Nano-imprinting technology applied in pentacene films

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ABSTRACT

Charged carrier transport efficiency and patterned issues in organic semiconductors (OSCs) limit the potential of organic devices toward nanoscale microelectronic and optoelectronic applications. We demonstrate high-performance organic field-effect transistors (OFETs) with mobility of near 2.5 cm^2/Vs using a nanogroove gate-dielectrics accomplished by nanoimprinting technology. Meanwhile, the flow of charged carriers in OFETs prefers parallel the nanogrooves to result in high electrical anisotropic ratio (above 200), thus achieving built-in auto pattern OSC function with nanoscale resolution. In this study, we also investigate the impact of nanostructural surface properties in relation to the mechanism of the pentacene growth, the polymorphism of the pentacene films. Interestingly, the polymorphism transported from the thin-film phase to the bulk phase is significantly affected by the width of the PI-nanogrooves.

Keywords: pentacene, OFETs, naonoimprinting, nanostructure, polymorphism

1 INTRODUCTION

An electronics revolution using a new class of materials commonly known as organic semiconductors (OSCs) has become possible in this century. The enormous progress in this field has been driven by the expectation of new applications of organic/polymeric nanostructures in microelectronics and optoelectronics, which have now demonstrated a high potential for high-performance devices (e.g., diodes, transistors, switches, and solar cells), especially nanoscale devices.[1] Since the OSCs are integrated into nanostructures, the possibilities of the organic devices being scaled down in size to nanometer range can be realized. Scaling down the size of electronic devices requires advanced methods of patterning. However, many nanolithographic approaches for patterning inorganic materials are severe for OSCs, so OSCs are patterned with difficulty for submicron or deep-submicron processes.[2]

Organic semiconductor-based thin-film devices hold the promise of flexible displays, thin-film solar cells, and inexpensive organic electronics, but patterning of OSCs in integrated circuits is a serious issue.[3] In this study, we show a nanogroove substrate achieved with nanoimprinting technology to realize a high performance organic field-effect transistor (OFET, field-effect mobility near 2.5 cm^2/Vs) with high anisotropy of charge transport (i.e., the mobility ratio between the parallel and perpendicular to the nanogrooves is above 200), which were outstanding compared with other reports in the literature.[4, 5] This study also investigates the impact of nanostructural surface properties in relation to the mechanism of the pentacene growth, the polymorphism of the pentacene films, and the electrical characteristics of OFETs. Furthermore, the mechanism of carrier transport in the OFETs on the nanostructal substrate is explained using a barrier model. This nanoimprinting technology can be used to develop advanced nanoscale and lithography-free patterning of organic devices.

2 EXPERIMENT

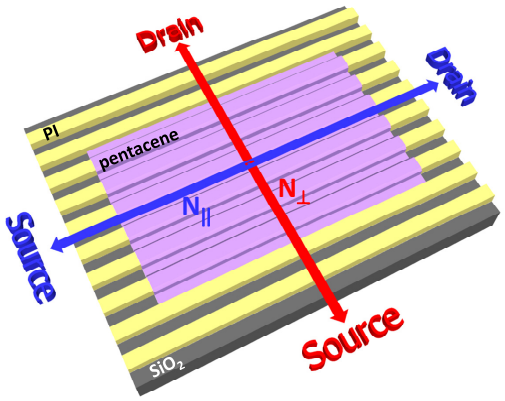

Fig. 1 Schechmatic diagram of OTFT with nanogrooves. Symbol $N_{||}$: I_{DS} parallel to the nanogrooves; $N_{\perp}$: I_{DS} perpendicular to the nanogrooves

In this study, the CMEL[6] imprinting technology was used to fabricate the nanogroove. Figure 1 shows the sketch of OFET device. A chromium (Cr) coated silicon mold was prepared for the nanoimprinting processes. Four periods of nanogrooves (800, 1200, 1600, and 2400 nm) are used in this study and the ratio of ridge to trench in the nanogrooves was approximately 1. Starting from a 100-nm-thick polyimide (PI) film acting as both the modification and aligned layer, a sacrificial layer, polymethylmethacrylate (PMMA) film, was spun on the PI layer. A loading force was applied for a few minutes to imprint the mold into the PMMA layer. After baking, the PMMA film was hardened during the imprinting process.

Separating the mold from the substrate, Cr-gratings was embedded in the PMMA layer to function as an etching mask. After reactive ion etching (RIE) and releasing the PMMA layer, the PI-nanogrooves were formed. A 60-nm-thick pentacene film was deposited on the PI-nanogroove substrate at a deposition rate of approximately 0.2 Å/s through a shadow mask. Finally, the Ag source and drain electrodes were deposited on the top of the pentacene film to completely form an OFET.

3 DISSCUSSIONS

Figure 2(a) shows output characteristics of pentacene-based OFETs: $N_{\parallel}$, $N_{\perp}$, and control (pentacene film was grown on native SiO_2) devices. Obviously, the drain current (I_D) of $N_{\parallel}$ device is 7- and 75-fold than that of SiO_2 and $N_{\perp}$ device, respectively. It is believed that the PI layer modified the interface between organic material (pentacene film) and inorganic material (SiO_2 dielectric); furthermore, the PI-nanogrooves affected the current flow of $N_{\parallel}$ device and $N_{\perp}$ device. The current flow is parallel to the electric field of source-drain ($\vec{E}_{SD}$) in the $N_{\parallel}$ device; however, in the $N_{\perp}$ device, the current flow is perpendicular to $\vec{E}_{SD}$ when carriers transfer across the sidewall of nanogrooves. This distinction influence the different mobility between $N_{\parallel}$ device and $N_{\perp}$ device. The $N_{\parallel}$ device with a 1600-nm-perodic PI-nanogrooves had the highest carrier mobility about 2.45 cm^2/Vs. Fig. 2(b) shows the mobility anisotropic ratio of OFETs with periods of PI-nanogrooves. The carrier mobilities of $N_{\perp}$ device with various periodic nanogrooves are similar, so that the $N_{\parallel}$ device with a 1600-nm-perodic PI-nanogrooves has the highest anisotropic ratio about 225.

It is believed that the bulk phase structure has high electronic coupling between adjacent pentacene molecules; thus, widely recognized that the carrier transport properties of the bulk phase are better than those of the thin-film phase.[7, 8] Therefore, considerable attention has been placed on the control of the pentacene polymorphism transformation from the thin-film phase to the bulk phase for improving the carrier mobility (μ) of OFETs.[9-12] The past study also indicated that the bulk phase of the pentacene film is a more stable phase than the thin-film phase because the bulk phase having a lower binding energy than the thin-film phase. However, thin-film phase dominated the polymorphism of pentacene film when pentacene film was grown on a plane surface.

In previous studies, the thin-film phase dominated the polymorphs at the early stage of growth.[13] Carrier transport properties, however, depend on the first few layers of pentacene films. Transforming the thin-film phase to the bulk phase in the first few layers is expected to improve the electrical characteristics. In usually, deposition substrate temperature or solvent exposure are usually used to control the polymorphs of pentacene film.[10, 14] Although the bulk phase forms with a large thickness, it does not efficiently influence the electrical characteristics. In the present study, PI-nanogrooves was used to control the polymorphism of pentacene film to induce the bulk phase to form in the early stage of growth. Mayer *et al.* reported using a rough surface to induce the bulk phase growth at the early stage.[15] Here, the PI-nanogrooves was used as a rough surface to restrict the diffusion of pentacene molecules, inducing three-dimensional growth.[14]

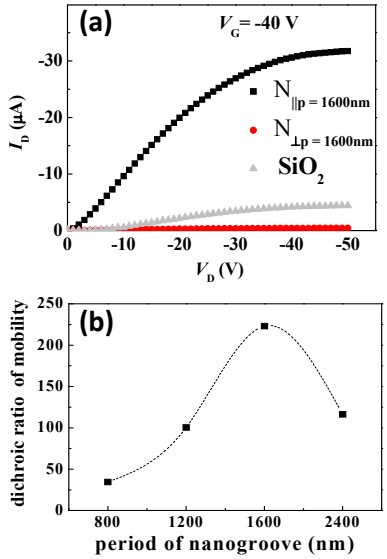

Fig. 2 (a) The output electrical characteristics of OFETs grown on 1600-nm-perodic PI-nanogrooves and SiO_2 substrate. (b) mobility anisotropic ratios of OFETs versus period of the PI-nanogrooves

In this investigation, the pentacene polymorphism transfered from thin-film phase to bulk phase as the period of PI-nanogrooves decreasing. In the previous reports,[7] the electrical performances and stability of pentacene film with the stable bulk phase are believed superior to that with metastable thin-film phase. It is interesting that there is anisotropism of phases in the sample with the PI-nanogrooves. Accordingly, the phase of the pentacene film can be controlled by varying the period of the PI-nanogrooves.

Figure 3 shows the XRD spectrum of pentacene film grown on the 1600-nm-perodic PI-nanogrooves. Obviously, the XRD spectrum is different from the pentacene film grown on flat surface.[13] The thin-film phase is the dominated phase of pentacene film grown on flat surface. However, the bulk phase dominated the polymorphism of the pentacene filme grown on a 1600-nm-perodic PI-nanogrooves. The XRD spectra of pentacene film grown on PI-nanogrooves with various film thickness from 6.2 to 60 nm is shown in inset of Fig. 3. The thin-film phase and the bulk phase can be observed vaguely in the 20 nm thick film; however, the thin-film phase and the bulk phase were

clearly observed when the film thickness was 40 nm. Interestingly, the proportion of the bulk phase to the thin-film phase increased with increasing thickness. The past investigations indicates that the bulk phase dominated the polymorphism above a thick thickness 100nm. In our study, the bulk phase become the dominated phae at a thickness of 50 nm. We believe that the PI-nanogrooves provided a driving force, similar to substrate heating or solvent treatment providing a perturbation, which induce that the phase formation of bulk phase. The geometry, which pentacene film grown on, effect the formation of pentacene polymorphism.

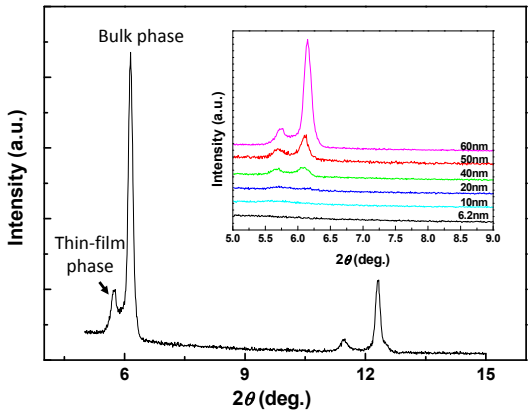

Fig. 3 XRD spectrum of pentacene film grown on the 1600-nm-perodic PI-nanogrooves. The inset is XRD spectra of pentacene films with various thicknesses grown on the 1600-nm-perodic PI-nanogrooves.

4 CONCLUSIONS

In summary, the dielectric with PI-nanogrooves is applied to grow multiple polymorphous pentacene films and successfully demonstrated a high performance and electrically dichroic OFET with the PI-nanogrooves. The morphology of nanogrooves not only achieves anisotropic characteristics in the electrical properties of OFETs but also controls the polymorph of pentacene films. The anisotropic electrical characteristics have a potential effect on circuit design—for example, to isolate neighboring components without a large spatial separation. Furthermore, an organic active layer would no longer require patterning during the manufacturing process. It is expected that the same conclusions can be held true for other organic semiconductors.

We used substrate geometry to transform the polymorphism of pentacene film from a metastable thin-film phase to a stable bulk phase. PI-nanogrooves provided a perturbation that induced the bulk phase to form in the early stage of pentacene film growth. Both the thin-film phase and bulk phase formed in the early stage of pentacene film growth, which has not been observed in the investigations, indicating that the polymorphisms of pentacene films depend not only on the film thickness and the substrate temperature, but also on the surface morphology. Accordingly, the surface geometry of the dielectrics can induce the pentacene molecules to form a stable polymorph.

REFERENCES

[1] Lyshevski, S.E., ed. "Nano and Molecular Electronics Handbook (Nano- and Microscience, Engineering, Technology, and Medicine Series)." CRC Press, 2007,

[2] Afzali, A., C.D. Dimitrakopoulos, and T.O. Graham, "Photosensitive pentacene precursor: Synthesis, photothermal patterning, and application in thin-film transistors," Advanced Materials, 15**,** 2066, 2003.

[3] Nabok, A., ed. "Organic and Inorganic Nanostructures." Artech House, 2005,

[4] Kang, S.J., Y.Y. Noh, K.J. Baeg, J. Ghim, J.H. Park, D.Y. Kim, J.S. Kim, J.H. Park, and K. Cho, "Effect of rubbed polyimide layer on the field-effect mobility in pentacene thin-film transistors," Applied Physics Letters, 92**,** 052107, 2008.

[5] Chou, W.Y. and H.L. Cheng, "An orientation-controlled pentacene film aligned by photoaligned polyimide for organic thin-film transistor applications," Advanced Functional Materials, 14**,** 811, 2004.

[6] Lee, Y.C. and C.Y. Chiu, "Micro-/nano-lithography based on the contact transfer of thin film and mask embedded etching," Journal of Micromechanics and Microengineering, 18**,** 075013, 2008.

[7] Coropceanu, V., J. Cornil, D.A. da Silva, Y. Olivier, R. Silbey, and J.L. Bredas, "Charge transport in organic semiconductors," Chemical Reviews, 107**,** 926, 2007.

[8] Cornil, J., J.P. Calbert, and J.L. Bredas, "Electronic structure of the pentacene single crystal: Relation to transport properties," Journal of the American Chemical Society, 123**,** 1250, 2001.

[9] Ji, T., S. Jung, and V.K. Varadan, "On the correlation of postannealing induced phase transition in pentacene with carrier transport," Organic Electronics, 9**,** 895, 2008.

[10] Gundlach, D.J., T.N. Jackson, D.G. Schlom, and S.F. Nelson, "Solvent-induced phase transition in thermally evaporated pentacene films," Applied Physics Letters, 74**,** 3302, 1999.

[11] Kakudate, T., N. Yoshimoto, and Y. Saito, "Polymorphism in pentacene thin films on SiO2 substrate," Applied Physics Letters, 90**,** 081903, 2007.

[12] Kang, S.J., M. Noh, D.S. Park, H.J. Kim, C.N. Whang, and C.H. Chang, "Influence of postannealing on polycrystalline pentacene thin film transistor," Journal of Applied Physics, 95**,** 2293, 2004.

[13] Bouchoms, I.P.M., W.A. Schoonveld, J. Vrijmoeth, and T.M. Klapwijk, "Morphology identification of the thin film phases of vacuum evaporated pentacene on SIO2 substrates," Synthetic Metals, 104**,** 175, 1999.

[14] Steudel, S., D. Janssen, S. Verlaak, J. Genoe, and P. Heremans, "Patterned growth of pentacene," Applied Physics Letters, 85**,** 5550, 2004.
[15] Mayer, A.C., A. Kazimirov, and G.G. Malliaras, "Dynamics of bimodal growth in pentacene thin films," Physical Review Letters, 97**,** 105503, 2006.