Inkjet Printing of Single-Crystal Organic Semiconductors

We have developed a printing technology to manufacture single-crystalline organic semiconductor films. This "double-shot inkjet printing" method introduces a technique of antisolvent crystallization into the microfluidic inkjet printing processes. We found that the sequential deposition of an antisolvent and a semiconductor solution can trigger the controlled formation of exceptionally uniform thin films. The observed out-of-plane and in-plane Bragg diffractions clearly demonstrated the single crystal nature of the films. Using this approach, we obtained printed single-crystal organic transistors with very high carrier mobility.

Printing technology is usually used to reproduce characters or pictures such as photographs on paper by the patterned deposition of inks. However, the technology has recently attracted considerable attention in the field of electronics as a new way of manufacturing electronic products: fine electronic circuits could be produced, or printed, with micrometer resolution on a plastic sheet, and the technology would make electricity-hungry vacuum facilities unnecessary. In addition, the use of plastic sheets should lead to "flexible electronic" products which are light-weight, thin, and impact-resistant, revolutionizing the electronics industry. In order to realize such "printed electronics", the most important challenge is to produce high-performance thin-film transistors (TFTs), indispensable building blocks for large-area electronics products such as active-matrix flat panel displays, by a printing method.

In 2011, a new printing technology was successfully developed to produce single-crystal thin films of organic semiconductors with molecularly flat surfaces under ambient conditions [1]. The novel "double-shot inkjet printing" technique involves the alternating print deposition of microliquid droplets both of ink composed of a dissolved organic semiconductor and of another ink that prompts crystallization of the organic semiconductor. Figure 1 presents a schematic of this printing technique. The crystallization ink is first deposited from an inkjet head, and the semiconductor ink is then over-printed from another inkjet head to form an intermingled microliquid droplet. Here, C_8-BTBT (2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene) [2] was used as the organic semiconductor. A supersaturated state of the organic semiconductor is immediately formed in the intermingled droplet, which results in the slow film growth of the organic semiconductor at the liquid-air interface of the droplet. Particularly, it was found that by appropriately designing the deposited pattern on the sheets, the growth direction of the semiconductor layer could be controlled. Thus the technique allows the production of semiconductor thin films with highly uniform thickness at arbitrary positions reproducibly, which is extremely difficult to achieve by conventional printing techniques.

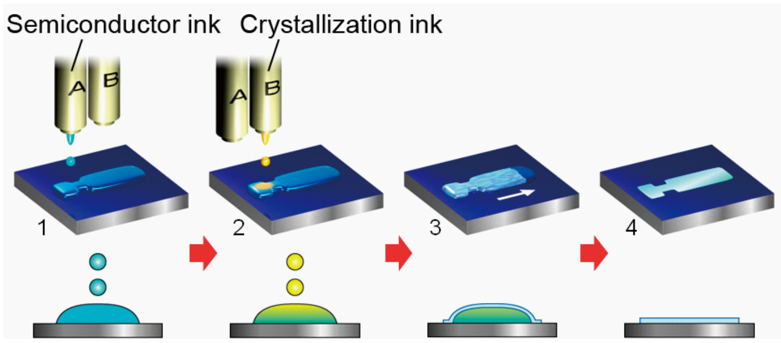

Figure 1
Schematic for producing semiconductor single-crystal thin films by the double-shot inkjet printing technique [1].

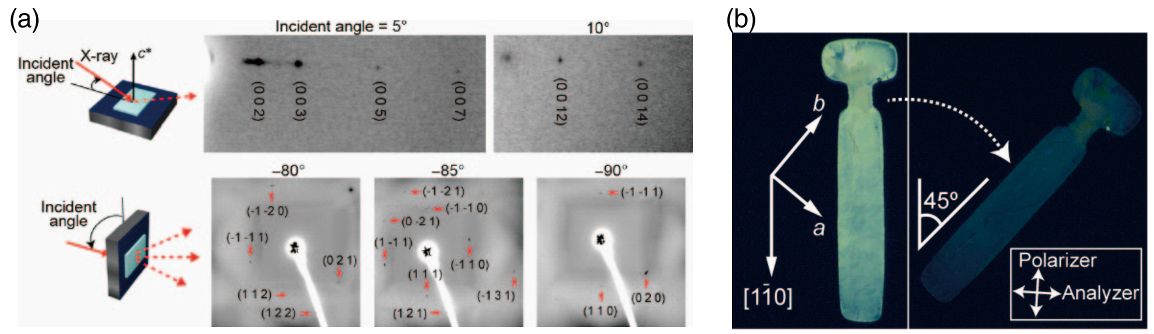

Figure 2
(a) Synchrotron X-ray oscillation photographs of the organic semiconductor single-crystal thin films. Out-of-plane (upper) and in-plane diffractions (lower), (b) Crossed-Nicols polarized micrographs for the organic semiconductor single-crystal thin films [1].

The single crystal nature of the films was investigated by synchrotron X-ray diffraction at the Photon Factory of KEK. It was found that all the diffractions were observed as clear spots [Fig. 2(a)]. The observation of Bragg reflections up to the 14th order indicates that the films have a highly crystalline nature. At high incident angles of the X-rays, we observed 16 Bragg reflections including an in-plane component. The refined unit cell based on the analyses of the observed diffractions is consistent with that of C_8-BTBT. The films were also investigated by a crossed-Nicols microscope. It was found that the color of almost the entire film uniformly changes from bright to dark when the film was rotated around an axis perpendicular to the film surface [Fig. 2(b)]. This indicates that the whole film is uniformly optically anisotropic. From these results we conclude that the inkjet-printed semiconductor thin films are composed of single-domain crystals. Organic TFTs composed of the inkjet-printed C_8-BTBT single crystal films exhibit high mobility reaching as high as 16.4 cm^2/Vs on average. The on/off current ratio is larger than 10^5, and the sub-threshold slope is about 2 V per decade. The mobility value is more than 10 times higher than that of amorphous silicon TFTs which are used in conventional liquid-crystal displays, and 100 times as high as that of organic TFTs produced by the conventional printing methods.

The newly-developed double-shot inkjet printing technique will be useful for manufacturing organic semiconductor thin films with high uniformity and for improving the performance of the TFTs, which have been major challenges in the printed electronics technology. This technology will greatly accelerate the research and development of flexible electronic devices.

REFERENCES

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