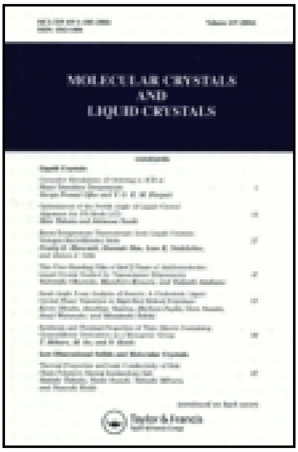

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Epitaxial Growth of TTF Films on Alkali Halides

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EPITAXIAL GROWTH OF TTF FILMS ON ALKALI HALIDES

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Abstract TTF films deposited on three kinds of alkali halides were studied by atomic force microscopy(AFM). In this study it was found that TTF displays epitaxial growth below room temperature. On the other hand, it has been reported that TTF does not grow at room temperature by vacuum deposition.

INTRODUCTION

In order to apply organic thin films to electronics and optical devices it is necessary to control the constituent molecular orientations within a thin film[1]. For these reasons it is very important to understand the nucleation and growth mechanisms of organic films[2]. Vacuum deposition is one of the promising techniques to fabricate thin films with the desired crystal structures. On the other hand, it has been reported that TTF does not grow at room temperature by vacuum deposition[3].

Figure 1(a) shows the structure of a TTF(tetrathiafulvalene) molecule. TTF is an important electron donor often used in thin films. TTF is both a parent compound of TTF-TCNQ, one of the first organic metals, and also a basic compound of BEDT-TTF, a compound from which many organic superconductors have been derived. Figure 1(b)-(d) show the molecular arrangements of the crystal, which were determined by X-ray diffraction, projected onto the *ab*-plane, *ac*-plane and *bc*-plane, respectively[4]. The crystal is monoclinic, belonging to space group $P2_1/c$, with lattice constants of : $a = 0.7364$ nm, $b = 0.4023$ nm, $c = 1.3922$ nm, $\beta = 101.42°$. The molecules form stacks along the *b*-axis, along which the crystal has the largest conductivity [4].

TTF films deposited on three kinds of alkali halides were studied by atomic force microscopy(AFM). In this study it was found that TTF epitaxially grew on three kinds of alkali halides below room temperature.

EXPERIMENTAL

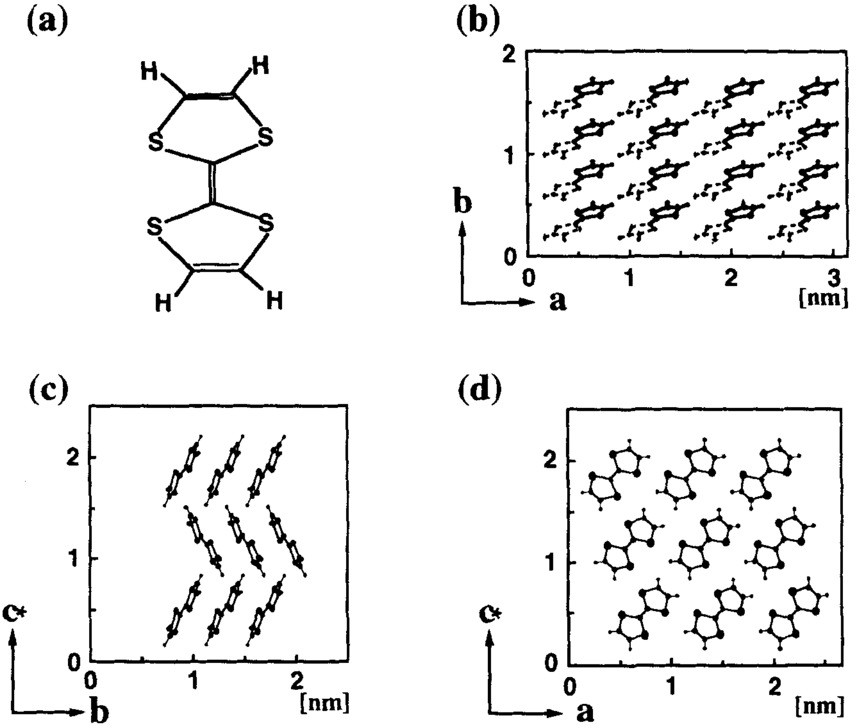

FIGURE 1 (a) Molecular structure of TTF. (b) Molecular arrangement projected onto the *ab*-plane. (c) *bc*-plane. (d) *ac*-plane.

TTF single crystals parchased from Tokyo Kasei Kogyo Ltd. have needle-like shapes with typical dimensions in the range of 0.5-2 mm long, 0.05-0.1 wide and 0.01-0.05 thick. The crystals were sublimated at the temperature of 70°C in a quartz crucible and deposited on the three kinds of substrates, NaCl, KCl and KBr,which had previously been air-cleaved and annealed at 200°C during 1 hour in a pressure of 1×10^{-4} Pa. The temperature of the substrates were kept from -100°C to 20°C in 5×10^{-4} Pa during deposition. The substrates were fixed onto the holder, which was controlled by an electric heater and filling the liquid nitrogen in thetrap outside. The sample's temperatures were measured by a thermocouple. After the deposition the substrates were annealed to 20°C at the rate of 10°C/min and kept at the temperature for 10 min in N_2 gas atmosphere and then they were taken out from the chamber. AFM observation was performed in air at room temperature by using NanoScope II and III (Digital Instruments, Inc., Santa Barbara, CA, USA).

RESULTS AND DISCUSSION

The incident molecular fluxes to the substrates were precisely controlled. The evaporation rate of TTF as a function of the temperature was obtained by using the thermogravimetry[5]. It is around 1 x 10^{22} [molecules/m^2·s] at 70°C. The incident molecular flux to substrate would be $R = \sim 10^{19}$ [molecules/m^2·s], after it was corrected by Clausing's factor of crucible and the $1/R^2$ distance correction factor (R:the distance between the aperture of the crucible and the substrate)[6].

Figure 2 shows AFM images of TTF films deposited on three kinds of alkali halide for 5 minutes at the substrate temperature of -20°C. For these substrates the films consisted of islands which longitudinal axes were parallel to the two equivalent <110> directions of alkali halides.The dimensions of typical islands are 1-10 μm in length, 0.3-2 μm in width and 0.5-1 μm in height. These anisotropic shapes are similar to those of the single crystals grown in solution. It suggests that there is strong intermolecular interactions between TTF molecules stacked along the *b*-axis. This means that TTF films grow parallel to the surfaces of alkali hailides. The number of islands which did not align along the <110> direction increased as the substrate temperature was lower. When the temperatures of these substrates were -100°C, most TTF islands arranged randomly with round-like shapes and did not show the axial relationship between molecular crystals and substrates.

The critical temperatures at which TTF films were able to be deposited on the substrates depend mainly on the kinds of substrates, incident fluxes and substrate

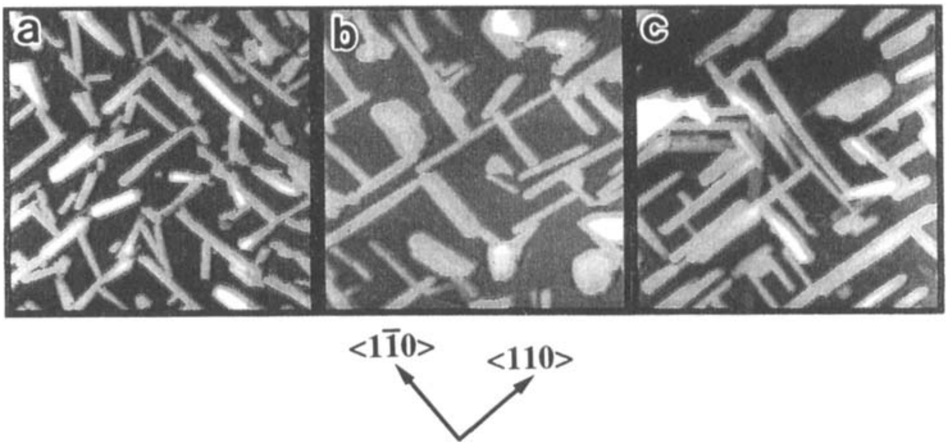

FIGURE 2 AFM images (13.4μm x 13.4μm) of TTF films deposited for 5 minutes at the substrate temperature of -20°C. (a) NaCl. (b) KBr. (c) KCl.

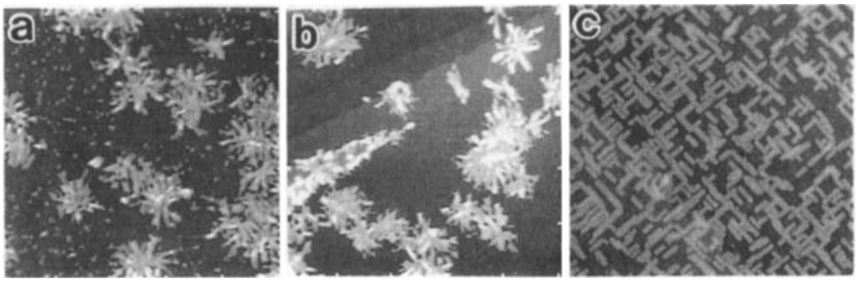

FIGURE 3 AFM images (125μm x 125μm) of TTF films deposited for 5 minutes at the substrate temperature of -10°C. (a) NaCl. (b) KBr. (c) KCl.

temperatures. For the flux $R = \sim 10^{19}$ [molecules/m^2·s], those were -10°C for NaCl and KBr and 10°C for KCl, respectively. Figure 3 show AFM images of TTF films deposited for 5 minutes at the substrate temperature of -10°C. The characteristics to the NaCl and KBr substrates are dendritic aggregation of islands. These aggregations are observed only when the substrate temperatures were -10°C for the NaCl and KBr substrates. These results could be interpreted as follows. The substrate temperatures, -10°C, are high enough to move and aggregate for TTF islands, but not high enough to coalesce each other moving around. And higher temperatures than -10°C are too high even to reach critical sizes for TTF clusters. On the other hand, all islands grow epitaxially on the KCl substrate.

Figure 4(a) and (b) show AFM images of TTF films deposited on KCl substrates for 10 minutes at substrate temperatures of 0°C and 10°C, respectively. All islands grow epitaxially at these temperatures and TTF are not able to be also deposited at higher temperature. No dendritic aggregation of islands could be observed at various conditions

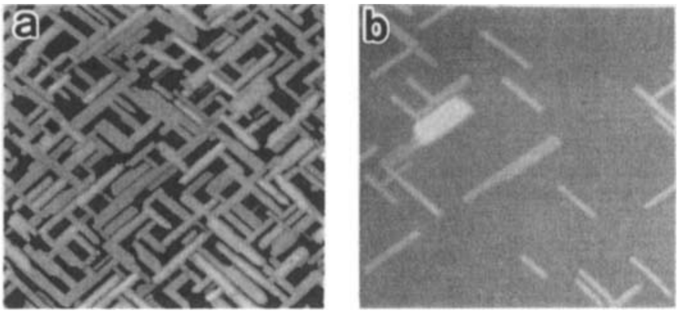

FIGURE 4 AFM images (50μm x 50μm)of TTF films deposited on KCl substrates for 10minutes at the substrate temperature of (a) 0°C. (b) -10°C.

for KCl substrates. This means that TTF islands were absorbed on KCl substrates more stably than on NaCl and KBr substrates. Figure 5 shows schematic diagram of epitaxial growth of TTF on these three kinds of alkali halides depending on substrate temperatures.

The differences between the stability of TTF islands on substrates and these critical temperatures could be explained by considering the differences of the surface energy and interfacial energy. In general, from a thermodynamical point of view, when usual atoms or molecules are deposited on several substrates, the larger the surface energy of substrate is and the smaller the interfacial energy is, the stronger the binding of the film to the substrate is. The value $\Delta = \sigma_S - \sigma_{FS}$ is a order of the strength of the binding of the film to the substrate. (σ_S : the surface energy of substrate, σ_{FS} : the interfacial energy between a substrate and a film.) From the experimental results the following relation is obtained. : $\Delta(\mathrm{NaCl}) \sim \Delta(\mathrm{KBr}) < \Delta(\mathrm{KCl})$. Since the surface energies of three alkali halides were estimated as $\sigma_S(\mathrm{NaCl}) = 0.438\ \mathrm{Jm}^{-2}$, $\sigma_S(\mathrm{KBr}) = 0.229\ \mathrm{Jm}^{-2}$ and $\sigma_S(\mathrm{KCl}) = 0.264\ \mathrm{Jm}^{-2}$, respectively[7], the following relations are obtained. : $\sigma_{FS}(\mathrm{NaCl}) > \sigma_{FS}(\mathrm{KBr})$, $\sigma_{FS}(\mathrm{NaCl}) > \sigma_{FS}(\mathrm{KCl})$. The relation between $\sigma_{FS}(\mathrm{KBr})$ and $\sigma_{FS}(\mathrm{KCl})$ can not be obtained only from these disussion.

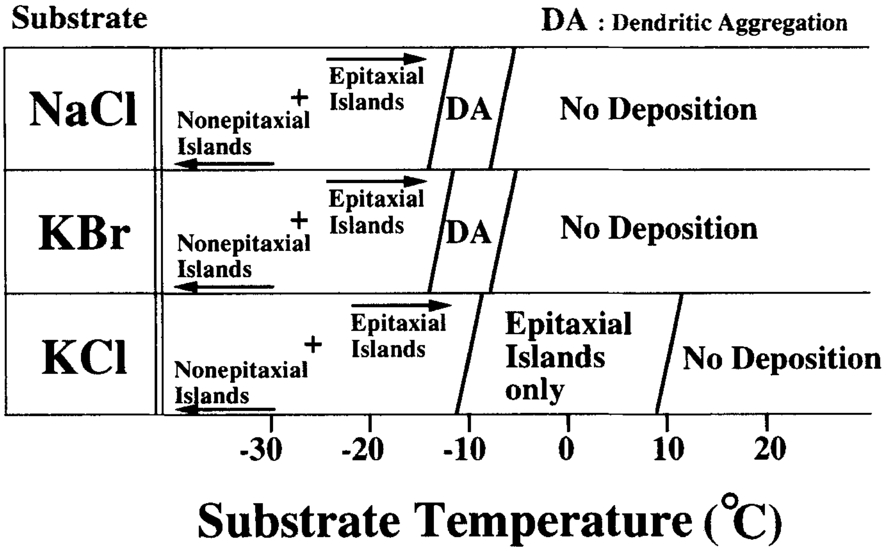

FIGURE 5 Schematic diagram of epitaxial growth of TTF on three kinds of alkali halides depending on substrate temperature.

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REFERENCES

1. *Molecular Electronic Devices*, edited by F.L.Carter (Marcel Dekker, New York, 1982) : *Molecular Electronic Devices II*, edited by F.L.Carter (Marcel Dekker, New York, 1987) : *Molecular Electronic Devices*, edited by F.L.Carter, R.E.Siatkowski and H.Wohltjen (North Holland, New York, 1988)
2. N.Ara-Kato, K.Yase and A.Kawazu, Synthetic Metals, in press: K.Yase, N.Ara and A.Kawazu, Mol.Cryst.Liq.Cryst. 247, 185(1994)
3. K.Yase,O.Okumura,T.Kobayashi and N.Uyeda, Bull.Inst.Chem.Res.Kyoto Univ., 62, 242 (1984)
4. W.F.Cooper, J.F.Edmonds, F.Wudl, and P.Coopens, Cryst.Struct.Comm.,3, 23 (1974)
5. K.Yase, Y.Takahashi, N.Ara-Kato,A.Kawazu, Jpn.J.Appl.Phys. to be submitted
6. P.Clausing, Z.Physik, 66, 471 (1930) ; L.Y.L. Shen, J.Vac.Sci.Technol., 15, 10 (1978)
7. G.C.Benson and K.S.Yun, J.Chem.Phys., 42,3085(1965)