In-situ measurements of the formation of conductive organic thin films during solvent evaporation

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1. Introduction

Organic light emitting diodes (O-LEDs) have been attracting much attention as new displays and room lighting devices because of its physical flexibility, high luminance efficiency and low energy consumption. Recently, wet coating is highly focused as the fabrication process of organic thin films.[1] However, controlling the structure of thin film by coating processes have some difficulties and the electric and optical properties of O-LEDs are often inferior to those by vacuum processes. To solve this problem, understanding the film formation kinetics during coating is indispensable. [2] Wet coating processes include a solvent evaporation and a solute precipitation. To determine when "solid" organic thin films are formed from "solvated" organic molecules in solvent, we carried out in-situ measurements of evaporation rates, temperature changes and variation in scattered light intensity from the top surface of coated solution during drying. The temperature and concentration at the point of the solidification affect the structure of organic thin films.

2. Experimental

2.1 Materials and film formation methods

We chose a toluene (Wako Pure Chemical Industries)/(N,N'-Bis[4-[bis(3-methyl phenyl)amino]phenyl]-N,N'-diphenylbenzidine (DNTPD, Chemipro Kasei Kaisha) solution as a coating solution. Organic thin films were formed via the evaporation of the solution with drop casting or spin coating methods on glass or ITO substrates. Substrates were cleaned by 5 min ultrasonication in Semico-clean (Furuuchi Chemical)

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solution. After ultrasonication, 5 min washing in pure water was carried out twice and further 5 min washing in IPA (Isopropyl alcohol, Kanto Chemical) was also conducted. After the washing, we finally performed IPA vapor washing and cooled the substrates in air to room temperature. All chemicals are used as received without further purification.

2.2 *In-situ* measurements of temperature and scattered light.

Temperature of the coated dispersion decreases due to solvent evaporation and the loss of the latent heat of solvent. On the other hand, the concentration of DNTPD increases. To determine the temperature and DNTPD concentration at the point of film formation, we set up an *in-situ* measurements system shown in Fig. 1. Temperature of the film is measured by a radio thermometer and the change in mass of the coated solution is recorded by an electric balance. Time evolution of the solute concentration in solution is calculated from measured mass. We determined the point of film formation by detecting the scattered light intensity from the top of the evaporating film.

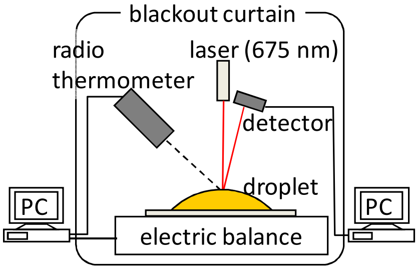

Fig. 1 *In-situ* measurement system.

2.3 Numerical model for solution evaporation

To analyze the kinetics of the coating process, we made two numerical models for pure solvent evaporation and DNTPD toluene solution. In our model, heat and mass balances during solvent evaporation were considered. In our model for pure solvent evaporation, we assumed following three simplified conditions, i) the shape of droplet is cylindrical, ii) the thickness of film is constant and only the radius of the cylinder decreases due to evaporation of solvent and iii) uniform temperature in the droplet. Under these assumptions, mass balance (or evaporation rate) and heat balance are expressed as,

$$\frac{dm}{dt} = -k\frac{MS}{RT}P_{sat}(T), \qquad (1)$$

$$\frac{dT}{dt} = \frac{1}{\rho C_p V}\left\{\frac{H}{M}\frac{dm}{dt} - \alpha S(T - T_{air})\right\} \qquad (2)$$

where S [m^2] is the top surface area of the cylindrical droplet and V [m^3] is the volume of droplet as,

$$S = \pi R^2, \qquad (3)$$

$$V = \frac{4}{3}\pi R^3 \qquad (4)$$

For solution evaporation, we referred previous study [3] which described the surface skin formation during solvent evaporation by simple 1D model (Fig. 2). In this report, the thickness of droplet h [m] and the height of the bottom of the skin layer h_g [m] are expressed as,

$$h = h_0 - J(1-\phi_0), \tag{5}$$

$$h_g = h_0 - \frac{J\phi_g(1-\phi_g)}{\phi_g-\phi_0}t\,. \tag{6}$$

The concentration of solute was roughly obtained by using the value of h and h_g under the assumption that the concentration of solute is uniform in the droplet.

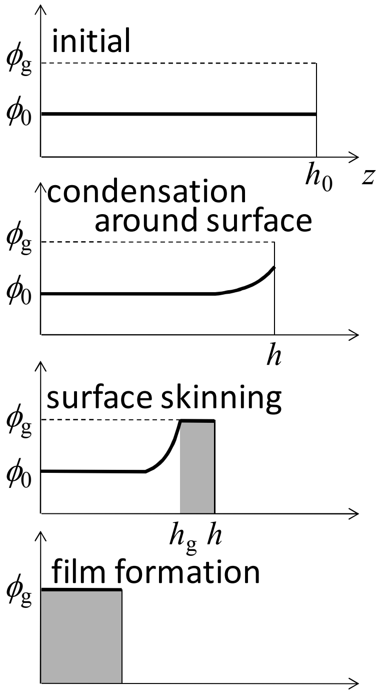

Fig. 2 1-D model for solution evaporation.

3. Results and Discussion

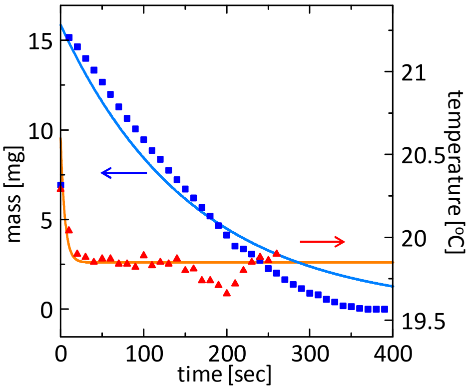

Fig. 3 In-situ measurement results of 20 μL toluene. Plots represent experimental results and lines represent those of numerical.

Figure 3 shows a typical example of in-situ measurement. The initial volume of the droplet was 20 μL. Calculation result of evaporation of pure toluene solution is also shown in Figure 3 as the solid lines. Due to the evaporation of solution, mass of droplet decreased with time. Temperature of the droplet drastically decreased in the initial stage of evaporation due to the loss of latent heat. Then, temperature was constant at 19.9 °C by balancing the loss of latent heat and heat conduction from the surroundings. Our estimation result by mathematical model agreed with the experimental results. From Figure 3, we determined two parameters as $k = 5.0 \times 10^{-3}$ m s^{-1} and $\alpha = 30$ W m^{-2}K^{-1}. Fig. 4a and 4b show the *in-situ* measurement result of scattered light intensity with an initial solute concentration of 1.75 wt% and 3.30 wt%, respectively. Scattered light intensity showed fluctuation until ca. 130 s after drop casting. This would be because most part of the coated solution is still liquid and the top surface acts as a free liquid surface. After that the sudden decrease in the fluctuation of the intensity was observed. We considered that this sudden stop of fluctuation is caused by the formation of "solid" organic thin film at the surface. Due to the formation of solid surface, the top surface is almost fixed, resulting in the less fluctuated surface displacement and less scattered light intensity. We defined this point as the onset of film formation. From the results of the mass and temperature measurements, the concentration of solution is estimated to be 10 wt% for the initial concentration of 1.55 wt% and 25 wt% for the initial concentration of 3.30 wt% About 80 sec after the sudden decrease in scattered intensity fluctuation, the fluctuation became completely zero in both cases. As Fig. 4 shows, the numerically obtained concentration line that leached to 100 wt% at that point. We consider that the point of the no fluctuation represents the completion of film formation. These results show that the critical concentration for skinning is increased with an increase in the initial concentration of solution. We estimated that the mass transfer coefficient is equivalent to 2.3×10^{-6} m s^{-1} from the value of J [s^{-1}] which was obtained from our model. Comparing to the value in the pure solvent case, the mass transfer coefficient for evaporation of solutions is ca. three orders of magnitude smaller than that of pure solvent evaporation. We think that the difference arose from the slow diffusion of toluene molecules in solid phase skin.

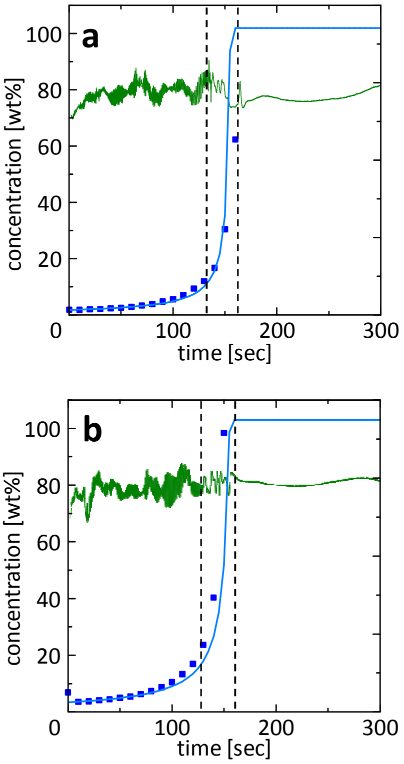

Fig. 4 In-situ measurement results of a) 1.75 wt% and b) 3.30 wt% toluene solution of DNTPD. Plots represent experimental results of concentration evolution and with lines obtained numerically. Fluctuating lines shows the intensity of scattered light from the surface of droplet. We drew two dotted line at the point of surface skinning and film formation.

4. Conclusion

We have established a novel method to observe the kinetics of film forming wet process. The concentration of solute at the onset of the film formation depends on the initial solute concentration. In our presentation, we introduce the relationship between the critical concentration and properties of organic thin film

References

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3. Okuzono T., *et al.*, *Phys. Rev. Lett.*, **97** (2006), 136103

Table 1 Nomenclature

α : heat transfer coefficient [$J\cdot s^{-1}\cdot m^{2}\cdot K$]
C_p : specific heat of solvent [$J\cdot kg^{-1}\cdot K^{-1}$]
ϕ : molar fraction of solute [-]
ϕ_0 : initial molar fraction of solute [-]
ϕ_g : critical gelation molar fraction of solute [-]
H : latent heat of solvent [$J\cdot mol^{-1}$]
J : mass transfer coefficient for solution evaporation [s^{-1}]
k : mass transfer coefficient for solvent evaporation [$m\cdot s^{-1}$]
m : mass of droplet [kg]
M : molar mass of solvent [$kg\cdot mol^{-1}$]
P_{sat} : saturated vapor pressure [Pa]
ρ : density of solvent [$kg\cdot m^{-3}$]
t : time [s]