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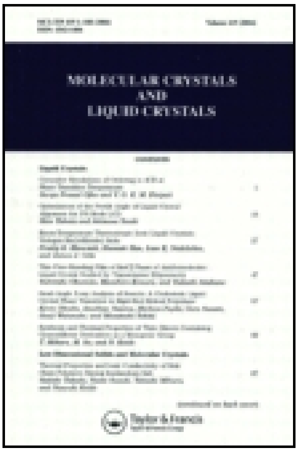

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Effect of Co-evaporant Induced Crystallization on Needle Growth of Phthalocyanine Thin Films

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Needle growth control of metal-free phthalocyanine (H_2Pc) films was performed by using a recently proposed method, "co-evaporant induced crystallization." Nominally 200 nm of H_2Pc films were grown on indium tin oxide (ITO) coated glass substrates with substrate heating of 70 and 40°C. The morphologies were observed by using scanning electron microscopy (SEM), and the crystallinities were confirmed by X-ray diffraction (XRD). Various lengths of needles were observed in the H_2Pc films grown without co-evaporant. With co-evaporant, in contrast, rather uniform and shorter needles with larger diameters were grown. These results suggest that the co-evaporant enhances rather 2-dimensional-growth than 3-dimensional-growth of organic films.

Keywords Organic photovoltaics; organic solar cells; phthalocyanine; thin film growth

Introduction

Structure control of organic thin films is important for fabricating high performance organic electronic devices, such as organic transistors [1] and organic solar cells (OSCs) [2]. Especially, needle growths of organic semiconductors sometimes roughen their film surface and the electronic devices composed of such films lose their robustness [3]. Recently, we have proposed a new method of organic film growth, "co-evaporant induced crystallization," and succeeded in crystallizing donor-acceptor blends, the key part of OSCs, based on small molecules by using a liquid as a non-sticking co-evaporant source during vacuum deposition of the blend film and showed striking enhancements of photocurrent [4]. In this study, this new method is utilized for controlling the needle growth of H_2Pc thin films.

Experimental

Nominaly 200 nm of H_2Pc thin films were grown on ITO-glass substrates by the apparatus depicted in Fig. 1a after air plasma treatment. The deposition rates for the H_2Pc were 1.0 $Å \cdot s^{-1}$, while the deposition rate was kept at 0.2 $Å \cdot s^{-1}$ for the co-evaporants. The substrates were heated to 70 and 40°C during the deposition. Water cooled quartz crystal microbalances (QCMs) were used to monitor the deposition rate independently after calibrations. In this study, we examined three polydimethylsiloxanes (PDMSs) with different chain lengths as co-evaporants: $C_3H_9SiO(C_2H_6SiO)_nSiC_3H_9$, where n∼13 (PDMS13), 41 (PDMS41)

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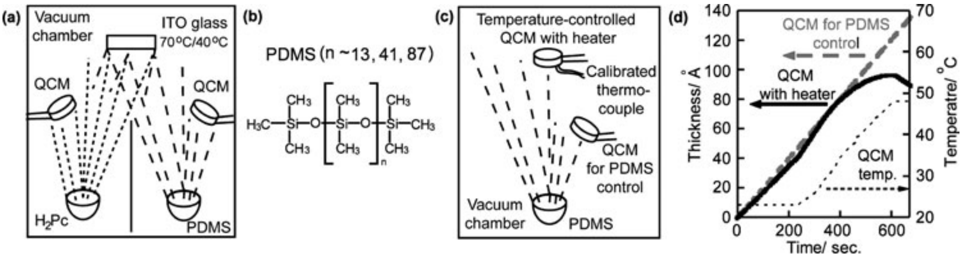

Figure 1. Apparatus of this study. (a) H_2Pc film growth. (b) Molecular structure of PDMSs. (c) Volatilization temperature measurement. (d) Volatilization temperature measurement result of a co-evaporant, PDMS41, under arriving rate of 0.2 Å/s.

and 87 (PDMS87) (see Fig.1b) since the PDMS41 drastically crystallized H_2Pc:C_{60} blend films in the former study [4]. The difference of the chain length results in the change of the volatilization temperature. At room temperature, these all co-evaporants are liquid oils in the vacuum system, while typical pressure of our system was about 1×10^{-3} Pa.

The measurements of volatilization temperature of co-evaporants were performed in the same vacuum system used for the film growth, using temperature-controlled QCM equipped with a tungsten heater and a thermocouple (see Fig.1c). In Fig.1d, while elevating the temperature of the quartz crystal, deposition rate of the co-evaporant on the crystal gradually decreased, despite the arriving rate was kept at 0.2 Å·s^{-1} by monitoring with another QCM. After the equilibrium at 0 Å·s^{-1} was performed, finally, the direction of the deposition rate was inverted from increase to decrease, i.e. emission rate became larger than the arriving rate of 0.2 Å·s^{-1}. Above this critical temperature of inversion, which we denote as volatilization temperature, the co-evaporant will not condense on the substrate. The volatilization temperature of each co-evaporant was the following: 26°C for PDMS13; 48°C for PDMS41; and 103°C for PDMS87.

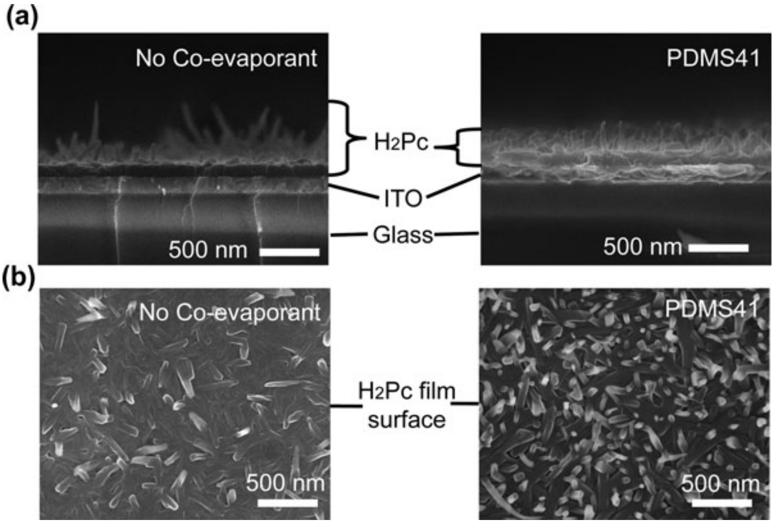

Figure 2. SEM images of 200-nm-thick H_2Pc film grown at 70°C without co-evaporant/with PDMS41. (a) Cross-sections. (b) Film surfaces.

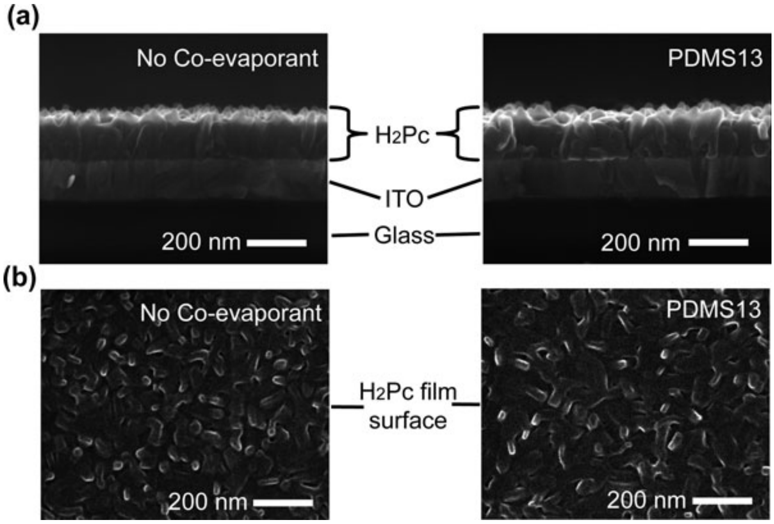

Figure 3. SEM images of 200-nm-thick H_2Pc film grown at 40°C without co-evaporant/with PDMS13. (a) Cross-sections. (b) Film surfaces.

The morphologies and crystallinities of the grown films were observed by SEM and XRD with a field emission scanning electron microscope JSM-6700F (JEOL) and a powder X-ray diffractometer RINT UltimaIII (Rigaku), respectively.

Results

Figure 2 shows SEM images of H_2Pc thin films grown at the substrate temperature of 70°C with and without a co-evaporant, PDMS41, which volatilization temperature, 48°C,

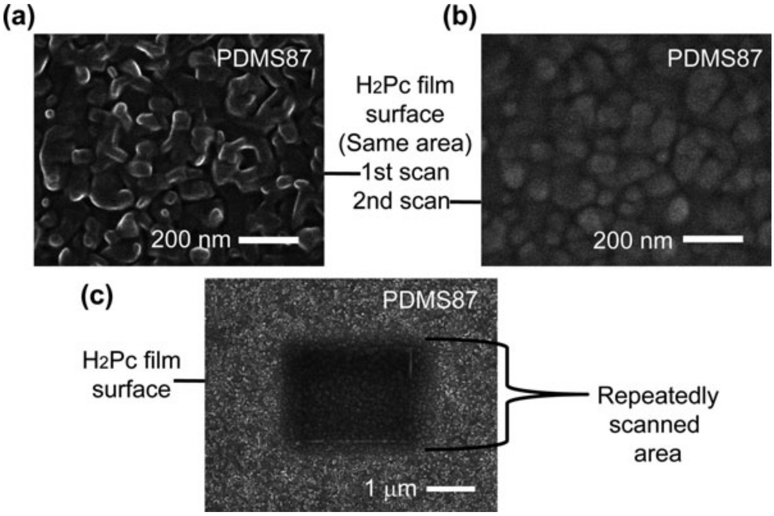

Figure 4. Surface SEM images of 200-nm-thick H_2Pc film grown at 40°C with PDMS87. (a) First scanning. (b) Second scanning. (c) Wide-scanned image after the continuous observation.

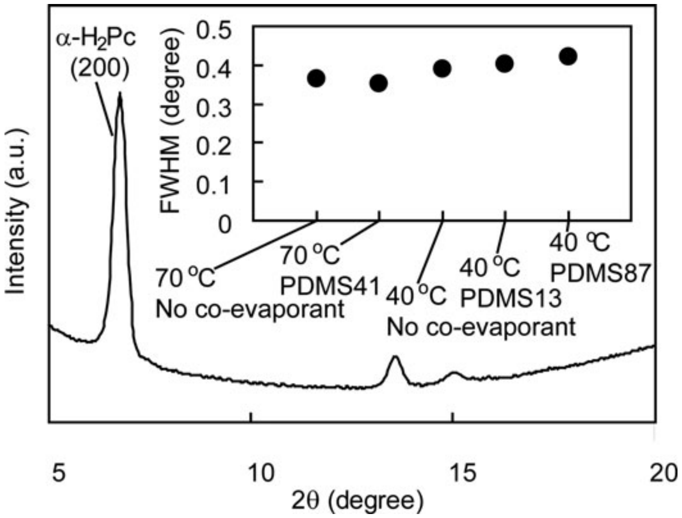

Figure 5. XRD pattern of 200-nm-thick H_2Pc film grown at 70°C without co-evaporant. The inset shows FWHM of the α-H_2Pc(200) peak at different growth conditions.

is lower than the substrate temperature of 70°C, so, it is considered not to remain on the substrate after the deposition. Various lengths of H_2Pc needles are observed in the film without co-evaporant. With PDMS41, in contrast, rather uniform and shorter needles grew. This difference implies that the co-evaporant itself does not induce the needle growth, and that the needle growth is caused by the substrate heating, which is conventionally known effective for the crystallization of organic thin films [5–7].

For the clarification of each effect, co-evaporant and substrate heating, we again grew the 200-nm-thick H_2Pc films, at lower substrate temperature of 40°C. Here, co-evaporant with lower volatilization temperature of 26°C, PDMS13, was utilized not to be condensed on the substrate at 40°C. The SEM images in Fig. 3 clearly show that this temperature lowering successfully suppressed the needle growth of H_2Pc films compared to the growth at 70°C in Fig. 2 and confirm that the needle growth is the effect of substrate heating. From grain size comparison in Fig. 3, the effect of the co-evaporant is clearly noticed as the grain size enlargement typically from 20 to 50 nm.

We also grew an H_2Pc film with PDMS87, which volatilization temperature is 103°C, obviously higher than the substrate temperature of 40°C, and should be condensed on the substrate. Only with this film, we found a curious phenomenon during SEM observation where fast expansion of H_2Pc film occurred (see Fig. 4). This might be because of the electron-beam irradiation of remained PDMS liquid. Since this did not occur with other films, it is confirmed that such residual PDMS exists only in this case.

Finally, crystallinities of all these films were confirmed by XRD as shown in Fig. 5. Different from the case of blend films [4], almost all films showed high crystallinity enough to saturate the full width at half maximums (FWHMs) of α-H_2Pc(200) peak [8].

Conclusion

We have demonstrated the needle growth control of metal-free phthalocyanine (H_2Pc) films by using a recently proposed method, "co-evaporant induced crystallization." High temperature of the substrate induced needle growth of H_2Pc, while the co-evaporant acted for the enlargement of H_2Pc grains in horizontal direction and made the needles rather uniform and shorter. These results suggest that the co-evaporant enhances rather 2-dimensional-growth than 3-dimensional-growth of organic thin films.

*This manuscript has not been published elsewhere and has not been submitted simultaneously for publication elsewhere.

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[8] FWHM narrowing is limited because of thin film thickness and measurement condition of XRD.