

Nanostructure and electrical properties of organic semiconductor thin films

prepared by wet and dry processing:

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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. We have already reported that the solvent influences crystal growth kinetics and crystal structures of polycrystalline organic semiconductor thin films in solution process ^[1]. In this work, we focus on amorphous organic semiconductor films and investigate the effect of dry/wet processes on the characteristics.

2. Experimental details

In this study, we use three types of precursors, where they have different crystallinity, solubility for toluene, and melting point as shown in table 1. Evaporation coating was performed for these organics (PVD process). Solution process of spin coating was also performed. Single crystal and precipitated powder were

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obtained by drying up solution.

Table 1. Low molecule organic materials in this study.

material	csyattallinity	solubility
A	crystal	~1.5
B	amorphous	~13
C	amorphous	~40

The characterizations of structures were performed by 2θ X-ray diffraction (XRD) with Cu $K\alpha$ radiation operating at 50 kV and 300 mA on an X-ray diffractometer (Rigaku, ATX-G), transmission electron microscopy (TEM; JEOL, JEM-4010) operating at 400 kV or 200 kV, electron diffraction, and Fourier transform infrared spectroscopy (FTIR; Perkin-Elmer, Spectrum One). Thermo analysis was also performed by a Thermogravimetry-Differential Thermal Analysis and Mass Spectrometry (TG-DTA-MS; Rigaku, Thermo plus) to identify the residual solvent in precipitated powder and scraped powder from spin coated films on Si substrates. Optical properties were measured by UV-vis spectrometer (Hitachi, U-4100) and photoluminescence.

3. Results and discussions

3-1. PVD films

Figure 1 shows typical XRD patterns of PVD films deposited below the crystallization temperature. The films had amorphous structure and each XRD pattern showed a halo peak around 20° . The d-spacing corresponding to the intermolecular distance was determined from the halo peak. Despite the substrate temperature, it took constant value based on each

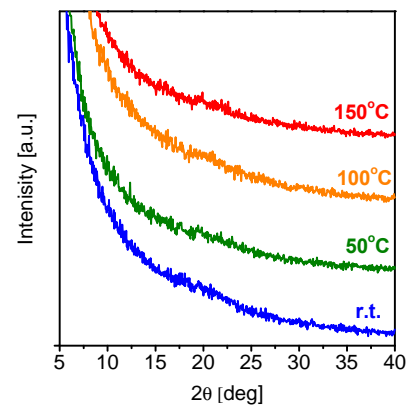


FIG. 1. XRD spectra of PVD films

organic material. Optical energy gap was obtained from absorption edge wavelength, and it also took the constant value based on each organic material.

3-2. Spin coated films

From XRD and TEM observation, spin coated films were confirmed to have amorphous structure independent of spin rate. D-spacing between molecules and optical energy gap of spin coated films was determined and it was found that spin rate affected the properties of the films. A higher spin rate, which corresponds to a higher drying rate, results in a smaller d-spacing value and a smaller optical energy gap. By focusing on the relationship between d-spacing and optical energy gap as shown in Fig. 2, it is obvious that the

energy gap decreases with the decrease of d-spacing probably due to the development of π - π conjugation.

To understand the effect of solvent, we determined the precipitated powder from toluene and THF solution, by drying up with different rate. The precipitated powder has amorphous structure when dried up fast, and has polycrystalline structure when dried up slowly. In the thermal analysis of precipitated powder, a three-step weight loss was observed due to solvent molecule. With increasing drying rate, the desorption of solvent corresponding to the second peak decreased, and the one corresponding to the third peak increased. We consider that precipitated powder contains solvent with three different modes, the first one caused by the solution from powder surface, the second one caused by the solvent adsorbed with molecules on the domain boundaries, and the third one, which is desorbed at melting point, caused by the solvent adsorbed much stronger than the second one with molecules in the domains.

We observed a phase transition from a toluene solution to a solid thin film during spin coating process using in-situ measurements of the PL spectra and the variation of scattered light ^[2]. As shown in Fig. 3, the gradual decrease in PL intensity was observed from 0 to τ_1 due to the formation of a solid-like surface. The sudden increase in PL intensity was observed between τ_1 and τ_2 , and the variation of the scattered light intensity that represented the fluctuation of the top surface suddenly decreased at τ_2 . We consider that τ_1

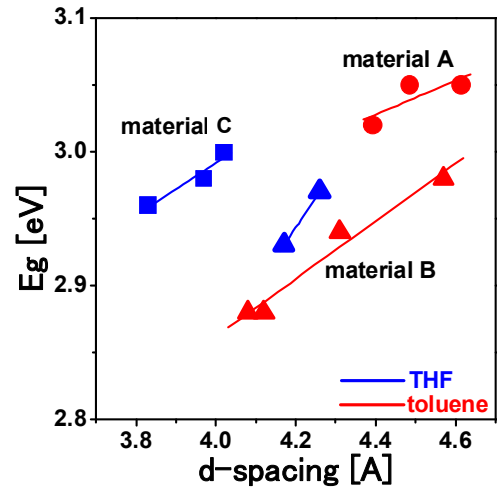


FIG. 2. Relationship between d-spacing and optical energy gap of spin coated films.

corresponds to the onset of the formation of the solid film, which should be a critical super-saturation point on the solubility curve, and the phase transition of the solute to the solid is completed at τ_2 .

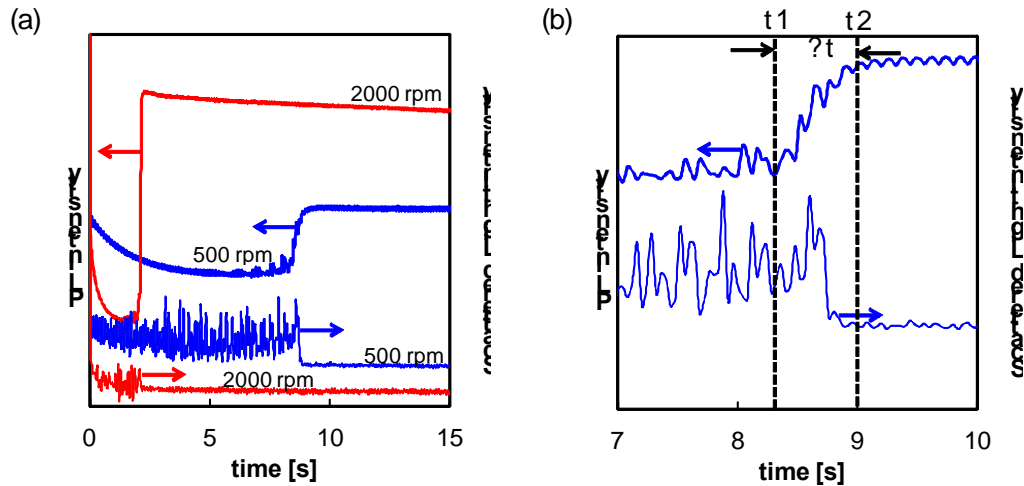


FIG. 3. In situ measurements of PL and scattered light during spin coating. (b) shows the magnified spectra between τ_1 and τ_2 .

Basically when the drying rate is fast, the solution concentration at critical super-saturation point is higher, causing the higher nucleation frequency, so that the domain size would be small. When the domain size is small, the diffusion length of residual solvent decreases and it becomes easy to diffuse solvent outside to the atmosphere, and introduces the small amount of residual solvent in the domains. And then, d-spacing tends to small, results in small optical energy gap.

4. Conclusions

We focused on the amorphous low molecular organic semiconductor films, and clarified the relationship among “process” including wet process and evaporation process, “structure” (d-spacing between molecules), and “property” (optical band gap or photoluminescence property). Though d-spacing and E_g were independent of process parameters in PVD films, they strongly depend on process parameter in spin coated films. The structure of the film is estimated by considering the dynamics of film formation, and the optical property is determined by d-spacing between molecules.

References: [1] Y. Tsuji, K. Uehara, E. Narita, A. Ono, N. Mizuno, and Y. Yamaguchi, Pacifichem 2010, Honolulu, Hawaii, USA, Dec. 17th-20th, 2010. [2] K. Oku, S. Inasawa, Y. Tsuji, and Y. Yamaguchi, Dry. Technol., 30 (8), 832-838 (2012).