

Simple Push-coating for High-Performance Polymer Thin-Film Transistors

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1. Introduction

The solution processability of organic semiconductor materials is a crucial advantage in the industrial application of organic electronic devices, because the solution processing under ambient conditions should permit the low-cost production of large-area, light-weight, and flexible electronic products. In the processes, the solvent affinity with substrate surfaces plays a crucial role. For example, it is known that the use of spin coating becomes increasingly difficult as the hydrophobicity of the substrate surface increases, since the solution is readily lost before the film can grow [1]. In addition, it is necessary for the complete film fabrication on that substrate to use low surface tension solvents or some surfactant in order to decrease surface tension energy of the solution. Meanwhile, it has been shown that the use of highly hydrophobic gate dielectrics and high boiling-point solvent improve various device characteristics of thin-film transistors (TFTs), such as the mobility and the current–voltage (IV) hysteresis [2,3,4].

Here, we report a novel technique for manufacturing thin films of organic semiconductor, which we call “push coating”. The process is applicable to highly hydrophobic substrate surfaces and a wide variety of solvents. It is found that the technique allows us to produce highly crystalline poly(3-hexylthiophene) (P3HT) and poly(2,5-bis(3-hexadecylthiophene-2-yl)thieno[3,2-b]thiophene)(PB16TTT) films that afford high performance TFTs[5,6,7].

2. Experimental

We prepared P3HT semiconductor material with a molecular weight of 71 kDa, a polydispersity index of 1.67, and a regioregularity of 96% by purifying the commercially available product (Merck Co., Ltd.) through Soxhlet extraction with hexane and dichloromethane. The purified polymer was dissolved in 1,2,4-trichlorobenzene (TCB) to give a 0.1 wt% solution. The PB16TTT with a molecular weight of 38 kDa, a polydispersity index of 1.98 (Merck Co., Ltd.) were used without further purification. The PB16TTT was dissolved in 1,2-dichlorobenzene (DCB) to give a 0.25wt% solution. The substrate consisted of *n*-doped silicon with a 300-nm-thick thermally grown layer of SiO₂. Before formation of the semiconductor film, patterned source and drain electrodes consisting of a 30-nm-thick layer of Au evaporated onto a 5-nm-thick lay-

er of Cr were manufactured by photolithography. The SiO₂ surface was thoroughly cleaned by wet and dry techniques, and then rendered highly hydrophobic by treatment with a silane coupling agent [hexamethyldisilazane (HMDS) or trichloro(octyl)silane (OTS-8) or trichloro(octadecyl)silane (OTS-18)].

The push coating technique is illustrated schematically in Figure 1. In this process, a 1-mm-thick stamp of PDMS elastomer [8] is used to squeeze a droplet of the semiconductor solution so that the solution spreads over the SiO₂ surface. The amount of solution that we used was as little as 35 μ L for a substrate with an area of 20 \times 25 mm. The

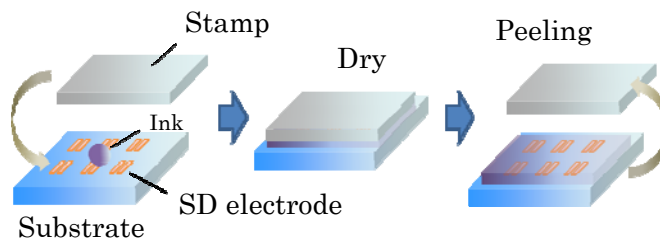


Fig. 1. Schematic of the push coating technique

stamp adhered uniformly and closely to the substrate surface so that a thin layer of solution formed between the stamp and the substrate. The assembly was annealed for several minutes, during which time the solvent was slowly absorbed by the PDMS stamp. Finally, the stamp was peeled off, leaving the polymer film adhering to the substrate. The stamp was swollen as a result of absorption of the solvent. Finally, all the P3HT films were annealed at 423K for ten minutes and then at 438K for five minutes and all the PB16TTT films were annealed at 373K for five minutes and then at 418K for twenty minutes on a hotplate under an atmosphere of N₂.

3. Results and Discussions

The out-of-plane X-ray diffraction (XRD) profiles were measured for both the push-coated and spin-coated P3HT films, and the results are shown in Figure 2. We found that the (100) peak intensity for the push-coated film was stronger than that for the spin-coated films. In addition, the full width of half-maximum of the peak for the push-coated films was narrower than that for the spin-coated films. These results clearly show that the push-coated films had a

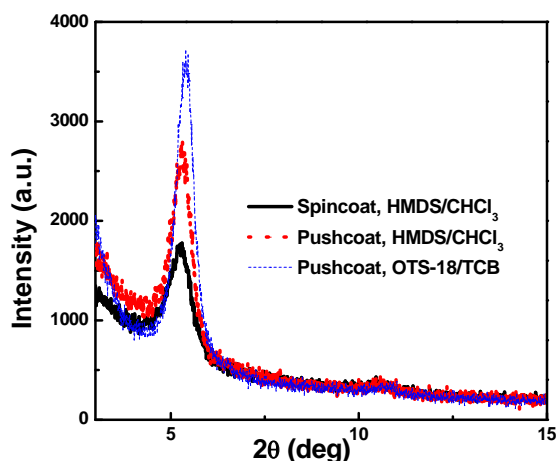


Fig. 2. XRD patterns of the push-coated and spin-coated P3HT films

greater crystallinity than the spin-coated films.

Figure 3 shows the transfer (I_D - V_G) characteristics of the push-coated and spin-coated P3HT films. The mobility of the P3HT TFTs fabricated by push coating was estimated to be $0.50 \text{ cm}^2/\text{Vs}$, which was ten times as high as that of the TFTs fabricated by spin coating. We concluded that this improvement can be ascribed to the greater crystallinity of the push-coated P3HT films [9]. Similarly, the mobility of the push-coated PB16TTT TFTs rose to $0.60 \text{ cm}^2/\text{Vs}$.

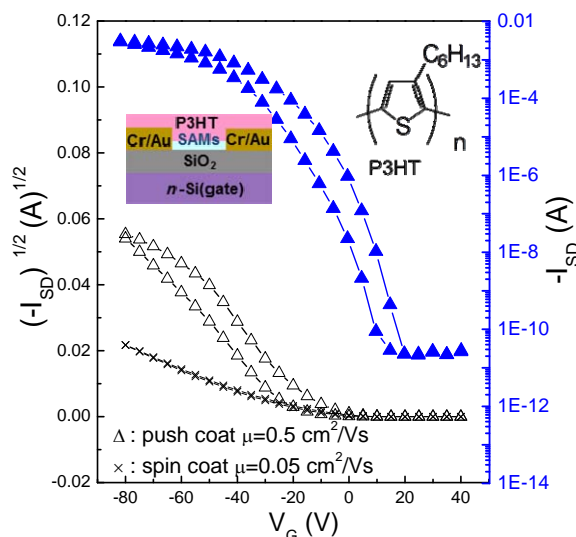


Fig. 3. Transfer characteristics of the push-coated and spin-coated P3HT TFT

4. CONCLUSION

We successfully prepared high-performance polymer TFTs exhibiting a mobility as high as $0.50 \text{ cm}^2/\text{Vs}$ by means of a simple push-coating technique. The technique uses a tiny volume of a solution of a semiconductor that is compressed by a PDMS elastomeric stamp to form a thin layer of solution confined between the stamp and the substrate. Because of the swelling of PDMS, the stamp can be

easily peeled off from the films. Since many kinds of solvent including high boiling point solvents were utilizable on highly hydrophobic surface in the method, we can fabricate the highly-crystalline films easily compared to conventional solution processes.

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