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Precipitation of thin film organic single crystals by a novel crystal growth method using electrospray and ionic liquid layer

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Abstract

The use of single crystal organic semiconductors is one promising way to improve the performance of organic devices. We propose a new organic single crystal growth method which uses an ionic liquid as a crystal growth field and supplies source solution as atomized droplets by electrospray. In this study, we investigated the behavior of crystal precipitation of four low molecular organic materials (Alq_3, NPB, PBD, TPD) at room temperature (25℃) under atmospheric pressure. When the material was supplied at the same speed, thin film single crystals with longest diagonal length of 97~35 μm were obtained by 180 min growth. It was found that the larger the solubility of material, the larger the size of the precipitated crystals. This is probably because in the solute with high solubility, the supersaturation degree in the ionic liquid becomes lower than that of the solute with low solubility, so the spontaneous nucleation density decreases, and the larger thin film single crystal grows more easily. By 16 hour growth, large Alq_3 hexagonal plate crystals with longest diagonal length of 393 μm were successfully obtained.

1. Introduction

Organic single crystals have features such as high charge mobility, high current density tolerance, and large transition dipole moment. Therefore, organic single crystal is a promising material for realizing high performance organic transistor and organic semiconductor laser. In the growth of organic single crystals, a solution method which utilizing supersaturation of a solute in a solvent or a vapor phase method which recrystallizing in a low temperature region by sublimation are widely used. Recently, the method which can control the position and shape of organic single crystal thin film by the inkjet method has been reported [1].

In order to grow large thin film single crystals for high performance organic devices, we have proposed a new crystal growth method which use an electrospray [2] for solute supply and an ionic liquid which is a liquid state salt at room temperature as a crystal growth field. By this crystal growth method, we succeeded in growing a large thin film single crystal of tris-(8-hydroxyquinoline) aluminum (Alq_3) known as a low molecular material which is difficult to grow large thin film crystal and acicular crystals tend to precipitate.

In addition, a general fluorescent low molecular materials of 2-(4-Biphenylyl)-5-(4-tert-butylphenyl) -1,3,4-oxadiazole (PBD), N,N'-Bis(3-methylphenyl),-N,N'-diphenylbenzidine (TPD) and N,N-di(naphthalene-1-yl)-N,N-diphenyl-benzidene (NPB) were used to investigate the dependence of solute solubility and precipitated crystal size for this crystal growth method.

2. Experiment instructions

ITO coated glass was used as the substrate, and 1-Ethyl-3-Methyl-imidazolium dicyanamide was used as the ionic liquid. Four kinds of source materials, Alq_3, PBD, TPD, and NPB were used as solute. A saturated ionic liquid was prepared by dissolving each solute in a saturated amount in ionic liquid at room temperature (25°C). The solubilities of Alq_3, PBD, TPD and NPB in ionic liquid were 5.0~5.5, 2.5~3.0, 0.7~0.8 and 0.3~0.5 mg/ml, respectively. After the substrate was soaked in piranha solution (concentrated sulfuric acid: hydrogen peroxide solution = 3: 1), ultrasonic washing was carried out for 15 min, and then each saturated ionic liquid layer about 5-μm-thick was formed on ITO substrate. A solution of each material was sprayed from above the saturated ionic liquid film by electrospray, to attempt to grow single crystals in a liquid film. For the spray solution, each material solution (0.3 mg/ml) in chlorobenzene (CB) with 20 vol% dimethyl-sulfoxide (DMSO) was prepared. Figure 1 shows a system configuration and a conceptual diagram of crystal growth. For the crystal growth, the electrospray conditions of the solution feed rate, the solution feed time and the substrate temperature were set to be 2.0 μl/min, 180 min and 25 °C, respectively.

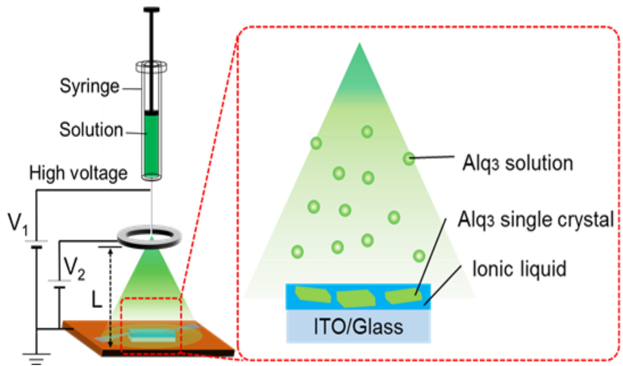

Fig.1 Schematic of electrospray system and conceptual diagram of crystal growth method.

3. Results and discussions

Figure 2 shows a fluorescence microscope images of obtained crystals in the ionic liquid films. Lower row pictures are SEM bird's eye view of crystals taken out from the ionic liquids. It was confirmed that single crystals grew in four types of fluorescent low molecular materials. It is considered that the precipitation driving force of the crystal is supersaturation of the solute concentration in the ionic liquid film due to evaporation of the high vapor pressure solvent supplied by the electrospray.

Table 1 shows the relationship between the length and volume of one crystal precipitated in each material and the solubility of each solute to ionic liquid (25 °C). Typical lengths (volumes) of Alq_3, PBD, TPD and NPB are 97 μm (4270 μm³), 86 μm (1450 μm³), 52 μm (1350 μm³) and 32 μm (330 μm³), respectively. The relationship between crystal size and saturated solubility showed same trend, and it was found that a material with higher saturated solubility in ionic liquid precipitated larger crystals. It can be considered that, in this experiment, since the supply rate of solute to the ionic liquid film was constant, the supersaturation degree of the higher solubility material in the ionic liquid became relatively low compared with lower solubility ones. Therefore, the higher solubility material would have lower crystal nucleation density and a longer diffusion length. Consequently, as well known, longer diffusion length causes lower density of nuclei and solute molecules were supplied to a smaller number of crystals, consequently grow larger thin film single crystal.

For Alq_3, we demonstrated the long-time growth of 16 hours, and succeeded in growing a large hexagonal plate-like single crystal with a maximum length of 400 μm as shown in Figure 3.

4. Conclusions

We proposed a new organic thin film single crystal growth method using ionic liquid and electrospray. This method was applied to four low molecular materials of Alq_3, PBD, TPD and NPB and found that the larger the solubility of material, the larger the size of the precipitated crystals. In addition, we succeeded in growing large hexagonal plate-like single crystals with a longest diagonal length about 400 μm for Alq_3 which is known to be difficult to grow thin film crystals.

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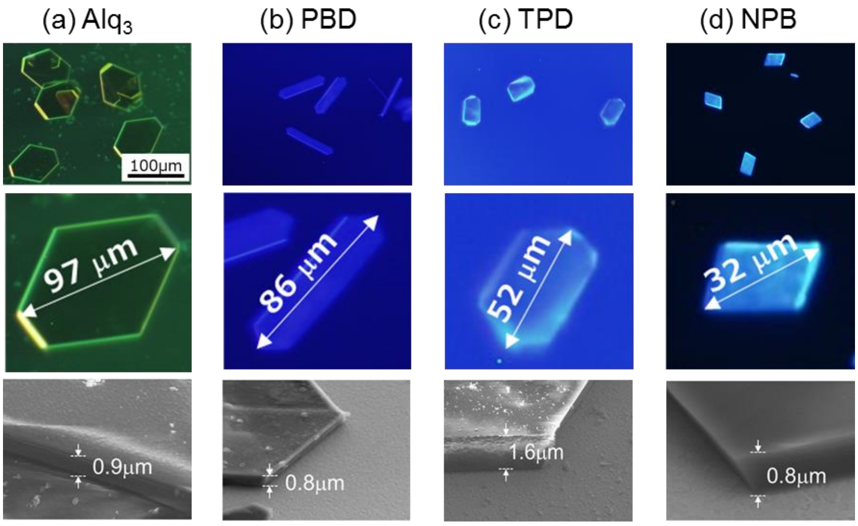

Fig.2 Fluorescence microscopy images of the precipitated crystals in ionic liquid after 180 min growth (upper row) and enlarged view of single crystal (middle row). And SEM bird's eye view of crystals taken out from ionic liquid (lower row).

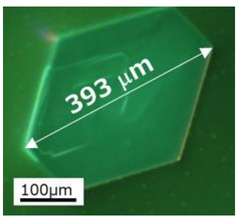

Fig.3 Large-sized Alq_3 thin film single crystal about 400 μm precipitated for 16 hours.

Material	Alq_3	PBD	TPD	NPB
Longest diagonal length (μm)	97	86	52	32
Volume (μm³)	4270	1450	1350	330
Solubility (mg/ml)	5.0~5.5	2.5~3.0	0.7~0.8	0.3~0.5

Table.1 Relationship between the saturation solubility of each material in ionic liquid at 25 °C, longest diagonal length and volume of precipitated crystal.