Studies of Thin Film Deposition of Organic Light Emitting Diode by Using Rapid Expansion of Supercritical Solution

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This research investigated the film deposition mechanism of organic material Alq3 through rapid expansion of supercritical solution (RESS) to organic light emitting diode (OLED) application. The depressurization of supercritical carbon dioxide ($SCCO_2$) into ambient environment produced a rapid supersaturated precipitation. The high speed particles imprinted the substrate and aggregated to form a membrane. It was found that $SCCO_2$ at 30.6MPa, 35℃ has higher solubility to obtain finer particles and to form a thin film with 4.1nm roughness. Moreover, with a suitable addition of co-solvent Ethyl alcohol to increase the solubility of Alq_3, it can save up to 40% of $SCCO_2$ producing 70nm thickness of Alq_3 thin film was re-agglomerated to reduce roughness to 3.2nm. For the OLED electrical test, layers of NPB and LiF were generated by evaporator to improve the electron and hold transition ability. The OLED device (ITO/ NPB (35nm)/Alq_3 (70nm)/LiF (0.5nm)/Al (100nm)) has turn on voltage at 6V and 300mA/cm^2 current density at 10V, which meets the requirements of the OLED device.

INTRODUCTION

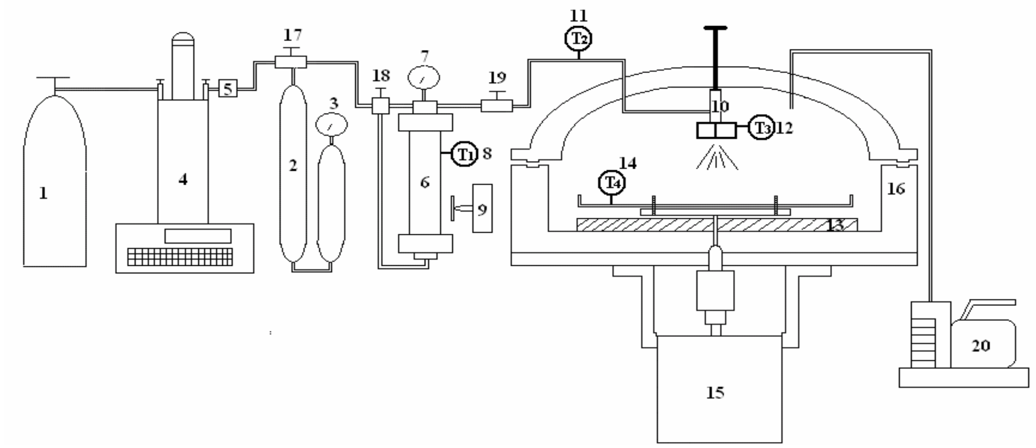
Organic light-emitting diode (OLED) is a light-emitting diode (LED) whose emissive electroluminescent layer is composed of a film of organic compounds. The layer usually contains small molecules or polymers that allow suitable organic compounds to be deposited. A significant benefit of OLED displays over traditional liquid crystal displays (LCDs) is that OLEDs do not require a backlight to function. Thus they draw far less power and, when powered from a battery, can operate longer on the same charge. OLED-based display devices also can be more effectively manufactured than LCDs and plasma displays. Hence, it is an important issue to fabricate the electroluminescent layer in less cost and effectiveness.

An OLED is composed of an emissive layer, a conductive layer, a substrate, and anode and cathode terminals [1]. The layers are made of special small or organic polymer molecules that conduct electricity. Their levels of conductivity range from those of insulators to those of conductors, and so they are called organic semiconductors. Small molecules commonly used in OLEDs include organo-metallic chelates (for example Alq3, used in the first organic light-emitting device) and conjugated dendrimers. In the past, the ways of fabricating the layer of organo-metallic chelating molecules include spin coating, ink jet printing, vacuum evaporation, screen printing. However, each of these fabricating methods has its disadvantages, e.g., difficult to allocate color pixels for spin coating, high cost and time consumption for vacuum evaporation, and solvent residual for ink jet printing and screen printing.

To cope with these problems, the method of rapid expansion of supercritical solutions (RESS) has been proposed in this study to generate a uniform thin layer of Alq3. High diffusivity and lower viscosity compared to organic solvents make supercritical fluid (SCF) more attractive as a reaction medium to transport reactants and products in several processes, such as extraction, separation, and reaction [2,3]. Since supercritical carbon dioxide ($SCCO_2$) is nonflammable, virtually inert, essentially nontoxic, it has been called as a green solvent. Recently, $SCCO_2$ has been applied to clean the integrated circuits without causing shrinking or cracking damage [4]. As to the RESS, it is a promising new technology for particle formation [5,6,7]. When a supercritical solution that contains a dissolved solute is expanded across a micro-orifice, the solvent density decreases dramatically and the solute is rejected from solution [8]. The absence of liquid organic solvents, the mild processing temperatures, and the purity of the final product make this process particularly attractive for various applications. In this study, we would like to investigate the operating parameters for fabricating the thin film of Alq3 by using RESS process.

MATERIALS AND METHODS

The RESS experimental apparatus for fabricating thin film is shown schematically in Figure 1. It consists of three major units: a $SCCO_2$ resource system with an ISCO syringe pump, a piston extractor with a temperature controlling jacket, and a glass-made decanter as an expansion unit. First, by syringe pump liquid CO_2 was pumped into a high-pressure stainless steel reservoir which can stand up to 40MPa. CO_2 in the reservoir was heated to supercritical condition by a controlled heating jacket. For dissolving Alq3, $SCCO_2$ was injected into one size of the piston extractor in which Alq3 has been deposited. In order to reach the saturated condition, the temperature and pressure of the extractor were maintained for a specific time. Then, through a 10-μm orifice the saturated-Alq3 $SCCO_2$ was sprayed into the glass-made decanter which was pre-vacuumed to prevent the substrate being polluted. The orifice was kept at a desired temperature no matter with/without $SCCO_2$. The rapid oversaturated precipitation generated nano-size Alq3 particles to deposit on the prepared ITO glass which was located 1cm from the orifice.



1.CO_2 Cylinder	2.Cooling tank	3.7. Pressure gauge
4. Syringe pump	5.Check valve	6.Extraction cylinder
8.10.11.12. Temperature controller	9.Magnetic stirrer	10.Nozzle
13. Heater	15. Stirrer	16.Expansion chamber
17.18.19. valve	20. Pump	

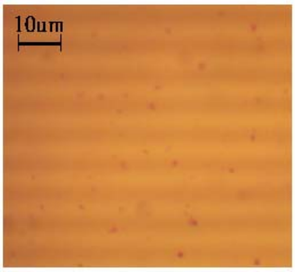
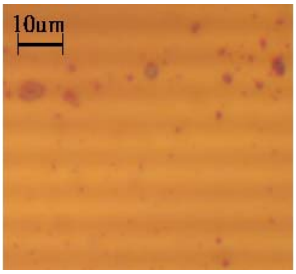
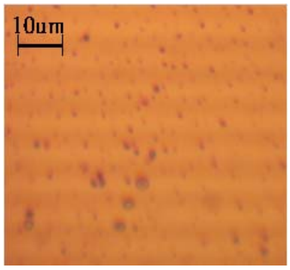
Figure 1. Scheme of RESS for fabricating the Alq3 thin film.

RESULTS

Effects of Pressure and Temperature of Extractor

Figure 2 shows the images of Alq3 thin film fabricated by different pressures and temperatures of extractor. From Fig.2, the fabricated thin film becomes smoother as increasing pressure to 30.6MPa for a fixed temperature. Although the large cluster existed in all pressure cases, the number and the size of large cluster gradually decreased and smaller at higher pressure. These phenomena can be explained by two mechanisms: First, at higher pressure the solution in the nozzle has higher and more stable solubility preventing particle from precipitation before expansion. On the other hand, at low pressure any fluctuation in pressure or temperature can cause instable in solubility, leading to precipitate particle easily in the nozzle. Second, the distance for producing mack number is longer at higher pressure. Hence, the precipitated particles were collected earlier at the same collecting distance before they collide together to form larger particles or clusters. Therefore, from Figure 3 scanned by AFM, the roughness (RMS= 4.1nm) of the thin film at 30.6MPa is smaller than that (RMS= 17.9nm) of 10.2MPa.

As proposed by Koch and Friedlander [9], the collision force between nuclei and particle can be increased with increasing temperature. Also, Wu and Friedlander [10] further proved that the solid-state diffusion coefficient around the boundary of nuclei is higher at higher temperature, which leads to the nuclei apt to coalescence in the nozzle. Hence, the number and size of cluster on the thin film is less and smaller at low temperature, as shown in Figure 2. The roughness

	30.6 MPa	17MPa	10.2 MPa
35°C			

(RMS= 4.1nm) of 35°C at 30.6MPa is smaller than that (RMS= 7.8nm) of 55°C. However, the temperature effect at higher pressure is more significant than that at lower pressure.

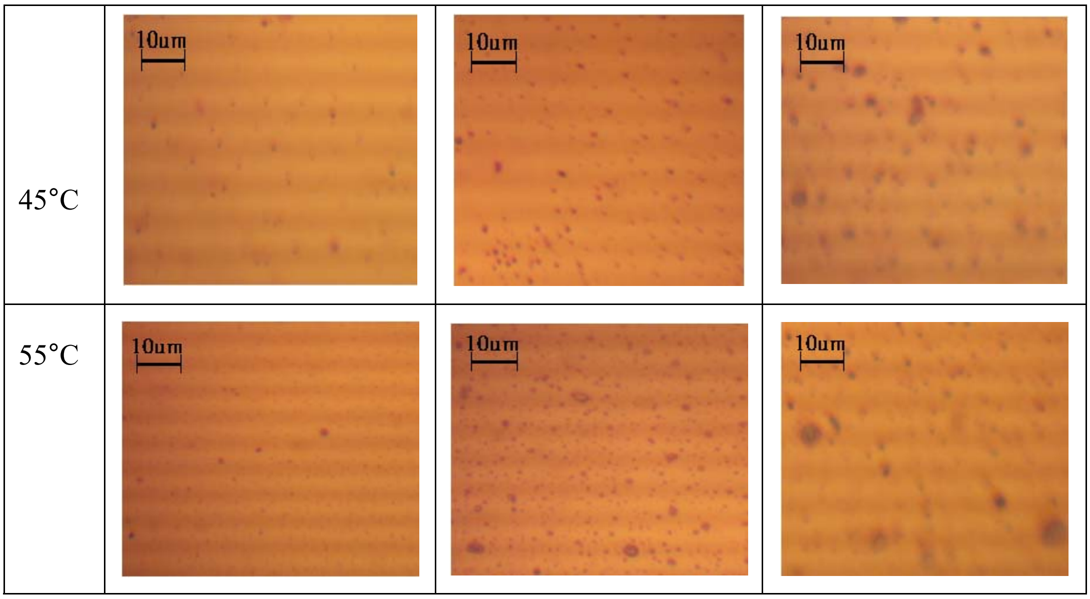
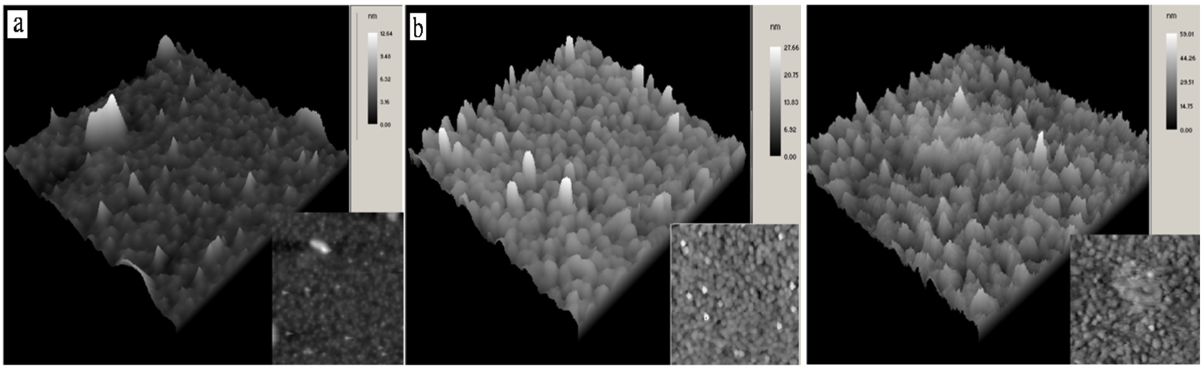


Figure 2. Images of Alq3 thin film fabricated by different pressures and temperatures of extractor.



(a)30.6MPa, 35℃<RMS=4.1nm>; (b)30.6MPa, 55℃<RMS=7.8nm>; (c)10.2MPa, 35 □<RMS=17.9nm >

Figure 3. AFM images and roughness of Alq3 thin film fabricated by different pressures and temperatures of extractor.

Effects of plasma etching and substrate temperature

By using plasma etching, the contact angle (surface tension) of glass substrate can be reduced, which can enhance the contact force between the thin film and substrate. Hence, the roughness can be dramatically improved, as shown in Figure 4. Besides, the roughness can be reduced by

increasing substrate tem

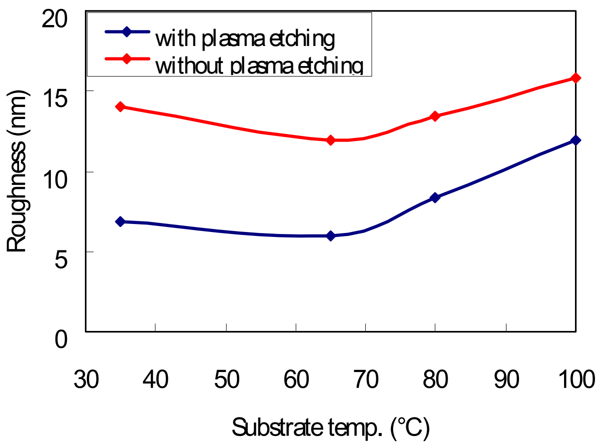


Figure 4. Effects of plasma etching and substrate temperature on the roughness of thin film

Optimal conditions

By testing all the operating parameters, a perfect Alq3 thin film with RMS= 3.2 nm can be made at 30.6MPa and 35°C of extractor, 30 wt% of ethyl alcohol to Alq3 as co-solvent, 80°C of nozzle, 10min of plasma etching, and 65°C of substrate temperature, as shown in Figure 5.

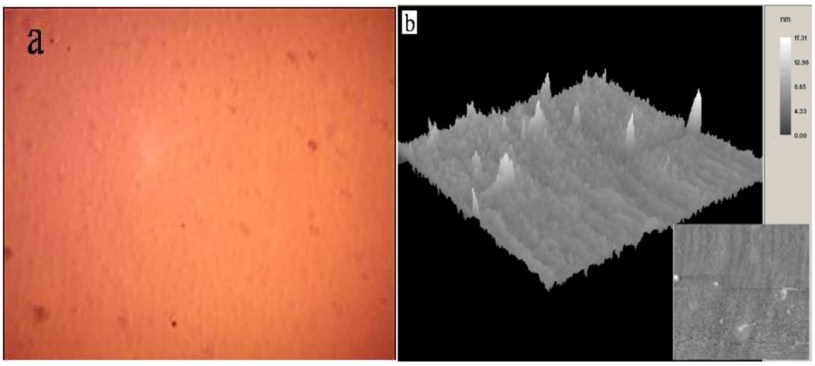


Figure 5. Images of the optimal Alq3 thin film with RMS= 3.2nm.

Electrical test

For the OLED electrical test, layers of NPB and LiF were generated by evaporator to improve the electron and hold transition ability, as shown in Figure 6. The OLED device (ITO/ NPB (35nm)/Alq_3 (70nm)/LiF (0.5nm)/Al (100nm)) has turn on voltage at 6V and 300mA/cm^2 current density at 10V, which meets the requirements of the OLED device.

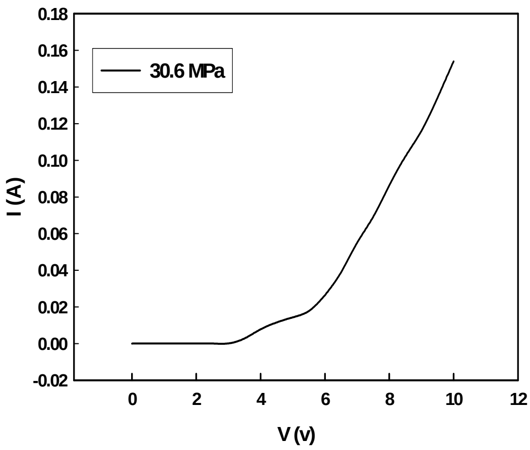


Fig. 6. I-V curve for OLED device (ITO/ NPB /Alq_3/LiF/Al) made at 30.6 MPa and 35^{o}C.

CONCLUSION

Using the process of RESS to fabricate OLED thin films has been proved successfully with examining the morphological and electrical characteristics. The optimal conditions for producing the perfect thin film are at 30.6MPa and 35°C of extractor, 30 wt% of ethyl alcohol to Alq3 as co-solvent, 80°C of nozzle, 10min of plasma etching, and 65°C of substrate temperature. The OLED device with optimal Alq3 (RMS= 3.2nm) has turn on voltage at 6V and 300mA/cm^2 current density at 10V, which meets the requirements of the OLED device.

REFERENCES :

[1] Sprengard, R., K. Bonrad, T. K. Daubler, T. Frank, V. Hagemann, I. Kohler, J. Pommerehne, C. Ottermann, F. Voges, B. Vingerling, Organic Light-Emitting Materials and Devices VIII, 2004, p. 173.

[2] McHugh, M.A. and Krukonis, V.J., Supercritical Fluid Extraction-Principles and Practice Butterworths, Stonham, MA, (1986).

[3] Yoon, S.H., Miyawaki, O., Park, K.H., Nakamura, K., J. Ferment. Bioeng., 82, 1996, p.334.

[4] Wang, Y.-P., T.-J. Lin, T.-C. Lee, J. Chinese Inst. Chem. Eng., to be published, 2008.

[5] Wong, J.M. and Johnston, K.P., Solubilization of Biomolecules in Carbon dioxide based Supercritical Solutions 2, Biotechnology press, 1986, p. 29.

[6] Debenedetti, P.G., AIChE J. 36, 1990, p. 1289.

[7] Reverchon, E., G. Donsì, J. Supercritical Fluids, 1993, 6, p.241.

[8] Petersen, R.C., D.W. Matson, R.D. Smith, I. Am. Chem. Soc., Vol. 108, 1986, p. 2102.

[9] Koch, W. and S.K. Friedlander, *J.Colloid and Interface Sci*,. Vol. 140**,** 1990, p. 419.

[10]Wu, M.K. and S.K. Friedlander, J. Aerosol Sci., Vol. 24, 1993, p. 273.