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Inkjet printing of small-molecule semiconductor thin films for high-performance organic transistors

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1. Introduction

Printed electronics is now regarded as a realistic paradigm for manufacturing large-area and flexible electronics devices by the patterned application of active electronic components. Among a variety of active semiconducting materials, organic semiconductors are most promising for the use into the printing processes because of the solution processability at ambient temperature. However, it is widely recognized that the high crystallinity of small-molecule organic semiconducting materials, that is indispensable for realizing high carrier mobility, might be incompatible with conventional printing processes, because their strong self-organizing nature prevents controlled thin-film formation.

Here we report novel inkjet-printing (IJP) technique to manufacture small-molecule-based organic semiconductor films having high crystallinity. By applying the method of antisolvent crystallization into the IJP process, we successfully controlled the formation of crystalline semiconductor films. In particular, we found that printed deposits of 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothio- phene form exceptionally uniform single-crystal films. We also show that the printed single-crystal films afford high-performance organic thin-film transistors whose mobility are much higher than the previous report for printed organic thin-film transistors, and can be comparable to the highest performance as obtained for organic single-crystal transistors.

2. Antisolvent-coupled inkjet printing

We applied the antisolvent crystallization into the microfluidic IJP processing through the use of the "double-shot" inkjet printing technique (DS-IJP) that had been developed to produce hardly-soluble charge-transfer (CT) compound films [1]. A solution of a semiconductor and an antisolvent for the semiconductor are utilized as the two kinds of inks, and are inkjet-printed individually at an arbitrary position to form microliquid intermixture between these inks on top of the substrates. A schematic illustration of the process is presented in Figure 1(a). We found that the optimized printing conditions provide supersaturated states within the microliquid droplet that undergo controlled formation of uniform single-crystalline or polycrystalline films. The essence of this method is in the temporal discrimination between solute crystallization and solvent evaporation within the microliquid. The ideal supersaturated state can be generated by adjusting the concentration and the solvent/antisolvent volume ratio as well as the substrate temperature, which enable the gradual growth of uniform thin films at the liquid-air interfaces. In addition, we found that the nucleation and the film growth direction within the droplets can be controlled through appropriate design of the droplet configuration which is shaped by the predefined hydrophilic area on substrate surfaces.

3. Inkjet-printed crystalline films

Figure 1(b) shows a microscope image of the obtained C_8-BTBT film. The observed stripe-like features with intervals of a few tens of micrometers can be ascribed to the step-and-terrace structure in C_8-BTBT films: Images of the film recorded by atomic-force microscopy (AFM) showed that the step height is about 2.6–2.8 nm which is consistent with the thickness of a molecular layer of C_8-BTBT. The films were also characterized by synchrotron radiated x-ray diffraction and polarized optical absorption spectra. From the results we conclude that the films are single-crystalline in nature with a long-range translational symmetry.

We fabricated thin-film transistors based on the C_8-BTBT single-crystal films with a top-contact/top-gate geometry, composed of Au films as the source and drain electrodes, and parylene C films as the gate dielectric layers. We found that the maximum mobility reached around 31 cm^2/Vs in the saturation regime, with the on/off current ratio of about 10^7. These values are much higher than the previous report for C_8-BTBT [3].

3. Conclusions

We developed a novel IJP technique to manufacture high-quality thin films of soluble organic semiconductors. Particularly, the method allows us to obtain exceptionally uniform single-crystal C_8-BTBT films which afford thin-film transistors presenting mobility as high as 31 cm^2/Vs. We also consider that the technique should be applicable to a broad class of functional soluble materials. Such a drop-on-demand, room-temperature and non-vacuum printing process of patterned high-performance films should be innovative to produce transistor arrays on top of plastic substrates, which are indispensable for realizing for large-area, light-weight, and flexible electronics products.

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References

[1] M. Hiraoka, T. Hasegawa et al., Adv. Mater. 19, 3248 (2007).
[2] T. Izawa et al., Adv. Mater. 20, 3388 (2008).
[3] T. Uemura et al., Appl. Phys. Express, 2, 111501 (2009).

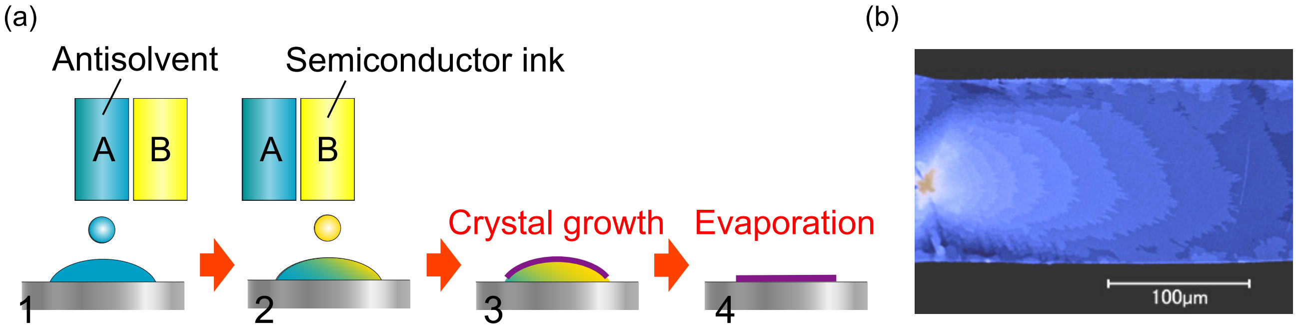

Figure 1. (a) Schematic representation of antisolvent-coupled inkjet printing process: 1, Antisolvent ink (A) is first inkjet-printed, and then 2, solution ink (B) is overprinted sequentially to form intermixed droplets. 3, Semiconducting thin films grow at liquid–air interfaces of the droplet, before 4, the solvent fully evaporates. (b) Micrograph of C_8-BTBT single-crystal thin film presenting stripes caused by molecular-layer steps.