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Growth of thin film organic single crystals with controlled in-plane doping profile by a novel method using electrospray and low vapor pressure solvent

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Abstract

Molecular doping for organic semiconductors which enables to control emission wavelength and carrier transport characteristics is expected to be a key technology in device application, but doping technology for thin film single crystals is still in its initial stage. In this report, we propose a molecular doping method with excellent controllability in concentration and demonstrated in-plane control of doping profile that is doped and non-doped area was steeply separated. The molecular doped thin film organic single crystals were grown by a novel growth system in which a low vapor pressure liquid thin film is used as a crystal growth field and fine droplets of solute are supplied from the liquid surface by an electrospray (ES) system. By use of this system, spatially controlling the doping region of DCM, which is red laser dye, for PBD thin film single crystals, which is wide gap fluorescent low-molecular material could be grown.

1. Introduction

Practical use of organic semiconductor devices is progressing with improving the performance of organic light emitting devices. Toward further prevalence of organic semiconductor devices, development of organic transistors and organic solar cells is accelerating, and it is desired to further improvement of performance and functionality of organic devices. Single crystal organic semiconductors are an attractive device material having characteristics such as high charge mobility, high current density tolerance, high-thermal stability, and large transition dipole moment. Development of a highly controllable doping technique for single crystal organic semiconductors will drastically expand the potential application of organic material [1].

Towards application to high performance thin film organic single crystal devices, we have proposed an organic single crystal growth method which use an electrospray (ES) system for solute supply and low vapor pressure liquid as a crystal growth field [2]. In this study, we investigated the molecular doping characteristics and tried to control the in-plane doping profile by use of this crystal growth method. In the experiments, 2-(4-Biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), which is wide gap fluorescent low-molecular material was used as host material and 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM), which is a red laser dye was used as dopant. By sequential suppling of splay solution without and with DCM, doping profile control was realized in the in-plane direction.

2. Experiments

Fig. 1 shows a schematic view of the thin film single crystal growth system using an ES method and a low vapor pressure liquid. Bis (2-ethylhexyl) sebacate (DOS) as the low vapor pressure liquid for thin film crystal growth field, PBD as the host single crystal material for the solute and DCM as the guest dopant material were used. First, saturated amount of PBD (2.5~3.0 mg/ml) was dissolved with low vapor pressure liquid of DOS at 25 ºC. Next, this PBD saturated DOS was coated with a thickness of about 5 μm on a hydrophillized ITO coated glass substrate. The nozzle applied voltage was 5.2 kV, the extraction electrode voltage was 3.0 kV, and the substrate temperature was 25 ºC.

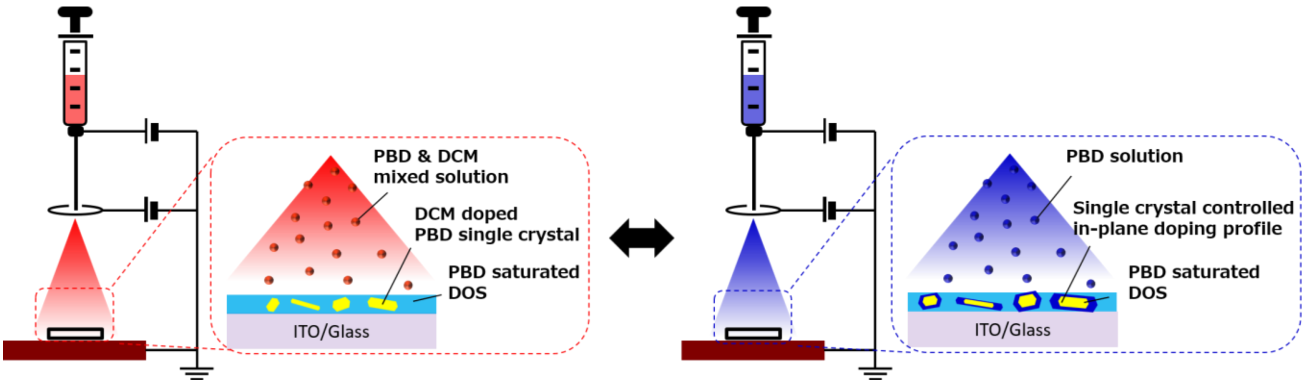

Fig.1 A schematic view of the thin film single crystal growth system using an ES method and a low vapor pressure liquid.

In the first experiment, in order to evaluate the DCM doping characteristic to the PBD thin film single crystals, solution of PBD and DCM dissolved at a concentration of 0.3 mg/ml in a mixed solvent of 80 vol% chlorobenzene and 20 vol% dimethylsulfoxide was sprayed by the ES to the liquid thin film surface. The dependency of the DCM concentration and influence of solution spraying speed was investigated. Next, attempts were made to create non-doped and DCM-doped regions in the in-plane direction by sequential spraying of DCM-free solution and DCM-5.0 wt% solution.

3. Results and discussion

For the case of different solution supply rate, PBD and DCM crystals precipitated independently at solution supply rates of 8.0 and 4.0 μl/min, but DCM was doped in PBD crystal at 2.0 μl/min. The DCM doped PBD thin film single crystals showed yellow emission under the UV light irradiation. It was confirmed that molecular doping can be occurred at lower growth rate condition than a threshold value. Under this condition, when the DCM concentration in the spray solution was changed to 0.2 to 50.0 wt%, the doping concentration was almost linearly widely controlled in two order of magnitude from 0.016 to 15.5 mol% as shown in Fig. 2.

Next, we tried to control the doping profile in the in-plane direction by sequentially spraying a solution without DCM and a solution with DCM concentration of 5.0 wt%. In this case, spraying times were set to 360 min for each. Fig. 3 shows fluorescence microscope images of typical crystals after the growth. Fig. 3 (a) shows a stripe-shaped crystal having a width of 100 μm with a DCM doping region with a width of 30 μm at the center region and Fig. 3 (b) shows a hexagonal plate-like crystal having a diagonal length of about 130 μm with a DCM doping region with a width of about 10 μm at the outer periphery. The blue-violet region which is the original light emission color of PBD and the yellowish region due to the DCM doping could be separately formed with steep interface in a single crystal. The room temperature PL spectra of a PBD crystal having doped and non-doped region measured by He-Cd laser (325 nm) excitation are shown in Fig. 4. In the region of blue-violet emission under fluorescence microscopy, a spectrum having a peak wavelength of 400 nm which corresponds to a PBD single crystal was obtained. On the other hands, in the region of yellowish emission under the fluorescence microscopy, double peaked spectrum with peak wavelengths at 400 nm from PBD and at 570 nm from DCM were obtained. It was shown that it is possible to grow a plate-like organic single crystal having steeply controlled in-plane molecular doping profile by a novel crystal growth method combining an ES and a low vapor pressure liquid thin film.

4. Conclusions

Characteristic of molecular doping for thin film organic single crystal was investigated using novel crystal growth method combining a low vapor pressure liquid as crystal growth field and electrospray as solute supply method. DCM doping to PBD single crystal were achieved at lower growth rate condition than certain threshold value. In-plane steep control of doping profile was demonstrated. This method is applicable to various organic single crystals and is expected to contribute to the progress of organic optoelectronic device technologies.

Acknowledgements

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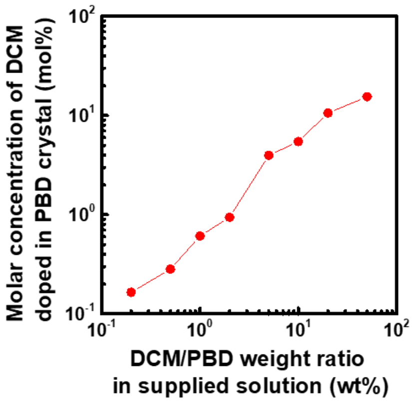

Fig. 2 Relationship between DCM concentration in supplied solution and doping concentration in PBD crystal.

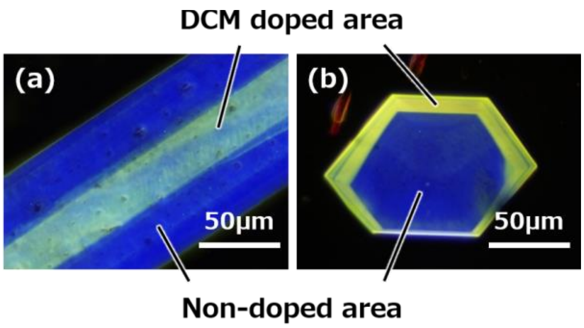

Fig.3 Fluorescence microscopy images of typical crystals precipitated at ITO substrate surface after spraying DCM concentration 5.0 wt% solution and DCM-free solution.

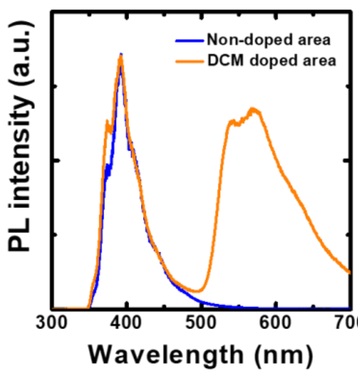

Fig. 4 PL spectra of non-doped area and DCM doped area of a PBD thin film single crystal.