Extended Abstracts of the 2018 International Conference on Solid State Devices and Materials, Tokyo, 2018, pp691-692

Growth Mechanism and Electrical Characterization of DPh-DNTT Films Prepared by Vacuum Deposition

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Abstract

The growth mechanism of Diphenyl-Dinaphthothienothiophene (DPh-DNTT) thin films on SiO_2 synthesized by vacuum evaporation was investigated. In particular, we focused on the influence of SiO_2 surface and substrate temepratures on the growth. Initially, the two-dimensional islands formed and grew laterally. Subsequent layers formed similarly in layer-by-layer growth mode. The nucleation density for the first layer decreases with incease in substrate temperature. Also, UV-O_3 or oxygen plasma surface treatment leaded to decrease in the nucleation density. In addtion, we characterized the top-contact field-effect transistors (FETs) to evaluate the synthesized films.

1. Introduction

Recently, DPh-DNTT has been receiving much attention as a novel organic material for organic transistors because of its high mobility and stability [1]. Vacuum deposition is a primary method for preparation of an organic thin film. However, the influence of deposition condition on the growth mechanism or crystallinity has not been clarified yet. Especially, the growth at initial or final stage is important for applications, since the interface between gate insulator and organic film dominates charge transport in FETs.

In this study, we investigated the growth mechanism of DPh-DNTT thin films at substrate temperatures (T_s) of 160–185 °C on a thermally grown SiO_2 synthesized by vacuum evaporation. The surface of SiO_2 was modified by some methods for comparison. In addition, the top-contact FETs were characterized to evaluate the synthesized films.

2. Experiment

The vacuum evaporation was conducted at ~2×10^{-4} Pa with a deposition rate of 0.05 Å/s which was measured by a quartz crystal microbalance (QCM). A thickness of film in a processing was measured by a QCM as nominal film thickness. A highly doped Si (100) wafers having thermally grown SiO_2 with a thickness of 40 or 90 nm was used as a substrate for deposition. To examine the influence of the surface conditions, the four kinds of the surface treatments were applied. (A) Acetone/IPA, the substrates were cleaned by sonication in acetone for 10 min, followed by cleaning in isopropyl alcohol (IPA) for 10 min. (B) UV-O_3, after the acetone/IPA cleaning, the substrates were exposed to UV-O_3 for 30 min. (C) Oxygen plasma, after the acetone/IPA cleaning, the substrates were exposed to oxygen plasma for 120 s. (D) HMDS, after the acetone/IPA cleaning, followed by exposing UV-O_3 for 15 min, the substrates were exposed to in hexamethyldisilazane (HMDS) vapor at 120 °C for 1 hour. After finishing these surface treatments, the substrates were immediately mounted in the evaporation chamber. Before starting deposition, the substrates were heated and kept at a target temperature more than 20 min for degas and a thermal equilibrium. The synthesized thin films were observed by an optical microscope and an atomic force microscopy (AFM) with tapping mode. For electrical characterization, Au electrodes with a thickness of 45 nm were deposited through a stencil metal mask on the DPh-DNTT film by vacuum evaporation. The channel length and width in top-contact FETs are 80 µm and 1000 µm, respectively.

3. Nucleation and growth

The optical dark-field microscopy image and AFM images in Fig. 1(a–c) shows the evolution of growth at 160 °C on acetone/IPA substrate for a nominal film thickness of 1.2 nm (a, b) and 3.5 nm (c), respectively. From the AFM image, the two-dimensional (2D) islands with a height of 2.3 nm were observed on the surface. The value of the height is close to the length in the long molecular axis of DPh-DNTT. This indicates that the molecules stand nearly in perpendicular to the substrate. The height for Fig. 1(c) is almost the same as that for Fig. 1(b) and the area covered with 2D islands for Fig. 1(c) is larger than that for Fig. 1(c). This suggests that the 2D islands isotopically grow in lateral direction without new nucleation. In other word, the nucleation density in Fig.1 (b) was almost saturated. In addition, it is possible that the re-evapo-

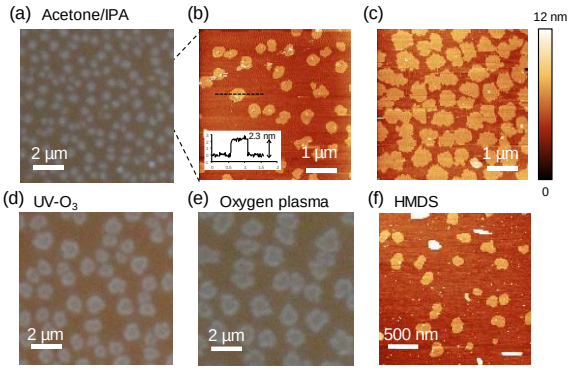

Fig. 1 Optical microscopic and AFM images for a nominal film thickness of 1.2 nm (a, b, d–f) and 2.4 nm (c) synthesized on UV-O_3 (d), Oxygen plasma (e), HMDS (f) substrate. Color bar applies to all AFM images.

ration occurred in the growth process since the source sufficient for formation of the first layer has been provided. In fact, the T_s adopted in this study is close to the upper limit temperature (~190 °C) to form a film.

Figure 1(d–f) shows the nucleation for different surface treatments, which are comparable to Fig.1(a). UV-O_3 or oxygen plasma treatment provides the large 2D islands. By contrast, the area of 2D islands for HMDS treatment is small. The nucleation density for each surface treatment is shown in Fig. 2 as a function of the inverse substrate temperature. The nucleation density decreases with increase in the substrate temperature, resulting formation of large area grain. Since the plot of log(N) versus $1/T_s$ is on a straight line, the nucleation density is expressed by Arrhenius's equation $1/N=A\exp(E/kT_s)$ [2]. Where, A and E are constants, and k is Boltzmann's constant.

Next, the growth mechanism on the first layer is discussed. Fig. 3 shows the optical bright-field microscope and AFM images for the film with a nominal film thickness of 25 nm, which was deposited on the UV-O_3 substrate at 160 °C. The color contrast in the optical image has been enhanced strongly by image processing. These figures show the formation of flat 2D islands with fractal shape on the top surface. This suggests that molecules continue stacking on the top and grow in the same manner after the first layer growth. Note that a similar morphology was observed in the different surface treatments. The observed morphology is quite different from a well-studied pentacene thin film, in which the mounds form on the surface [3]. Therefore, the flat DPh-DNTT film is appropriate for an organic semiconductor film for top-gate FETs.

The shape and the nucleation density of those on the top are different as compared with the 2D islands for the first layer. This is because formation of 2D islands depends on interaction with materials of under layer. Although the first layer grows on the SiO_2, the subsequent layers grow on the DPh-DNTT film. The influence of substrate on the formation of the first layer has been investigated using pentacene film [4]. Interestingly, similar 2D islands with a fractal-shape which was observed in the study forms on reactive substrate

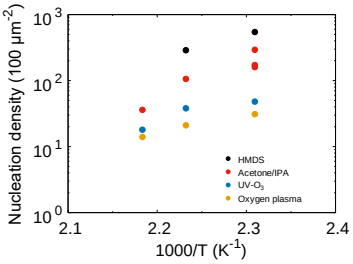

Fig. 2 Nucleation density depended on the surface treatments.

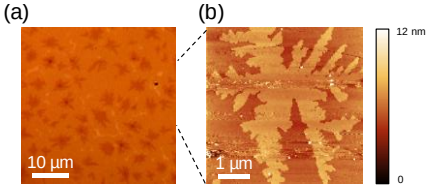

Fig. 3 Optical microscopic (a) and AFM (b) images for the surface of the 25-nm film synthesized on UV-O_3 substrate at 160 °C.

such as Si(001) and don't form on inert substrate such as oxide or polymeric material. Therefore, it is possible that the interaction of (DPh-DNTT)-(DPh-DNTT) are stronger than that of (DPh-DNTT)-SiO_2 in present case. The possibility causes the difference of the 2D islands.

4. Electrical characterization of top-contact FET

The 25-nm films which were synthesized on 40-nm SiO_2 (83 nF/cm^2) at 160 °C were evaluated in bottom-gate top-contact FETs. Figure 4(a) shows drain current (I_d) versus gate voltage (V_g) characteristics for the different surface treatments. The mobilities in the saturation regime are summarized in Fig. 4(b), which shows that mobilities get higher when the grain size of the first layer becomes small. Although the increase of grain boundary generally causes decrease of mobility in FETs, our results are inconsistent. The discrepancy might be related to the degree of coalescence of each grain in the first layer. Inadequate connection between grains interrupts charge transport. In fact, the nucleation of the second layer was observed before the first layer has not been completed. These experimental evidence and discussions suggest that the nucleation of first layer affects directly the performance of FETs.

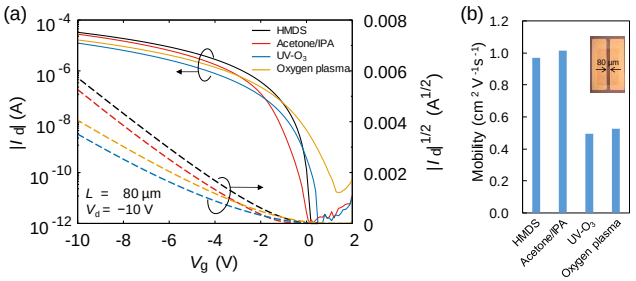

Fig. 4 Transfer characteristics of a DPh-DNTT FETs (a) for various surface treatments and calculated mobilities in the saturation regime (b).

5. Conclusions

The DPh-DNTT thin film grows in layer-by-layer mode, which process can be observed easily by an optical microscope. The size of grain in the first layer increases with increasing the substrate temperature and use of UV-O_3 or oxygen plasma surface treatment. However, to improve the performance of FETs, not only the study on the grain size but also the detail study on the transport properties of the interface between grains is required.

Acknowledgements

This work was partly supported by a Leading Initiative for Excellent Young Researchers program from the MEXT in Japan. The authors would like to thank Nippon Kayaku Co., Ltd. for supplying us DPh-DNTT.

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