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Oriented Growth of Sexithiophene Induced by Edge of Metal Electrodes

Susumu Ikeda[1], Yasuo Wada[2] and Koichiro Saiki[3]

[1] Graduate School of Science, Tohoku University, 6-3 Aza-Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8578, Japan
Phone: +81-90-6544-6728 E-mail: sikeda@m.tains.tohoku.ac.jp
[2] Graduate School of Interdisciplinary New Science, Toyo University, 2100 Kujirai, Kawagoe, Saitama 350-8585, Japan
[3] Department of Complexity Science and Engineering, Graduate School of Frontier Sciences,
The University of Tokyo, Kashiwanoha 5-1-5, Kashiwa, Chiba 277-8561, Japan

1. Introduction

Organic semiconductors have attracted much attention as promising materials for future electronic devices due to their flexibility, low energy, cheap production costs, and large area applications. Organic light-emitting diodes are already in practical use, and current research and development focus on organic thin film transistors (OTFTs) [1]. Since organic thin films generally grow as randomly oriented polycrystalline films, grain boundary resistance associated with misorientation angle between grains decreases the carrier mobility of OTFTs [2]. Thus, mobility is predicted to increase if the oriented growth of organic thin films can be achieved. One of the ways to obtain the oriented films is epitaxial growth. However, epitaxial growth is generally difficult because amorphous insulators such as thermally-oxidized Si are used as the substrates. Some techniques for oriented growth have been proposed, for example, the use of friction-transferred polymer films [3] or photo-aligned polyimide films [4,5] covering the surface of amorphous substrates as the templates of preferred orientation. Recently, we have shown that graphoepitaxy [6] of the small molecular weight organic semiconductor α-sexithiophene (6T; $C_{24}H_{14}S_6$) occurs on thermally-oxidized Si surface with the artificial periodic microgrooves fabricated by electron beam lithography [7]. We also found that the orientation of graphoepitaxy can be controlled by simple surface treatment [8] and graphoepitaxy can contribute to reduction of the grain boundary resistance [9]. Here, we report the new experimental results using the same concept of graphoepitaxy. We evaluated the possibility that the edge of the metal electrodes induces the oriented growth, same as the periodic microgrooves do. In this study, metal electrodes with narrow channel (2 μm) were fabricated. This channel length is smaller than the average size of 6T grains. If the graphoepitaxy is induced by the metal electrodes, it is expected that "oriented single grains" fill the narrow channel, leading to improvement of the carrier mobility.

2. Experiments

Electrodes

Au electrodes were fabricated on thermally oxidized Si substrates by photolithography. Cr (20 nm in thickness) was deposited prior to Au (30 nm in thickness) deposition. The channel length between source and drain electrodes was 2 μm and channel width was 3 mm. Surface of the substrates was cleaned by acetone, methanol and pure water and finally by UV/ozone treatment before loading them into a vacuum chamber.

Film growth

As a source material, 6T powder was purchased from the Aldrich Chemical Co. and was further purified by the vacuum sublimation technique. The 6T thin films were grown by molecular beam deposition (MBD) using a Knudsen cell under ultrahigh vacuum conditions ($1\text{-}3\times10^{-7}$ Pa). The substrate was kept at 110°C and 6T (35 nm in thickness) was deposited at a growth rate of 0.13 nm/min.

3. Results and discussion

Film structure

We observed the films using an atomic force microscope (AFM). Chain-like structure composed of oriented 6T grains was formed (Fig. 1). This connected structure can be seen only within the limited area along the channel as shown in Fig. 1(b). Thus, it is evident that the chain-like structure first nucleated in the channel or at the edge of the electrodes and grew spreading to both sides on source and drain electrodes. Although the data is rather qualitative, the *b*-axis directions of the connected 6T grains tend to be perpendicular to the channel as shown in Fig. 1(a). This probably indicates that oriented growth of 6T grains was induced by the edge of the metal electrodes. The orientation relationship between *b*-axis of 6T and the edge is similar to the graphoepitaxy using the periodic microgrooves treated by HMDS (hydrophobic condition) reported in our recent work [8]. Chemical affinity of Au for S atoms of 6T molecules presumably causes this configuration.

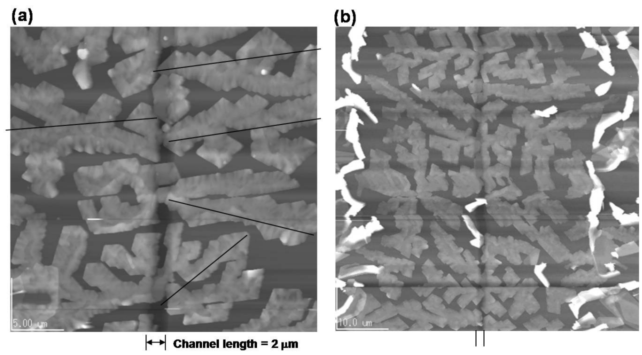

Fig. 1 AFM images around the narrow channel. (a) Area of 30 μm × 30 μm. Lines show *b*-axis directions of the connected 6T grains. (b) Wider 60 μm × 60 μm area.

Chwang and Frisbie [2, 10] showed the grain growth of 6T around Au electrodes and succeeded in making the single grain and double grain field effect transistors (FETs). Although the 6T grains seem to have grown from the Au electrodes, the authors did not mention the orientation relationship between 6T and the electrode shape.

Xu et al. have reported similar oriented growth of pentacene [11]. They fabricated a planarized bottom contact TFT with source and drain electrodes embedded in the dielectric layer, and succeeded in improving the carrier mobility. They made hollows on the thermally oxidized surface of Si substrates. In the hollows Pt/Cr electrodes were deposited as the surface level of the silicon substrate and electrodes was just the same. Finally they grew the pentacene film on the substrate by MBD. AFM observation revealed that pentacene began to grow from the crevice existing around the electrodes and spread over the channel region with preferred orientation. Our result in the present study is similar to their data. However, their conclusion is that the oriented growth was induced by the edge of the crevice of SiO_2 side, not the metal electrode. Therefore our experimental result, oriented growth induced by the edge of metal electrodes, is probably a new finding. If the orientation of organic thin films can be controlled by the electrodes, new design of device configuration might be possible by taking such effect into account.

FET characteristics

We measured FET characteristics of the device (the same sample shown in Fig. 1). Fig. 2 shows the output and transfer characteristics of the device. The estimated mobility was 1.2×10^{-4} cm^2/Vs (V_{th} ~ +3 V) and not so high. However, this low mobility is due to the fact that the channel is not filled with the 6T grains as shown in Fig. 1. The effective channel width is less than 10 % of the whole channel width (3 mm). Therefore, actual mobility of the 6T grains is higher, probably ranging from 10^{-2} to 10^{-3} cm^2/Vs. Based on these data, if the channel can be filled with the oriented grains induced by the edge of the electrodes, the improvement of the mobility is hoped for.

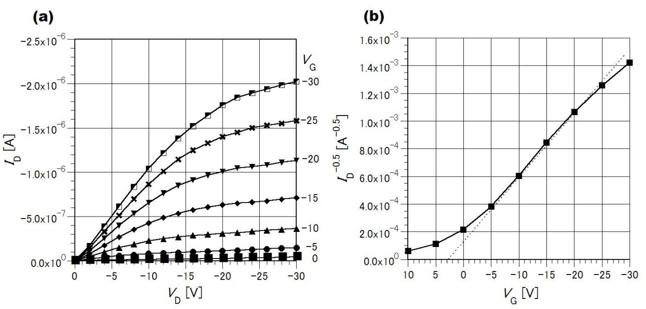

Fig. 2 (a) Output characteristics and (b) transfer characteristics of the 6T-TFT.

3. Conclusions

In this study, we showed the possibility of oriented growth of organic semiconductors induced by the edge of metal electrodes. This phenomenon is probably associated with the interaction between organic molecules and wall of the metal electrode edge. For the combination of 6T and Au electrodes, {010} planes of 6T crystals tend to face the Au wall probably owing to the chemical affinity of Au for S atoms of 6T molecules. Depending on the crystal structure of 6T (molecules are inclined in the unit cell), the probability of contact between Au and S atoms becomes high when the {010} planes of 6T crystals face the Au wall. If such oriented growth is applicable to OTFT devices, the fabrication process could be much simplified compared to the conventional graphoepitaxy requiring the microfabrication technique of the substrate surface.

Acknowledgements

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