

Precipitation process observation of dissolved organic semiconductor materials during drying

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1. Introduction

Solution processed electronic devices such as low molecule OLEDs are now attracting research interests because of the benefits of cost-effective mass production. To improve electric/optical properties, it is necessary to control the nanostructure of thin films on a macroscale. In the coating process, dissolved organic semiconductor materials are precipitated during drying and finally form a film. Drying is a non-equilibrium phenomenon which is an important factor to determine the film structure and properties.

In this study, we interpreted the nano-structure of precipitated material with solubility parameter of solute / solvent and saturated vapor pressure of solvent. We also observed the dynamics of precipitation process of semiconductor materials and tried to clarify the relationship between critical super-saturation and drying rate.

2. Nanostructure of precipitated Alq3 from various solutions

2-1. Experimental details

In this study, we used tris (8-hydroxyquinolinato) aluminium (Alq3), which is popular luminescence material of OLED, in tetrahydrofuran, chloroform, acetone, 1,4-dioxane, dimethylacetamide (DMA), N,N-dimethylformamide (DMF), nitrobenzene, and benzyl alcohol. The solubility parameter, vapor pressure, and Alq3 solubility [1] are shown in Table 1. The solubility parameter provides a numerical estimate of the degree of

interaction between solvent and solute, and vapor pressure reveals a good correlation with drying rate of solvent.

Table 1. Properties of solvents

	Solubility Parameter [cal/cm ³] ^{1/2}	Vapor pressure [kPa]	Solubility [1] [wt.%]
THF	9.1	18.9	0.36
chloroform	9.4	8.13	1.51
acetone	9.9	24.2	0.29
1, 4-dioxane	9.9	1.4224	0.42
nitrobenzene	10	0.02	0.61
dimethylacetamide	10.8	0.33	1.23
benzyl alcohol.	12.1	0.00306	4.13
N,N-dimethylformamide	12.1	0.3	1.30

The crystal structures of precipitated powders were determined by optical microscopy and X-ray diffraction (XRD) analyses.

2-2. Results and Discussion

Figure 1 summarized the structures of Alq3 precipitated powders from various solutions arranging on SP value and vapor pressure.

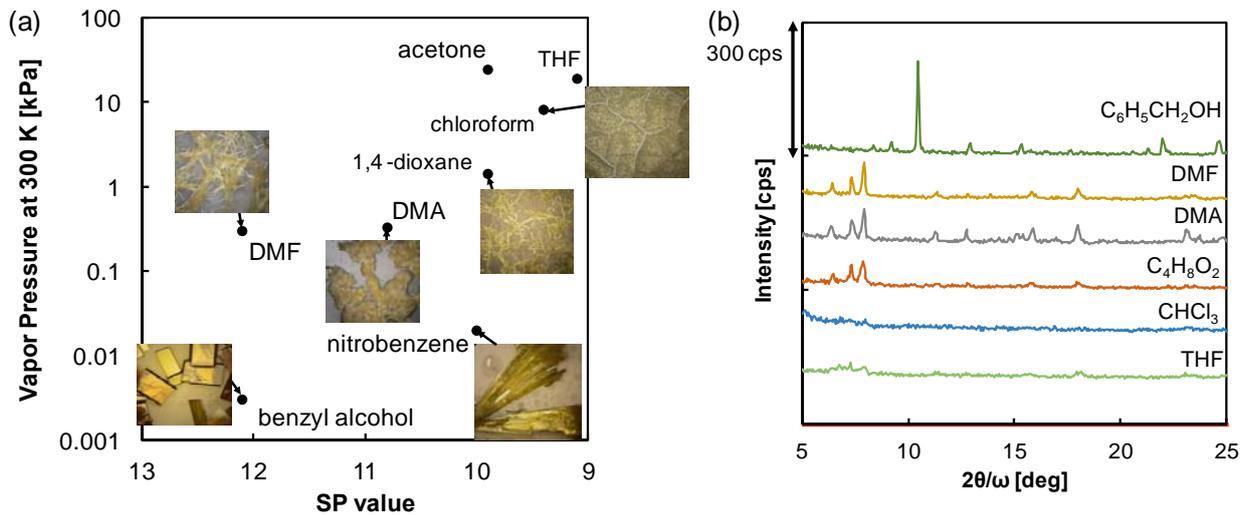


Fig. 1 (a) Optical microscopy, (b) XRD spectra of precipitated Alq3 from various solutions.

When SP value is large and vapor pressure is small, which means the interaction between solvent and solute is large and drying rate of solvent is slow, the precipitation occurs in equilibrium state and it causes the stable crystal structure of Alq3. Alq3 from benzyl alcohol solution shows the different structure of ones from others as shown in Fig. 1(b). On the other hands, when SP value is small and vapor pressure is large, the precipitation occurs in non-equilibrium state and it causes amorphous structure of Alq3.

3. The dynamics during drying process

3-1. Experimental details

In non-equilibrium drying process, it is important to determine the degree of supersaturation at nucleation point during phase transition from liquid phase to solid phase. The degree of supersaturation can be calculated from the liquid phase thickness at nucleation point. We set up the dynamic observation systems as shown in Fig. 2. For film thickness, we monitored the intensity of reflected laser light with 670 nm during spin coating [2]. With the decrease of liquid thickness, constructive interference and destructive interference occur alternately. We also monitored the intensity of scattered laser light with 780 nm during spin coating [3]. At the onset of the formation of the solid phase, the sudden intensity variation film occurs, which should be a critical supersaturation point.

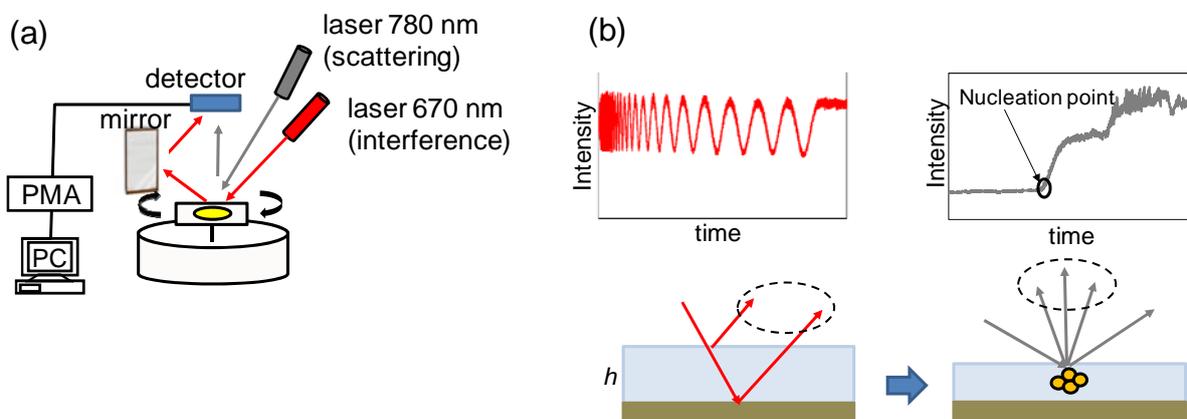


Fig. 2 Schematic illustration of (a) dynamic observation systems and (b) *in-situ* formation analysis.

3-2. Results and Discussion

Liquid phase thickness was calculated at constructive interference point and destructive interference point from the dynamic observation during spin coating of Alq3

film at 1000 rpm from DMA, DMF, and nitrobenzene with 1 wt.% Alq3 using eq. [1] and [2]. And the solution concentration was estimated from liquid phase thickness assuming that there was no concentration distribution in the liquid phase.

$$h = \frac{\lambda}{2n \cos \theta} \left(m - \frac{1}{2}\right) \quad \text{eq. [1] at constructive interference}$$

$$h = \frac{\lambda}{2n \cos \theta} m \quad \text{eq. [2] at destructive interference}$$

Figure 3 shows the solution concentration during spin coating. It is clear that nitrobenzene is the most equilibrium state during drying. The concentration at nucleation, where scattering suddenly increased, was estimated 19 wt.% in nitrobenzene solution, 16 wt.% in DMA solution, and 3 wt.% in DMF solution. Considering saturated solubility in Table 1, nitrobenzene has the lowest degree of supersaturation.

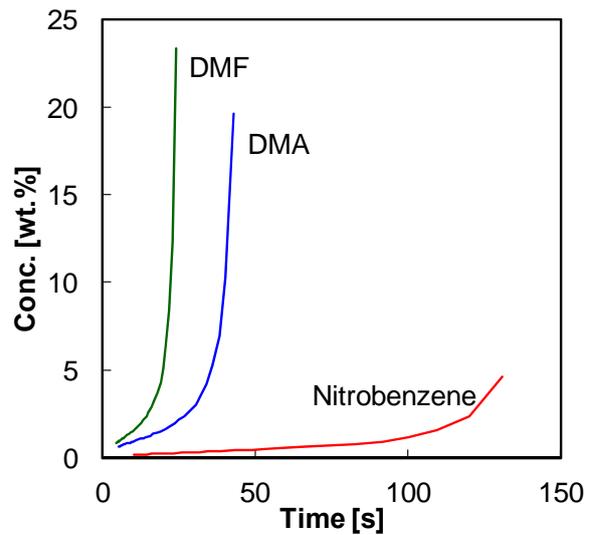


Fig. 3 Estimated variation of solution concentration during spin coating.

4. Conclusions

We focus on solubility parameter and vapor pressure to categorize the structure of precipitation material in the solution process, coating and drying. The condition with the small difference of solubility parameter between solvent and solute and the low vapor pressure of solvent reveals the equilibrium state in precipitation phenomenon. We also clarified the relationship between supersaturation point and equilibrium / non-equilibrium state.

References

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- [3] K. Oku, S. Inasawa, Y. Tsuji, and Y. Yamaguchi, *Dry. Technol.* 30, 832 (2012).