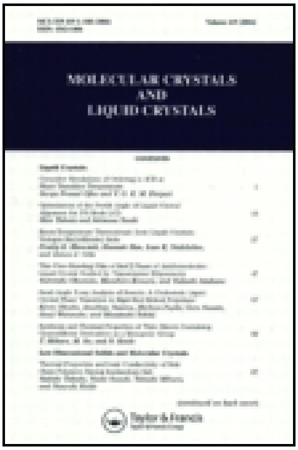

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Effect of Several Organic Buffer Layers on TTF-TCNQ Epitaxial Growth

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EFFECT OF SEVERAL ORGANIC BUFFER LAYERS ON TTF–TCNQ EPITAXIAL GROWTH

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Abstract The orientations of TTF–TCNQ films co–evaporated onto several kinds of organic buffer layers were investigated. The c^*–axis of TTF–TCNQ was normal to the substrates. However, the direction of the b–axis was random on CaF_2 and cadmium–stearate LB film deposited CaF_2 substrates. The b–axis of TTF–TCNQ evaporated on polytetrafluoroethylene (PTFE) rubbing layer arranged across the rubbing direction, but the film contained many grooves due to PTFE rubbing. TTF–TCNQ films on calcium–stearate/PTFE buffer layer had flat surface, even though the degree of the b–axis orientation was not high.

Introduction

The preparation of highly–oriented organic thin films by the vapor phase deposition is one of the important techniques for organic electronic device applications. The molecular orientation and the anisotropy of the organic thin films result in unique electronic and optical properties. A single crystal of TTF–TCNQ which is well known as a one–dimensional conductor shows a highly anisotropic electrical conductivity. The electrical conductivity along the stacking axis (b–axis) is 2 or 3 orders of magnitude higher than that of a– or c^*–axis[1–3]. If the TTF–TCNQ thin film with the b–axis arranged along a single direction in the sample surface is obtained, it will be useful to apply to the electronic devices. In general, the molecular orientation of the evaporated film strongly depends on the surface condition of the substrate. From this point of view, surface modifications of the substrate by physical and/or chemical methods are important. Thus,the introduction of organic buffer layers on the inorganic substrate is a promising technique to arrange the functional molecules in the desirable manner.

The molecular orientation in the surface direction has not obtained on the glass substrate. Even on the alkali halide substrates such as KCl, bioriented micro-grains were observed[4]. Therefore, it is necessary to introduce some treatments of the substrate surface in order to align the b-axis of TTF-TCNQ in the same direction. One of the promising techniques is to introduce well-oriented organic buffer layers such as Langmuir-Blodgett (LB) films[5,6], rubbing polymer films[7], evaporated organic films[8], etc.

Experimental

We have prepared three types of organic buffer layers on the calcium fluoride (CaF_2) substrates as shown in Fig. 1. CaF_2 substrates were used to evaluate the molecular orientation using infrared absorption measurements. First type is 5-monolayer cadmium-stearate (St-Cd) LB film deposited by a conventional vertical dipping technique and they have the Y-type structure. Second type is polytetrafluoroethylene (PTFE) layer rubbed onto the CaF_2 substrate kept at 130°C. PTFE layer was prepared by a same manner as reported by Wittmann et al.[7]. Highly-oriented PTFE layer was obtained in the rubbing direction, but the PTFE surface was rather rough due to the rubbing by force. As shown later, many grooves with various heights along the rubbing direction were observed in SEM images. Third type is two-layered organic buffer film consists of St-Ca/PTFE. The main aim of this type is to prevent the surface roughness and defects. The St-Ca layer is chosen to reduce the surface roughness without losing the highly-orientation of PTFE layer. Schematic diagram of molecular structure of St-Ca is shown in Fig. 1. It is known that the fatty acids like St-Ca exhibit two possible molecular orientations, the normal growth and the lateral growth, by changing substrate

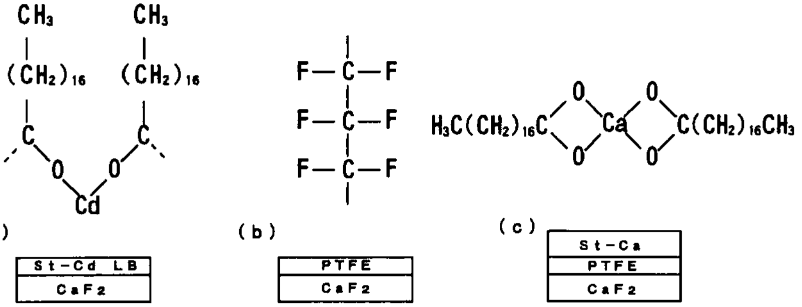


Fig. 1 The structures of the organic buffer layers and the chemical structures of the materials used as buffer layers.

materials, substrate temperature and growth rate during the evaporation[9]. We prepared the St–Ca buffer layers by evaporation to establish the lateral growth.

Onto these organic buffer layers, TTF–TCNQ thin films were deposited by using a co–evaporation technique in vacuum around 10^{-5} Torr. Schematic diagram of the co–evaporation system is shown in Fig. 2. TTF and TCNQ were sublimed from two crucibles and these temperatures were controlled independently. Substrate temperature during evaporation was room temperature and deposition rate was about 70nm/hr. The film thickness was about 200nm.

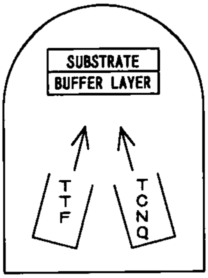


Fig. 2 Schematic diagram of co–evaporation system for TTF–TCNQ growth.

We investigated the molecular orientation of those samples by X–ray diffraction (XRD), scanning electron microscope (SEM) and Fourier–transform infrared absorption (FT–IR), including infrared reflection absorption spectroscopy (RAS). For RAS measurements, Au/Cr coated glass substrates were used. The wavenumber region of FT–IR measurement was from 4000 to 1000 cm^{-1}.

Results and Discussion

I. St–Ca buffer layer

First, we describe the molecular orientation of St–Ca buffer layers to help a clear understanding of TTF–TCNQ thin films. XRD patterns of St–Ca evaporated films on (a) glass substrate and (b) PTFE layer are shown in Fig. 3. As the diffraction planes shown in the figure, XRD peaks observed at low angle region $2\theta<7°$ and those at higher angle region $2\theta>21°$ correspond to the normal growth and the lateral growth of St–Ca, respectively. XRD results indicate that the lateral growth exist dominantly in the St–Ca film on PTFE layer, while the normal growth is dominant on glass substrate.

SEM images of St–Ca evaporated films on (a) glass substrate and (b) PTFE layer are shown in Fig. 4. We could see the rod–like images in both SEM images. According to the results by Yase et al.[9], these rod–like images correspond to the domains of the lateral growth. XRD patterns and SEM images indicate that the lateral growth of St–Ca is dominant on the PTFE layer. Furthermore, the lateral growth arranged in the single direction is observed only on the PTFE layer and the direction of long domains is perpendicular to the PTFE chains (rubbing direction).

Schematic view of the molecular arrangements for the normal growth and the lateral growth is shown in Fig. 3. Since St–Ca molecules have an anisotropic growth due to the interaction between the long-chain of the molecules, the lateral growth region tends to extend in the longitudinal direction against the long-chain of St–Ca molecule. Therefore, rod-like micrograins in Fig. 4(b) are formed on the substrate surface.

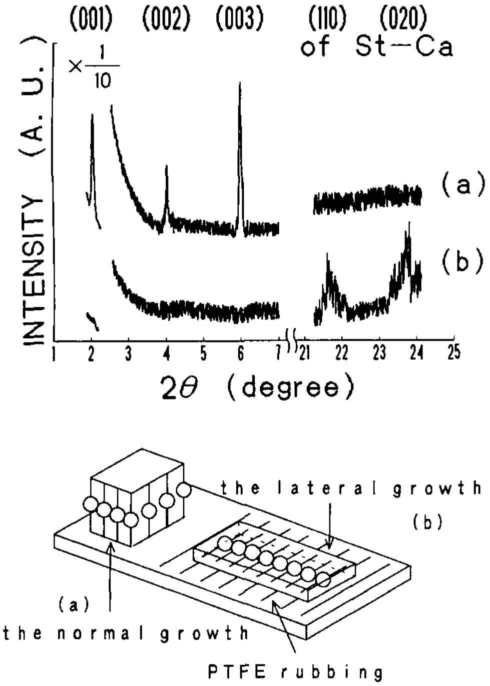
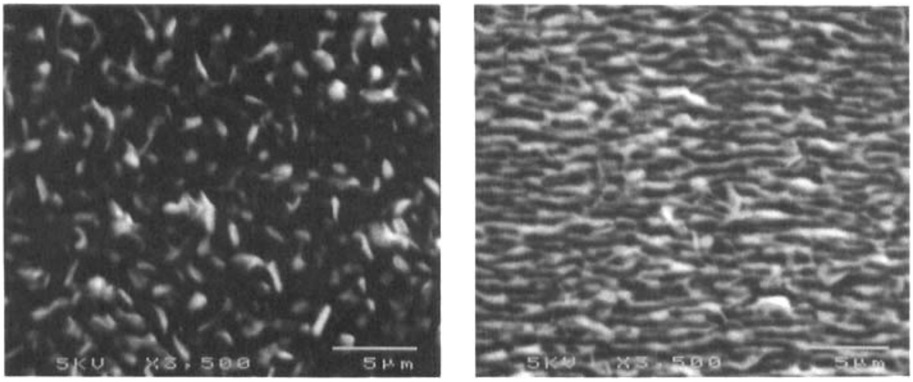


Fig. 3 XRD patterns of St–Ca films and the schematic diagram of the molecular arrangements on (a) glass substrate and (b) PTFE layer.



(a) On glass substrate (b) On PTFE layer

Fig. 4 SEM images of St–Ca evaporated films.

II. TTF-TCNQ co-evaporated films

XRD pattern of TTF-TCNQ/CaF$_2$ sample is shown in Fig. 5. Only peaks from (00n) plane are seen. This result indicates that the c*-axis of TTF-TCNQ is normal to the substrate surface. Fig. 6 shows FT-IR spectra, (a) transmission spectra of TTF-TCNQ/CaF$_2$ and (b) RA spectra of TTF-TCNQ/Au/Cr /glass. Intensity of the peak around 2200 cm^{-1} which is assigned to the C≡N stretching mode is large in the RA spectra compared with the transmission spectra. It indicates that TCNQ molecules are rather standing against the surface. The FT-IR results also indicate that the c*-axis of TTF-TCNQ is normal to the substrate. SEM image of the sample surface is shown in Fig. 7.

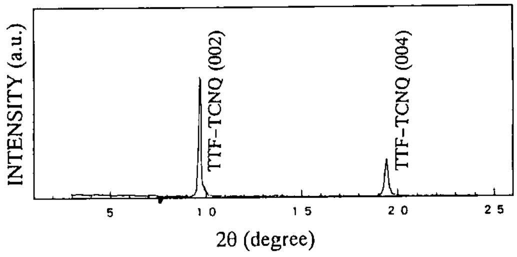


Fig. 5 XRD pattern of TTF-TCNQ/CaF$_2$.

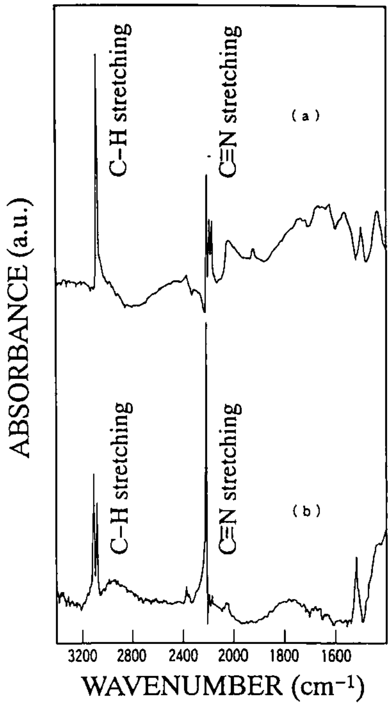


Fig. 6 FT-IR spectra, (a) transmission spectra of TTF-TCNQ/CaF$_2$ and (b) RA spectra of TTF-TCNQ/Au/Cr/glass.

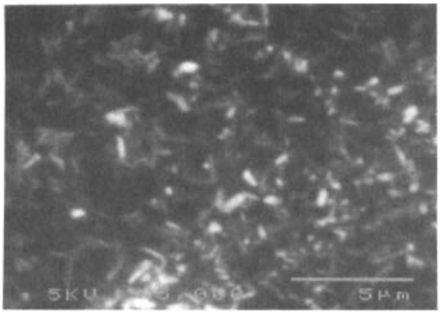


Fig. 7 SEM image of TTF-TCNQ/CaF$_2$.

The random network of the rod-like micro-grains along the b-axis of TTF-TCNQ crystal is observed in the SEM image. It is proved by these measurements that the c*-axis of TTF-TCNQ is controllable without any buffer layer, but the b-axis is random in the substrate surface.

XRD pattern and SEM image of TTF-TCNQ/St-Cd/CaF_2 are almost same as the TTF-TCNQ/CaF_2 sample. In the case of TCNQ evaporated film[6], the molecular orientation was strongly influenced by the St-Cd LB buffer layer, and the TCNQ molecular plane arranged to be parallel to the substrate by the introduction of St-Cd LB film. In the TTF-TCNQ films, however, the orientation of c*-axis is normal to the substrate and which is independent of the St-Cd buffer layer.

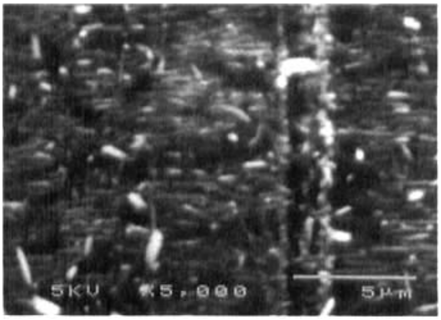


Fig. 8 SEM image of TTF-TCNQ/PTFE/CaF_2.

XRD results of TTF-TCNQ/PTFE/CaF_2 show almost the same patterns as TTF-TCNQ/CaF_2 sample. On the contrary, SEM image in Fig. 8 indicates that the rod-like TTF-TCNQ micro-grains arrange across the rubbing direction of PTFE. These results indicate that the b-axis of TTF-TCNQ arrange in perpendicular to PTFE chains. However, the grooves with about 2μm wide along the rubbing direction are observed in Fig. 8. This is probably due to the striped PTFE layer by rubbing. Thus, the TTF-TCNQ/PTFE has many defects and which may be a serious problem for applying to molecular electronic devices.

The grooves due to the PTFE rubbing were not observed all over the surface of TTF-TCNQ/St-Ca/PTFE/CaF_2 by SEM. It indicates that the flat surface was obtained by introducing the St-Ca buffer layer. However, the intensity of (00n) peaks in XRD pattern of this sample were weak compared with that of TTF-TCNQ/PTFE/CaF_2 sample. Moreover, the SEM image indicates that the orientation of the micro-grains is random in the surface direction. The control of both the surface flatness and orientation of the b-axis in the lateral direction is not easy at the present stage. However, highly-oriented TTF-TCNQ thin films will be obtained on the St-Ca/PTFE buffer layer by controlling thicknesses of each layer and deposition parameters of TTF-TCNQ film such as growth rate, substrate temperature, etc.

Conclusion

We have examined the effect of several kinds of organic buffer layers on the formation of high-quality TTF-TCNQ thin film. XRD patterns and IR spectra show that the c*-axis of the evaporated TTF-TCNQ was normal to the substrate for all the sample examined here. The b-axis of TTF-TCNQ arranged in perpendicular to the rubbing direction of PTFE layer. However, the surface roughness of TTF-TCNQ film due to the rubbing grooves of PTFE layer was observed. The flat surface was obtained in the TTF-TCNQ/St-Ca/PTFE/CaF_2 sample. In the present stage, however, the orientation of the b-axis of TTF-TCNQ was weak compare with the TTF-TCNQ/PTFE/CaF_2 sample. To obtain high-quality TTF-TCNQ epitaxial layers, the control of the thickness, deposition rate and substrate temperature for both the organic buffer layer and TTF-TCNQ film is important.

References

1. T.E.Phillips, T.J.Kistenmacher, J.P.Ferraris and D.O.Cowan, J.Chem.Soc.Chem.Commun., 471,(1973).
2. M.J.Cohen, L.B.Coleman, A.F.Garito and A.J.Heeger, Phys.Rev., B10,1298(1974).
3. T.Ishiguro, S.Kagoshima and H.Anzai, J.Phys.Soc.Jpn., 41,351(1976).
4. K.Yase, O.Okumura, T.Kobayashi and N.Uyeda, Bull.Inst.Chem.Res.,Kyoto Univ., 62,242(1984).
5. Y.Tomioka and S.Imazeki, J.Phys.Chem., 95,7007(1991).
6. K.Kudo, Y.Ueno, S.Kuniyoshi and K.Tanaka, Appl.Surf.Sci., 60/61,334(1992).
7. J.C.Wittmann and P.Smith, NATURE, 352,414(1991).
8. T.Kanetake, K.Ishikawa and T.Koda, Appl.Phys.Lett., 51,1957(1989).
9. K.Yase, T.Inoue, K.Inaoka and M.Okada Jpn.J.Appl.Phys., 28,872(1989).