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Stable growth of large-area single crystalline thin films from an organic semiconductor/polymer blend solution for high-mobility organic field-effect transistors

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ABSTRACT

We developed an effective and steady solution-processing technique for a small molecule–type semiconductor, **C_{10}–DNBDT–NW**, by adding an amorphous **PMMA** polymer to produce stable growth of a two-dimensional large-area single-crystalline thin film by effective phase separation at a crucially faster processing speed compared to the case without the addition of a polymer. By using this solution-processing technique, it is noteworthy that the single-crystalline films of **C_{10}–DNBDT–NW/PMMA** exhibit the highest and average mobilities of 17 and 10.6 cm^2/Vs, respectively. Furthermore, we also show the limitations of two-dimensional continuous growth of a single-crystalline film in terms of the solution technique.

1. Introduction

A major challenge in printed electronics technology is reproducibly building homogeneous large-area organic semiconductor thin films with charge carrier mobilities. Such technology will have a dramatic effect; it should open novel electronics markets based on organic field-effect transistors (OFETs), which are anticipated to be next-generation low-cost, flexible, light-weight, and large-area switching electronic components [1–5]. Consequently, reliable solution-processing techniques are highly desired toward high-speed device applications such as radio-frequency identification (RF-ID) tags and gate-driver circuits of active matrices necessary for fully flexible displays [6].

Among the various solution-processing techniques, one of the most common in the field of organic electronics is the spin-coating method, which can easily form thin films. However, spin-coating has some drawbacks; one is that a large amount of compounds is required because most of the semiconductor solution is spun-out and wasted. Another is that the polycrystalline films are randomly ordered in a radial fashion from the center area because organic semiconductors rapidly crystallize. These limitations result in a poor carrier mobility compared to the intrinsic mobility of organic semiconductors due to the inevitable crystal boundaries and interfacial traps, which are crucial for a high carrier mobility [7,8].

To reduce the amount of required materials and to grow crystalline thin films without grain boundaries, several recent approaches have focused on the development of promising solution processing techniques such as the double inkjet method [9] and the solution-shearing method [10] to grow single crystalline thin films with ordered and grain boundary-less natures [11]. These works have demonstrated the intrinsic high carrier mobility of organic semiconductors compared to less ordered cases. Our research group has developed a simple and easy solution-processing technique with minimal materials called the "*edge-casting* method" [12]. In our method, material thin films are prepared from a solution, including a semiconductor in the controlled direction using

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the edge structure, resulting in a highly uniform and highly crystallized single crystalline thin film that exhibits an intrinsic carrier mobility.

Very recently, we developed a continuous growth method of single crystalline thin films by the edge-casting method, called "*continuous edge-casting* method", toward practical large-area device applications [13]. Employing this method, we obtained a highly ordered inch-sized single crystalline film using a high performance 3,11-didecyldinaphtho[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (**C_{10}–DNBDT–NW**) organic semiconductor [14]. We also demonstrated transistor arrays with 25 transistors where the average carrier mobility reached 7.5 cm^2/Vs, indicating that the device performance is suitable for high-speed logic circuit applications [13]. However, this method has some drawbacks because single crystalline thin films are only obtained under optimal growth conditions in the representative parameters of the *concentration of organic semiconductor solution*, *substrate moving speed*, and *substrate temperature*, as illustrated in Fig. 1a. The difficulty in controlling single-crystal growth of small molecule–type compounds from a solution due to natural phenomenon has motivated us not only to develop more reliable and reproducible solution-processing techniques, but also to clarify the size limitations for growing large-area and high-quality single-crystalline films suitable for high-speed organic semiconductors TFTs using low-cost and high-throughput large-area printing.

Fig. 1a illustrates the concept of the continuous edge-casting method [13]. It has the following steps: 1) the semiconductor solution is supplied to the edge of the solution holding a blade. Simultaneously, the substrate on a hot plate at a certain temperature is moved toward the other side of the solution supply, which is depicted with an arrow. 2) The crystal nucleus emerges from the area of the contact line and then the crystalline film grows gradually to form an inch-sized single-crystalline film.

The most appropriate speed to form a smooth single-crystalline thin film of **C_{10}–DNBDT–NW** is reported to be 30 μm/s. A faster processing speed results in poor ordering and discontinuous single-crystalline thin films as described in Table 1 (the pictures of the upper row). The result indicates that single-crystalline thin films spread two-dimensionally due to a very narrow processing window in the reported processing conditions. Because a subtle change in the growth conditions has a drastic impact on film morphology, it is essential to maintain the appropriate processing conditions.

The formation of the poor ordering and a discontinuous single-crystalline thin film at a faster speed prompted us to investigate the mechanism of crystal growth in the continuous edge-casting method from the viewpoints of "*crystal growth*" and "*substrate moving*" using three cases. In case (1), crystal growth and the substrate move at the same speeds to realize single-crystalline film grow continuously and two-dimensionally. In case (2), crystal growth has a faster speed and the solution sticks to the crystals grown on the substrate. In case (3), the substrate moves faster, preventing the semiconductor solution from sticking to the crystals, and the shape of the solution in the contact region starts deforming, as illustrated in Fig. 1b. Consequently, in case (3), the contact line slips and the shape of the meniscus relaxes into a more stable shape, and the crystals stick again. Due to the well-known "slip-and-stick" movement of the contact line in faster growth conditions, poor ordering and discontinuous films are formed. Such details of the contact line movement and the nature of the solution deposition of nanoparticle assemblies have been reported [15,16].

To overcome such problems and eliminate the slip-and-stick movement of the contact line, we envisioned that adding a polymer would increase the viscosity of the semiconductor solution. In order not to impact the growth of the single-crystalline thin film or alter the charge-transport characteristics of organic semiconductors at the interface, we selected an amorphous, polar, and insulating polymer, whose physical properties differ from commonly designed organic semiconductors composed of a robust highly extended π-electron core and non-polar flexible long alkyl chains. As a result, the slip-and-stick movement of the contact line

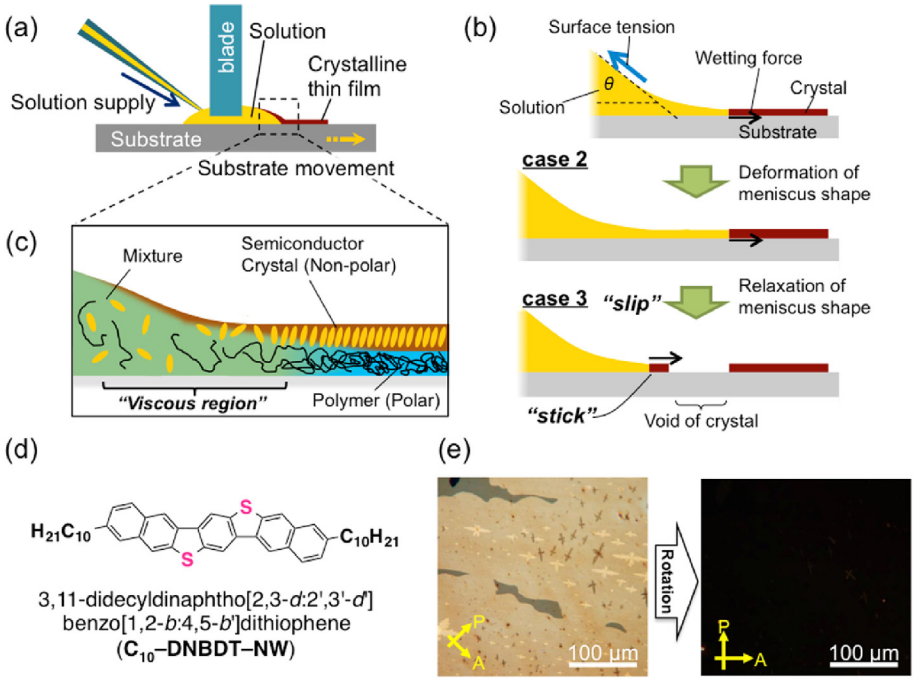

Fig. 1. (a) Schematics of the continuous edge-casting method. (b) Schematics of the growth instability. (c) Magnified figure of the contact region describing the mechanism of crystal-growth stabilization with a polymer additive. (d) Molecular structure of **C_{10}–DNBDT–NW**. (e) Cross-polarized optical microscopic picture of the thin film grown from a polymer/semiconductor blend solution. Crystalline thin film is grown at a speed of 80 μm/s.