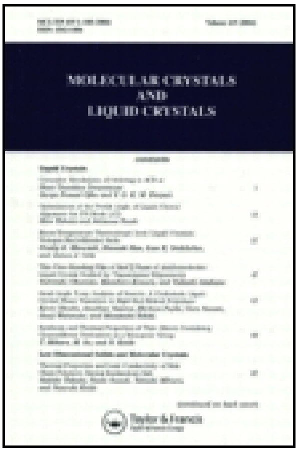

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GROWTH OF CO–EVAPORATED TTF–TCNQ FILMS ON SURFACE MODIFIED SUBSTRATES

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Abstract TTF–TCNQ co–evaporated films were fabricated on variously surface–modified substrates and the structural investigation was carried out by scanning electron microscope and X–ray diffraction measurements. It was indicated that the molecular orientation was controllable on a properly modified substrate by chosing an evaporation condition. Furthermore, the selective growth of the TTF–TCNQ film was achieved on the surface–modified substrate using a standard photolithographic technique.

INTRODUCTION

A number of organic materials have unique electrical and optical properties owing to the anisotropic structures of the composed molecules and they are expected as new materials for molecular electronic devices. In order to apply the properties derived from their anisotropic structures to molecular electronic devices, it is necessary to prepare highly oriented thin films of them. In general, the orientation of the film is strongly influenced by surface treatments of substrate and deposition parameters.[1-3] Therefore, it is important to control molecular–molecular or molecular–substrate surface interactions for the molecular orientation. For the promising technique, vacuum evaporations on several organic buffer layers were reported.[4,5] For example, tetracyanoquinodimethane (TCNQ) evaporated film show a different orientation by existence of the cadmium stearate buffer layer.[4] In other case, long and narrow grains aligned in a single orientation are observed in the tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) film co–evaporated on the poly(tetrafluoroethylene) (PTFE) buffer layer,[5] which was prepared by rubbing a substrate surface whose temperature was kept at 130°C in a single direction with a PTFE solid bar.[6] However, the precise mechanism of molecular orientations on the surface–modified substrates is unknown.

In this paper, we prepared TTF–TCNQ co–evaporated films on the Si substrates on which various grooves were artificially formed and investigated the molecular orien–

tation of them.

EXPERIMENTAL

We have prepared four types of surface–modified substrates (see Figure 1). The first type was prepared by rubbing the surface of a Si substrate in a single direction with an abrasive which had submicron–size particles (type–I). It had straight–line grooves and their widths were 0.1–1μm. The second type was a posi–type photoresist film (OFPR–800; Tokyo Ohka Kogyo) spin–coated onto a SiO_2 film (100nm thickness) formed Si(100) wafer (type–II). Other two types were prepared by a standard photolithographic technique on a SiO_2 film (100nm thickness) formed Si(100) wafer. The third type was 2μm, 5μm and 10μm line & space resist patterns formed SiO_2/Si substrate (type–III). The fourth type was line & space patterns formed SiO_2/Si substrate (type–IV), which was produced by etching the SiO_2 and removing the resist layer of the type III substrate.

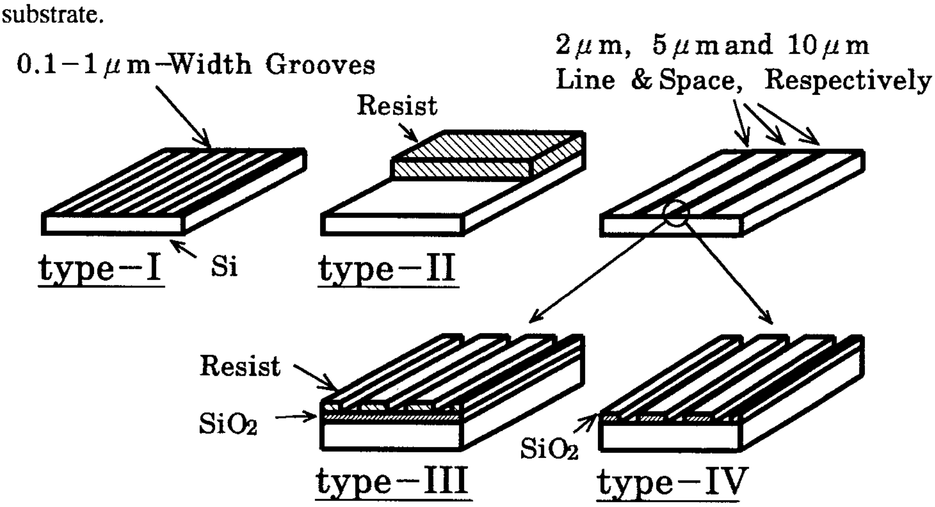

FIGURE 1 Surface–modified substrates used in this study.

TTF–TCNQ films, about 100nm thick, were deposited by co–evaporation technique at a base pressure of $1x10^{-5}$ Torr. TTF and TCNQ were sublimed from two crucibles whose temperatures were controlled at 57°C and 115°C, respectively, and TTF–TCNQ charge–transfer (CT) complex was formed on the substrate surface. The molecular structures of TTF and TCNQ and the crystal structure of TTF–TCNQ CT complex are shown in Figure 2 (a) and (b), respectively. The preliminary study revealed that slightly TTF–rich films were obtained at the substrate temperature of below 30°C. Three samples kept at different temperatures, 24°C, 31°C and 36°C, were

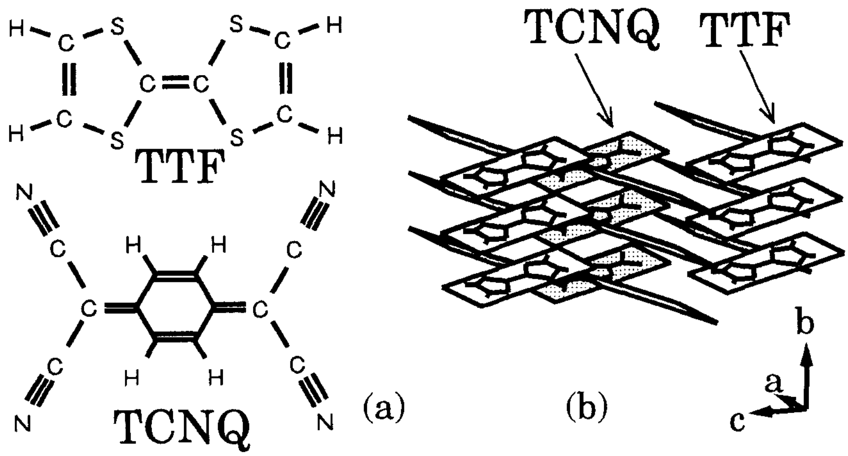

FIGURE 2 (a) Molecular structures of TTF and TCNQ, (b) crystal structure of TTF–TCNQ single crystal.

fabricated at a same time.

The structural investigation of the films was carried out by scanning electron microscope (SEM) and X–ray diffraction (XRD) measurements.

RESULTS AND DISCUSSION

1. Growth on the Groove–Formed Surface (type–I)

The SEM photographs of the TTF–TCNQ films grown at 24°C, 31°C and 36°C on the type–I substrate are shown in Figure 3 (a), (b) and (c), respectively. All the samples show that long and narrow grains selectively grow in the normal direction to the sub–

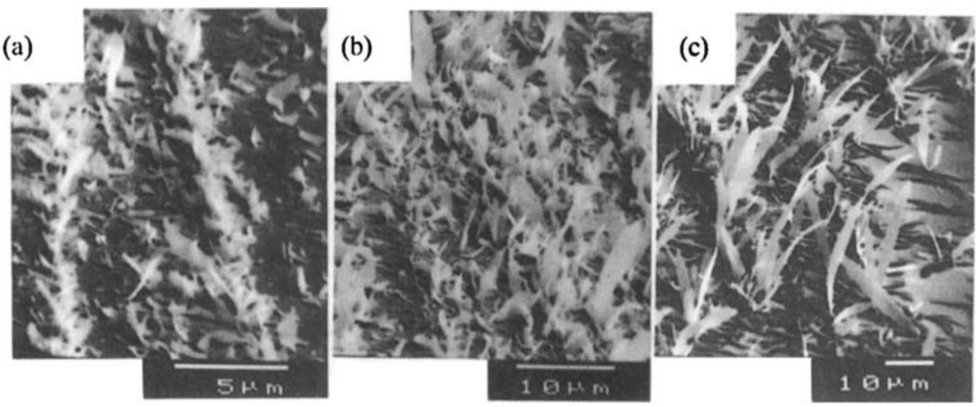

FIGURE 3 SEM photographs of the TTF–TCNQ films grown at (a) 24°C, (b) 31°C and (c) 36°C on the type–I substrate, respectively.

strate surface (normal grains) from grooves and the flat substrate surface is covered by the flat layer composed of grains that grow in the lateral direction to the surface (lateral grains). Especially, the film grown at 36°C is just like crops growing in a field. As the migration of the molecules in the surface becomes more active at higher substrate temperatures, normal grains grow larger up to 30μm at 36°C. The formation process of normal grains is considered as follows. TTF and TCNQ molecules evaporated on the substrate migrate on the surface and a nucleation occurs at a groove where both molecules are easy to adsorb and form the CT complex compared with a flat surface. Furthermore, molecules that come one after another climb the nucleus and the grains grow upward. Although the growth mode of normal grains depends on the molar ratio of TTF to TCNQ (TTF/TCNQ ratio), growth temperature and the growth rate, etc., it is not yet clear which factor is most effective for the growth mode in the present stage.

2. Growth on the Photoresist Film (type–II)

TTF–TCNQ film was co–evaporated on the photoresist coated Si substrate. The SEM photograph shown in Figure 4 displays the border between the resist film and the etched Si substrate. Normal grains exist both on the resist film and on the Si substrate. However, it seems most of grains show normal orientation on the resist film while the flat layer (lateral grains) exists among normal grains on the Si. Figure 5 shows XRD patterns of them. While only peaks from (00n) plane of the TTF–TCNQ complex are seen in the part of TTF–TCNQ/Si, no peak appears in the part of TTF–TCNQ/resist. On the other hand, clear peaks (00n) are observed in TTF–TCNQ films without normal grains that is grown on the SiO_2/Si substrates at higher temperature. Therefore the TTF–TCNQ/resist has

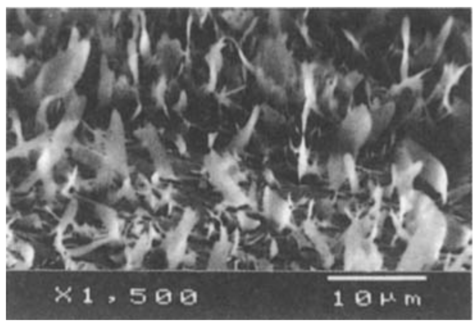

FIGURE 4 SEM photograph of the border between the resist film and the etched Si of the type–II substrate.

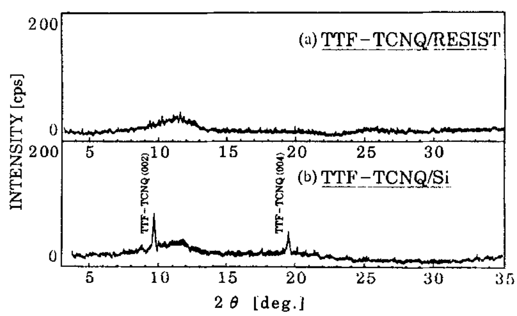

FIGURE 5 XRD patterns of (a) TTF–TCNQ/resist and (b) TTF–TCNQ/Si, respectively.

few lateral grains in which the c*-axis of TTF–TCNQ is normal to the substrate surface. This result indicates that the resist film has an effect to generate the nucleation for normal grains. Since both the surfaces of the resist film and the etched Si are flat according to the high-resolution SEM observation, it is not considered that normal growth is caused by the surface roughness. The growth of the nucleus in the normal direction may relate to a strong interaction between TTF–TCNQ molecules and dangling bonds (or irregular termination) of the Si surface or radicals of the resist film.

3. Growth on the Resist (Line) & SiO_2 (Space) Pattern (type–III)

The SEM photograph of the TTF–TCNQ film co-evaporated on the type–III substrate is shown in Figure 6. Normal grains grow selectively on the resist layers and lateral grains cover all over the SiO_2 layers. This is the one example giving a possibility to achieve the selective growth of the organic material, that is, the normal growth and the lateral growth are controllable on a same substrate. We varied the width of the line & space, 2μm, 5μm and 10μm, but, remarkable difference was not observed. These results of Figure 4 and 6 indicate that the migration length of molecules at this condition is larger than 5μm.

4. Growth on the SiO_2 (Line) & Si (Space) Pattern (type–IV)

The SEM photograph of the TTF–TCNQ film co-evaporated on the type–IV substrate is shown in Figure 7. Lateral grains cover all over the substrate surface regardless of existence of the SiO_2 grooves. Some normal grains grow at the step between the SiO_2 and Si layers. In spite of the resemble sample configuration between the type–I and type–IV substrates, they show the different orientation. It seems to be due to the sharpness of the step by the fabrication process.

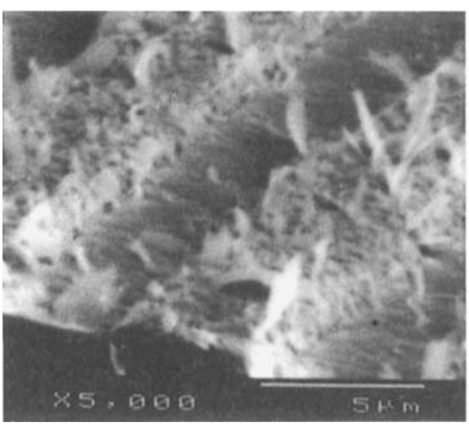

FIGURE 6 SEM photograph of the film grown on the type–III substrate.

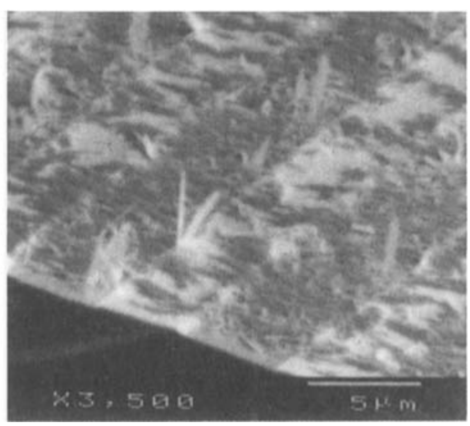

FIGURE 7 SEM photograph of the film grown on the type–IV substrate.

CONCLUSION

We have investigate the possibility for controlling the molecular orientation the Si substrate on which grooves were artificially formed. TTF-TCNQ films were co-evaporated onto the variously surface modified substrate, i.e., the substrate on which submicron to 10μm-width grooves were artificially formed. Long and narrow grains of TTF-TCNQ selectively grew in the normal direction to the substrate surface from the edge of grooves or on the resist film. Therefore, these results demonstrate the control of the molecular orientation is possible by evaporation in a proper condition onto an artificially modified substrate.

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