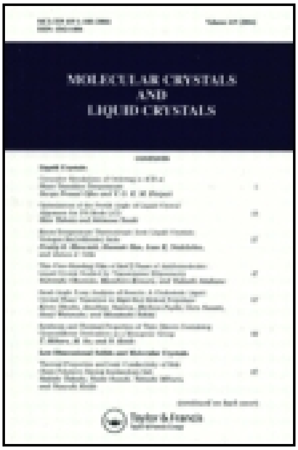

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Growth Mechanism of Thin Films of A Charge Transfer Complex, TTF-TCNQ, Formed on Alkali Halide

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GROWTH MECHANISM OF THIN FILMS OF A CHARGE TRANSFER COMPLEX, TTF-TCNQ, FORMED ON ALKALI HALIDE

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Abstract A charge transfer complex of tetrathiafulvalene and tetracyano-quinodimethane (TTF-TCNQ) is vacuum-deposited onto air-cleaved (001) planes of alkali halides, NaCl, KCl and KBr. The molecular orientation in thin films and surface morphology are characterized by transmission electron microscopy (TEM), and scanning tunneling microscopy (STM) and atomic force microscopy (AFM) to confirm the fine structure and dependence of nucleation and crystal growth on the kinds of substrate.

1. INTRODUCTION

Highly conductive charge transfer complexes of 2,2-bis-1,3-dithiafulvalene (TTF) and 7,7',8, 8'-tetracyanoquinodimethane (TCNQ),[1] and of bis(ethylene-dithio)tetrathiafulvalene (BEDT-TTF) and anions like I_3, $Cu(NCS)_2$, $KHg(SCN)_4$, $(NH_4)Hg(SCN)_4$, etc.[2] have been intensively investigated, and already established the single crystal structures and the origin of such sophisticated physical properties:

the former is characterized in column structure consisting of TTF and TCNQ molecules as donor and acceptor, respectively, while the latter has layer structures of the alternating stacking of cations and anions.[3] It has been well-known that the conductivity and superconductivity of these materials depends on the structures. According to the study by scanning tunneling microscopy (STM),[1,4-6] it has been also made clear surface morphology, structure defects and stacking faults, and electric states in crystals.

When the complex crystal of TTF-TCNQ (Fig. 1) was vacuum-deposited on the (001) planes of alkali halides like NaCl, KCl and KBr, it tended to grow epitaxially to form slender crystals crossing with each other.[8-11] The longitudinal direction of crystals is parallel to the b-axis and corresponds to the direction of molecular columns. The origin of such epitaxial growth was resulted that the anchoring of two CN groups in TCNQ molecules taken place just on any two cations on the (001) plane of alkali halide.[9] Misorientation was also observed by atomic force microscopy (AFM) to be defined the axial relationship between molecules and substrate.[10]

In this paper we will discuss the molecular orientation and growth mechanism in TTF-TCNQ thin films formed on the surface of alkali halides.

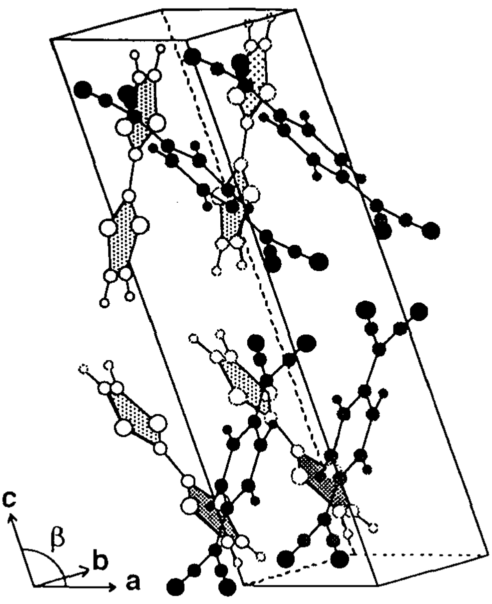

FIGURE 1 Crystal structure of TTF-TCNQ. The lattice parameters are a = 1.2298 nm, b = 0.3819 nm, c = 1.8468 nm, and ß = 104.46°.[7]

2. EXPERIMENTAL

Two solutions of TTF and TCNQ with same molar concentration in acetonitrile were mixed to precipitate the complex crystals. The dried sample was sublimated in a pressure of 1 x 10^{-4} Pa from K-cell type crucible kept at 373 K. The substrates used were air-cleaved (001) planes of NaCl, KCl and KBr maintained at 293 K after baked at 473 K for 2 hours. The deposition rate and final film thickness were 1 nm/min and 1 - 10 nm, respectively. After deposition, the samples were reinforced by carbon film with a thickness of 3 nm by using another vacuum system. The films were floated on the water surface to be stripped from the substrate and then scooped up by electron microscopic grids. Transmission electron microscope (TEM) and AFM used here are TOPCON ABT-002B and Digital Instruments NanoScope-II, respectively.

3. RESULTS AND DISCUSSION

3.1. Molecular arrangement in thin crystals of TTF-TCNQ

Figure 2 shows TEM image (a), and electron diffraction (ED) patterns (b) and (c) of thin films formed on the KCl substrate. The film consists of slender crystals aligning along two <110> axes of the substrate. The longitudinal direction of crystals corresponds to the b-axis along the direction of molecular column, in which TTF and TCNQ molecules stack in line. This molecular arrangement is also confirmed by the ED patterns with four-fold symmetry. The ED pattern taken from these sample consist of reflection spots and accompanying streaks as shown in Fig. 2(b). It was found that two equivalent directions indicated by a in Fig. 2(b) are inclined with an angle of 14° with respect to the basal ab-plane. So that these reflection spots can be indexed by (5,0,-2) and (10,0,-4). When the sample was tilted by 14° around the b-axis in TEM, the series of reflections indexed by (h00) appeared as shown in Fig. 2(c). In the previous paper,[9] one of the authors concluded that the origin of diffuse reflec-

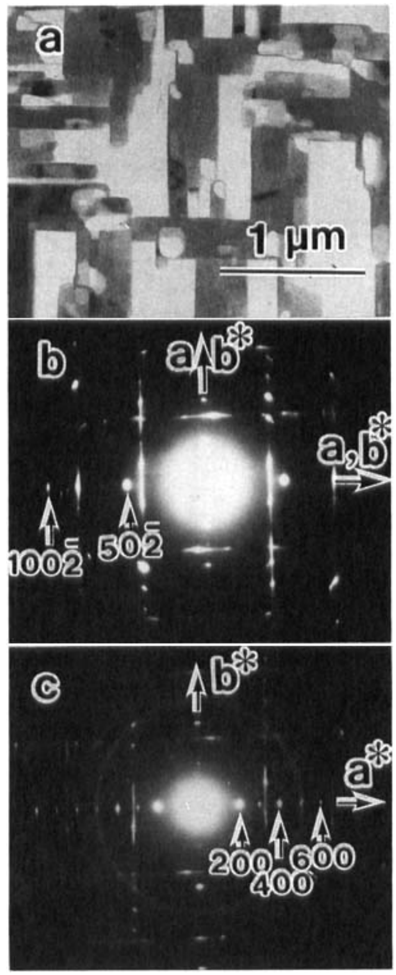

FIGURE 2 Transmission electron micrograph (a), and electron diffraction (ED) patterns (b) and (c) of thin films formed on the KCl substrate. The ED pattern (c) was obtained from the sample tilted in TEM with an angle of 14° with respect to the basal plane. The main reflection spots are indexed.

tion streaks was caused by the line defect along the b-axis.

To prove visually the line defect in thin films of TTF-TCNQ, high resolution TEM observation was performed. Figure 3 shows a high resolution image taken from the tilted sample in TEM. However, there are only the lattice fringes with a spacing of 1.2 nm corresponding to the (200) planes. There are no dislocation in one slender crystal to confirm that it whould be the single crystal. From the molecular arrangement in Fig. 1, the projection along the c-axis should represent only the superimposed images through either two crystallographically equivalent TTF or TCNQ molecules, which are connected with each other by the symmetric operation of $2_1/c$.[7] It suggests that some limit exists in the case of TEM observation in molecular level if molecules arranged in such manner.

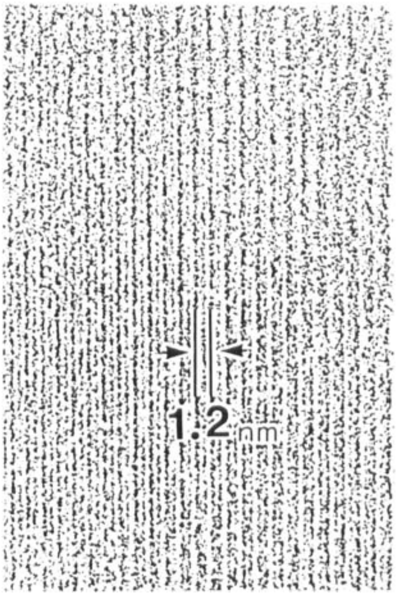

FIGURE 3 High resolution electron micrograph of thin film formed on KCl. The lattices with a spacing of 1.2 nm corresponds to the (200) planes.

It could be overcome by STM or AFM observation, because these technique performs the surface morphology in addition to imaging in atomic scale. Figure 4 shows STM image obtained from thin film on KCl substrate. Two CN groups and one C atom in TCNQ, and one thiol group in TTF can be visualized as dots. In fact, TTF and TCNQ molecules arrange in line along the b-axis to form the molecular columns.

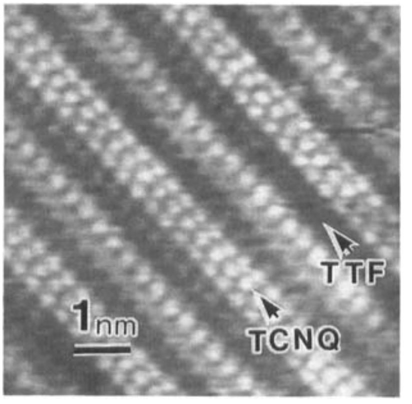

FIGURE 4 STM image of thin film formed on KCl. Each group in TTF and TCNQ molecules is visualized as dot.

3.2. Growth mechanism of epitaxial films of TTF-TCNQ

To make clear the epitaxial growth mechanism of TTF-TCNQ thin films, the initial stage was examined on the series of alkali halides. Figure 5 is AFM images of as-prepared thin films on three kinds of substrates; NaCl (a), KCl (b) and KBr (c). All the films consist of slender crystals orienting along the <110> directions of substrate surface.

In the thin film formed on KCl, there are rectangular crystals, which arrange parallel to the <100> or <010> directions of KCl. They were identified as K-TCNQ crystals by high resolution TEM observation. It is shown in Fig. 6. After deposition, K cations might diffuse into TTF-TCNQ film to substitute for TTF, because the ionization potential of K cation should be larger than that of TTF.

Nevertheless the same amount of complex molecules were evaporated onto these substrates, the amount of deposits would differ each other. It reveals that the condensation coefficient of such substrates might be in proportional to the surface energies of alkali halide: 0.438 Jm^{-2} for NaCl, 0.264 Jm^{-2} for KCl and 0.229 Jm^{-2} for KBr.[12] Such physical properties of substrate should affect to the nucleation of TTF-TCNQ.

In the other point of view, the rectangular crystals were formed on KBr, which should reflect the shape of single crystal. The slower crystal growth due to less adsorption onto the substrate surface might enhance the surface migration of molecules, so that slower crystal growth

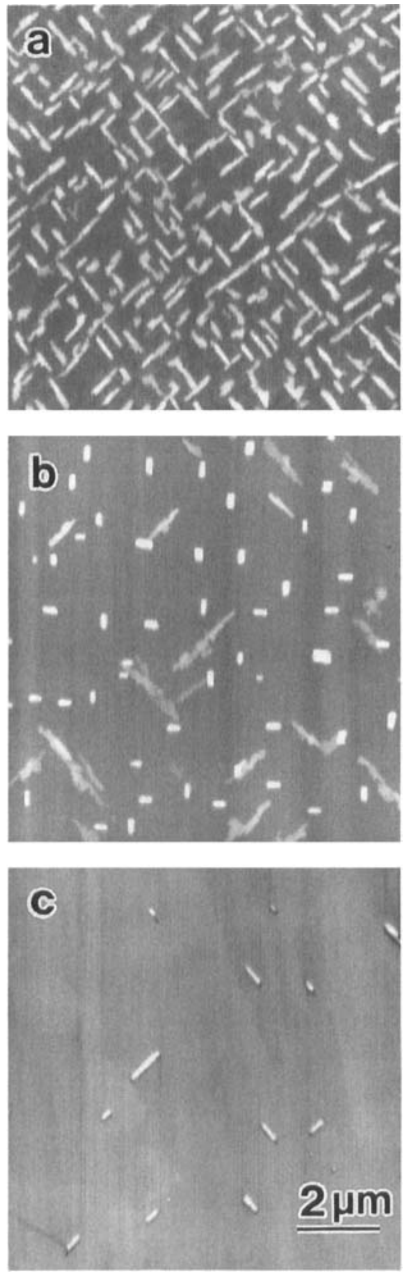

FIGURE 5 AFM images of thin films formed on NaCl (a), KCl (b) and KBr (c).

should occur to generate the single crystal. The same results were also obtained when the deposition was carried out onto the substrates kept at higher temperature.

In conclusion, the appropriate choice of deposition conditions; kinds of substrate having different surface energy and the temperature of substrate during evaporation could lead the proper nucleation with the density of nuclei comparable to the distance for surface diffusion of molecules deposited on the substrate.

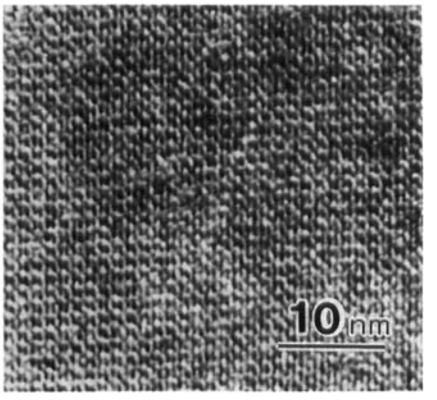

FIGURE 6 High resolution electron micrograph of K-TCNQ crystal found in TTF-TCNQ film on KCl.

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