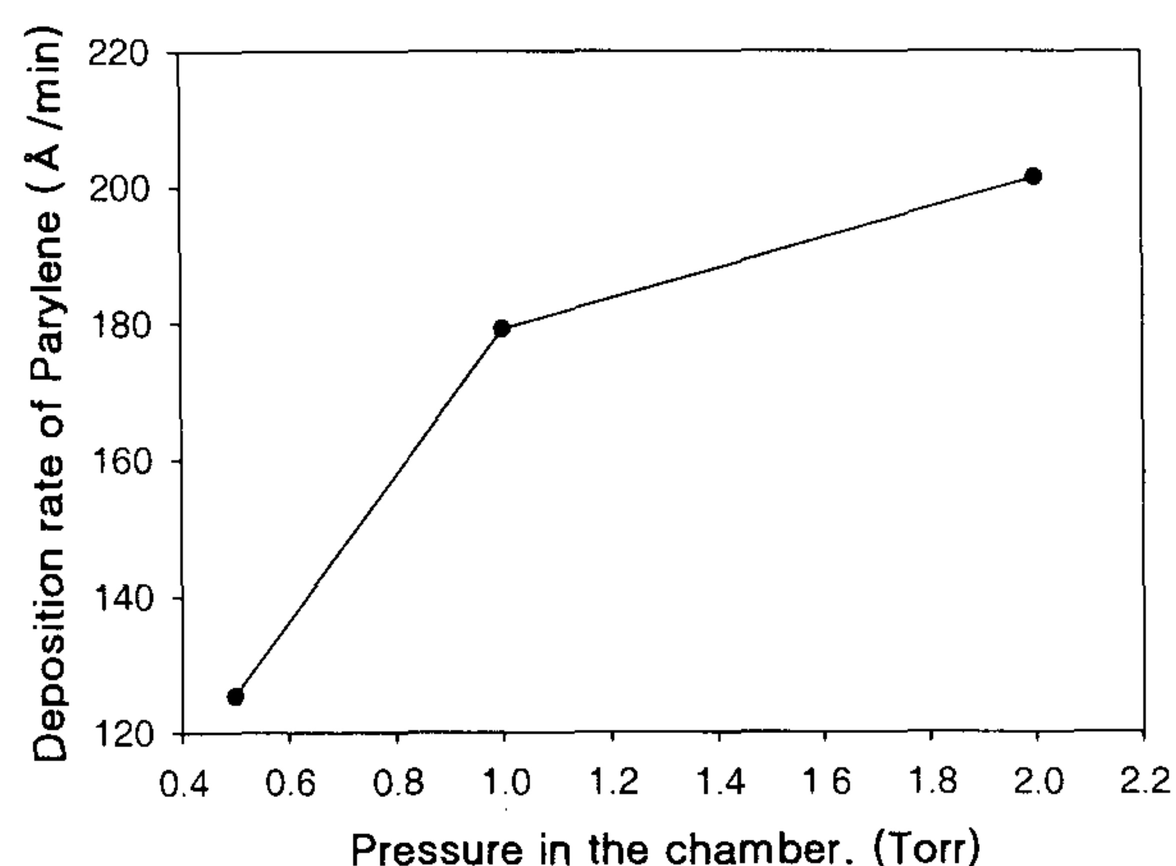

Fig. 4. Effect of reactor pressure on deposition rate: T_p = 660 ℃, T_s = 110 ℃, T_d = 1 ℃, F_T = 150 sccm.

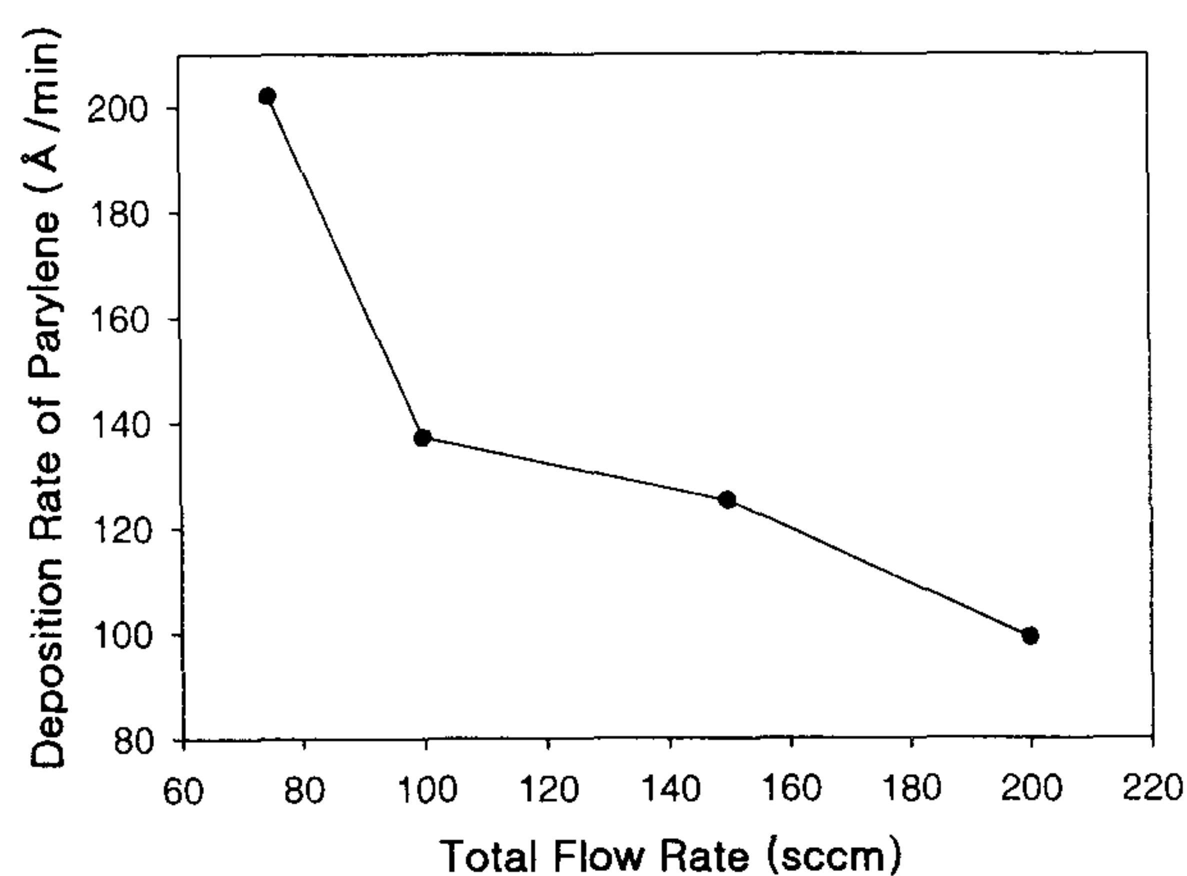

Fig. 5. Effect of total flow rate on deposition rate: T_p = 660 ℃, T_s = 110 ℃, T_d = 1 ℃, P =

0.5 Torr.

As clearly shown in Fig. 4, the deposition rate increases with reactor pressure. It was found that the deposition rate at 2.0 Torr was 202 Å/min with thickness uniformity of 18.3%.

Fig. 5 shows the effect of total flow rate on deposition rate, keeping the F_{He} constant at 50 sccm. In this case the deposition rate decreased monotonically with increasing total flow rate. The maximum deposition rate of 202 Å/min (1.2 ㎛/hr) could be achieved with the total flow of 75 sccm at 0.5 Torr reactor pressure. The modified inlet design with many exit holes facing downward seems to help improve the film uniformity. But further modification in the reactor inlet design and the process tuning seem necessary to improve the film uniformity with increased deposition rate.

Fig. 6 SEM photograph of the surface of deposited Parylene-N film: T_p = 660 ℃, T_s = 110 ℃, T_d = 1 ℃, P = 0.5 Torr, F_T = 75 sccm.

Fig. 6 shows the SEM image of Parylene-N surface deposited at the current optimum process condition, and it was seen that the surface of Parylene-N film was very smooth (AFM rms roughness of 250 Å), and dense film was formed without any void or pinholes.

4. Conclusion

The design modifications were made in the CVC reactor system to increase the deposition rate and its uniformity of Parylene-N passivation layer for the OLEDs. Different gas inlet designs were tested in this study, and it was found that shortening the distance between the outlet of dimer-cracking furnace and the substrate help increase the deposition rate by reducing the unwanted wall depositions inside the inlet tubing. Capped inlet tube design with many exit holes facing downward to the substrate further improves the deposition rate uniformity. After these modifications, the deposition rate was increased to the maximum of about 3 fold compared with that obtained before the modification. Deposition rate uniformity was also improved to 18.3%. Optimum process conditions obtained in this study were found to be T_s = 110 ℃, T_d= 1 ℃, F_T = 75 sccm, F_{He} = 50 sccm, and P = 0.5 Torr. The deposited Parylene-N films showed appropriate morphological properties without any voids and pinholes. Further study is, however, needed to fully realize the potential of CVC reactor system for commercial applications.

5. Acknowledgements

This work was supported by grant No. 1999-1-30700-003-3 from the Basic Research Program of the Korea Science & Engineering Foundation.

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