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Scanning tunneling microscopy of TTF-TCNQ single crystal and thin film

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Abstract

We have studied single crystals and thin films deposited on alkali halides of one-dimensional organic conductor, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), by scanning tunneling microscope (STM). The molecular structures of both samples imaged by STM were similar and the *I-V* (tunneling current - bias voltage) curves measured were both metallic at room temperature. However, when thin films were cooled from room temperature, some parts of films showed to be insulating at ~200K which is much higher than the critical temperature of the metal-insulator phase transition which was observed for the bulk single crystal (53K). The results may suggest that the charge density wave occurs at higher temperature in thin films as in the case of (BEDT-TTF)$_2$I$_3$ films.

1. Introduction

Since physical properties of organic materials depend on their constituent molecular arrangements, their characterizations on an atomic scale are very important both from foundamental and practical points of view. Scanning tunneling microscope (STM) is a powerful tool to investigate the geometric and electronic structures of materials with atomistic resolution at various temperatures1). We have studied single crystals and thin films deposited on alkali halides of one-dimensional organic conductor, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), by use of STM.

TTF-TCNQ is a charge transfer compex with quasi one-dimensional conductivity. The most characteristic property for TTF-TCNQ as one-dimensional conductor is a metal-insulater transition, which is called "Peierls transition", at 53K2).

The crystal TTF-TCNQ is monoclinic with lattice constants of a = 1.2298 nm, b = 0.3819 nm c = 1.8468 nm and β = 104.46° 3). The molecular arrangements projected onto *ab*-plane are shown in Fig.1. TTF-TCNQ grows epitaxially with its *ab*-plane parallel to alkali halide (001) surfaces and with its *b*-axis along the two <110> directions4,5).

2. Experimental

The single crystals studied were grown from acetonitrile solutions as decribed by Kaplan6) and were the typical dimenions of 0.03 x 1 x 3 mm. The films were deposited onto KCl substrates which were air-cleaved and annealed at 473 K for 2 hours in a pressure of 1 x 10^{-4} Pa. The thickness were around 300 nm. The substrate temperatures were kept at 293 K and the pressure was 3 x 10^{-4} Pa during deposition. STM observations were carried out in air at room temperature by using Nanoscope II (Digital Instruments, Santa Barabara, California) and *I-V* characteritics were measured in UHV from room temperature to 14 K by USM-501 (UNISOKU, Hirakata, Japan)

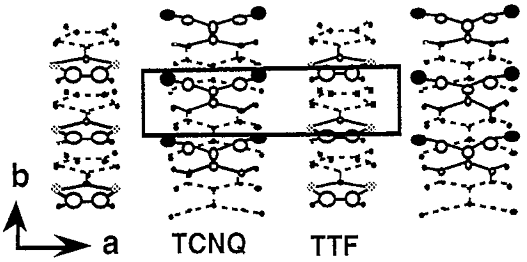

Figure 1. Molecular arrangement projected onto *ab*-plane

3. Results and Discussion

Figure 2(a) and (b) show STM images for a TTF-TCNQ crystal and a thin film measured in air. The tip bias voltage and the average tunneling current were 10.1 mV and 0.42 nA, respectively. The unit cell measured are 1.24 nm x 0.37 nm and 1.21 nm x 0.37 nm, respectively. They are in good agreement with that in the *ab*-plane of bulk crystal, 1.2298 nm x 0.3819 nm, which was determined by X-ray diffraction3). The resolutions are slightly different between two figures, but the characteristics are similar. Alternative two kinds of rows are seen in the figures; one is a column consisting of the triplet protrusions, indicated by "A", and another is that consisting of the single protrusions, indicated by "B". These features are similar to those of the images for the TTF-TCNQ crystal, which was obtained by Sleator and Tycko7) and Magonov et al.8), and for the films deposited on KCl9) and on mica10). According to their assignment, the triplets and the single balls correspond to the TCNQ molecules and the TTF molecules, respectively. These results indicate that the TTF-TCNQ films grow with its *ab*-plane parallel to the KCl substrate.

We also measured *I-V* curves (tunneling current - bias voltage) from room temperature to low temperature. The *I-V* curves measured were both metallic at room temperature. However, when thin films were cooled from room temperature,

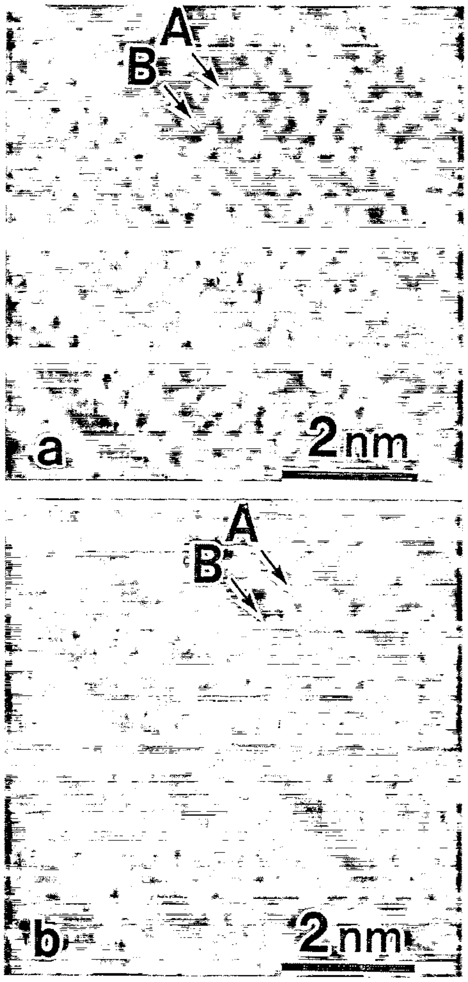

Figure 2. Current images of (a) the crystal and (b) the film

it was difficult to measure *I-V* curves stably and some parts of films showed to be insulating at ~200K which is much higher than the critical temperature of the metal-insulator phase transition which was observed for the bulk single crystal (53K). Figure 3(a) and (b) show the typical *I-V* curves both for the crystal and the film at 200K and the corresponding derivatives. The *I-V* curves of film display a gap of around 150mV. At the temperature below 150K, it was more difficult to measure them stably both for the crystal and the film. At the temperature below 80K, most parts showed to be insulating both for the crystal and the film. The gaps for the films varied widely from 200mV to 300mV, which is two to three times the value for a crystal obtained by Pan et al.[11] and four to six times that for a crystal obtained by dc conductivity measurement[12]. On the other hand, for the crystals those were from 100mV to 250mV. The results may suggest that the charge density wave occurs at higher temperature in thin films as in the case of $(BEDT\text{-}TTF)_2I_3$ films[13,14].

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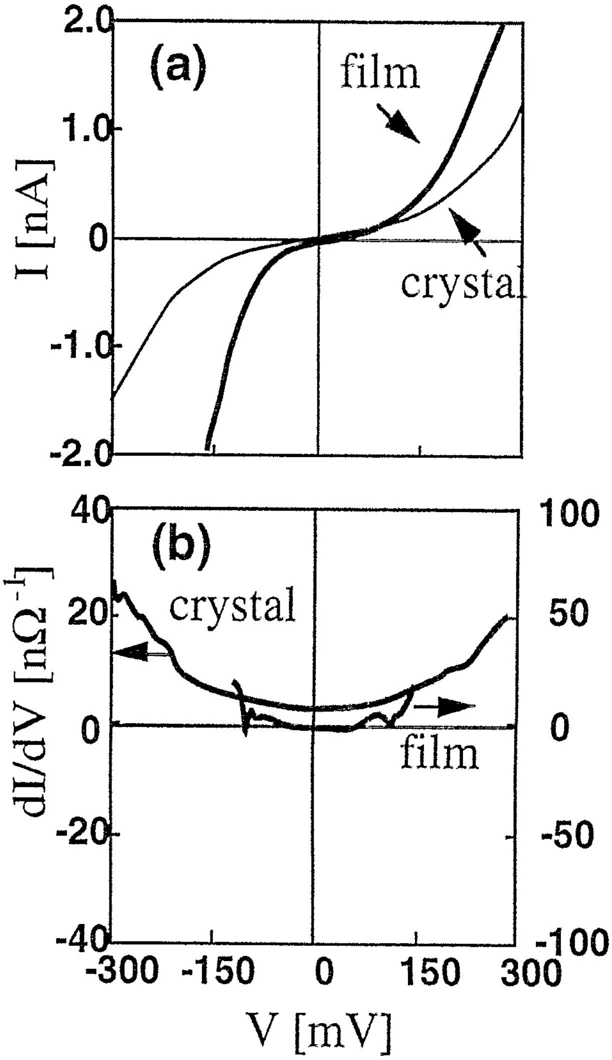

Figure 3. Current-voltage characteristics

REFERENCES

1) *Scanning Tunneling Microscopy and Related Methods*, edited by R.J.Behm, N.Garcia and H.Rohrer (Kluwer, 1989) : *Scanning Tunneling Microscopy Vols I through III*, edited by H.-J.Güntherodt and R.Wiesendanger (Springer Verlag, 1991-1992) : *Scanning Tunneling Microscopy*, edited by H.Neddermeyer (Kluwer, 1993)
2) J.Jerome and H.Shulz, Adv.Phys.**31**,299(1982)
3) T.J.Kistenmacher, T.E.Phillips, and D.O.Cowan, Acta Crystallogr. Sect.**B30**, 763 (1974)
4) K.Yase, O.Okumura, T.Kobayashi and N.Uyeda, Bull.Inst.Chem.Res., Kyoto Univ. **63** (1985) 383.
5) K.Nakajima, M Kageshima, N.Ara, A.Kawazu and M.Yoshimura, Appl.Phys.Lett. **62**, 1892 (1993)
6) M.L.Kaplan, J.Cryst.Growth **33** (1976) 161
7) T.Sleator and R.Tycko, Phys.Rev.Lett. **60**, 1418 (1988)
8) S.N.Magonov, G.Bar, H.-J. Cantow, J.Ren, and M.-H. Whangbo, Synth.Met. **62**, 159 (1994)
9) K.Yase, N.Ara and A.Kawazu, Mol.Cryst.Liq.Cryst. **247** (1994) 185
10) A.Kawazu, N.Ara, and M.Yoshimura, in *The Structure of Surfaces III*, edited by M.A.van Hove and K.Takayanagi (Springer-Verlag, Berlin,1991) p214
11) S.Pan, A.L.de Lozanne and R.Fainchtein, J.Vac.Sci.Technol., **B9** (1991) 1017
12) S.Etemad, Phys.Rev.**B13** (1976) 1792
13) K.Kawabata, K.Tanaka and M.Mizutani, Solid State Commun. **74** (1990) 83 ; Synthetic Metals **39** (1991) 191 ; Synthetic Metals **41** (1991) 2097
14) M.Yoshimura, H.Shigekawa, K.Kawabata, Y.Saito and A.Kawazu, Appl.Surf.Sci., **60/61**(1992)317