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STM study of organic thin films of BEDT-TTF iodide

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Thin films of α-BEDT-TTF iodide were studied and found to show a new structure besides its normal crystal structure; the periodicity in the direction of the a-axis is about two times as large as that of its crystal value. The appearance of this new structure is considered to be responsible for the anomalous metal–insulator transition reported previously. Similar structures were also observed for thin films of α_t-BEDT-TTF iodide.

1. Introduction

Since physical properties of organic materials strongly depend on the molecular structures, it is very important to develop techniques to control the molecular structures as expected to enable the derivation of their new functions. Among these techniques, vacuum deposition has been considered to be very hopeful for the growth of the designed thin films. However, in order to realize this procedure, characterization of the electronic structure of the thin films grown on an atomic scale is necessary.

Recently, Kawabata et al. [1] studied the properties of thin films of $(BEDT\text{-}TTF)_2I_3$ grown by a vacuum deposition technique, and reported that a metal–insulator transition was observed in this material, as in the bulk crystal, while the transition appeared at higher temperature and the change in the conductivity with temperature was rather gradual compared with that in the bulk crystal.

In order to clarify the peculiar properties observed for the thin films of BEDT-TTF iodide, we studied the surface structure of thin films of this material by scanning tunneling microscopy (STM).

2. Experimental

BEDT-TTF powder with iodine prepared by direct reaction was used as a raw material, which was sublimated at around 200°C in an alumina crucible and deposited on a glass substrate. The temperature of the substrate was kept at 70°C, and the pressure of the chamber was $\sim 1 \times 10^{-3}$ Pa during deposition. Typical thickness of the films obtained was $\sim$ 500 nm. Some of them were annealed at 90°C for 40 h in air in order to study the effect of annealing, and these will be referred to as "annealed samples" hereafter. The structures of the as-grown and the annealed thin films were examined by X-ray analysis and found to have α- and α_t-phases, respectively, and the films were observed to grow with the ab-plane parallel to the substrate [1]. In the case of bulk crystals, the α-phase is known to show a metal–insulator

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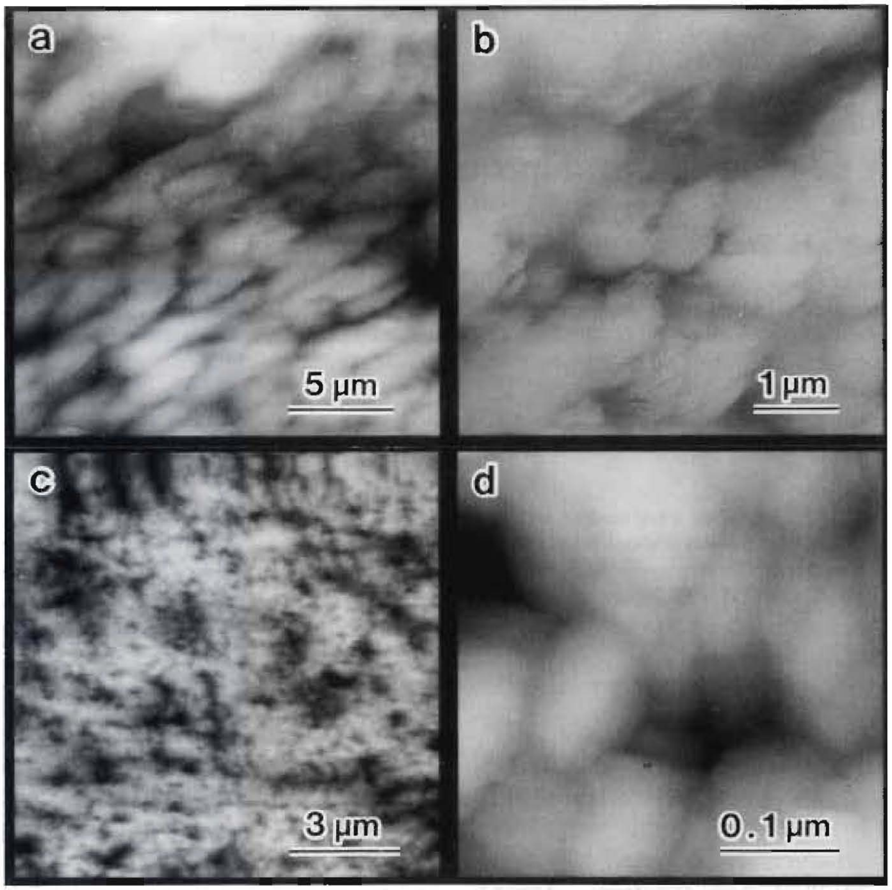

Fig. 1. Topographic images of as-grown ((a): $20 \times 20\ \mu m^2$, (b): $5 \times 5\ \mu m^2$) and annealed films ((c): $12 \times 12\ \mu m^2$, (d): $0.4 \times 0.4\ \mu m^2$).

transition, and the α_t-phase shows superconductivity at 5 K. The STM observations for these samples were performed in air and at room temperature with Pt–Ir tips.

3. Results and discussion

Fig. 1 shows wide-scan images obtained for the as-grown and the annealed thin film samples (fig. 1a as-grown $20 \times 20\ \mu m^2$, fig. 1b as-grown $5 \times 5\ \mu m^2$, fig. 1c annealed $12 \times 12\ \mu m^2$, fig. 1d annealed $0.4 \times 0.4\ \mu m^2$). These images depict island structures, the sizes of which are $\sim 1\ \mu m$ for the as-grown and $0.1\ \mu m$ for the annealed samples. Upon annealing, the surface seems to roughen and the size of the islands becomes smaller, which is considered to be caused by the sublimation of iodines from the surfaces.

Fig. 2 shows a closer image of the as-grown film obtained at the sample voltage of 10.1 mV. Two kinds of rows, each of which includes two kinds of protrusions, are observed. The size of its unit cell, in which there are four protrusions, is $\sim 0.93 \times 1.1\ nm^2$, and is in good agreement with that of the *ab*-plane of the α-(BEDT-TTF)$_2$I$_3$ crystal ($0.92 \times 1.09\ nm^2$), as is shown in fig. 3. Four kinds of protrusions can be assigned to the BEDT-TTF molecules in the *ab*-plane, as was done for the (BEDT-TTF)$_2$Cu(NCS)$_2$ crystal surface [2], and the direction of the rows is considered to be the crystal *a*-axis. As was observed for

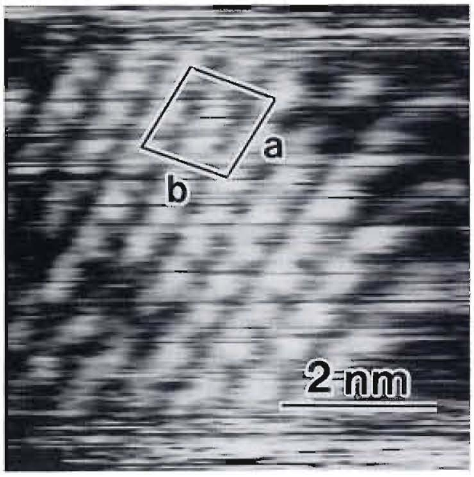

Fig. 2. Current image of the as-grown film obtained at the sample voltage of 10.1 mV (6.0×6.0 nm^2). Unit cell is drawn for reference.

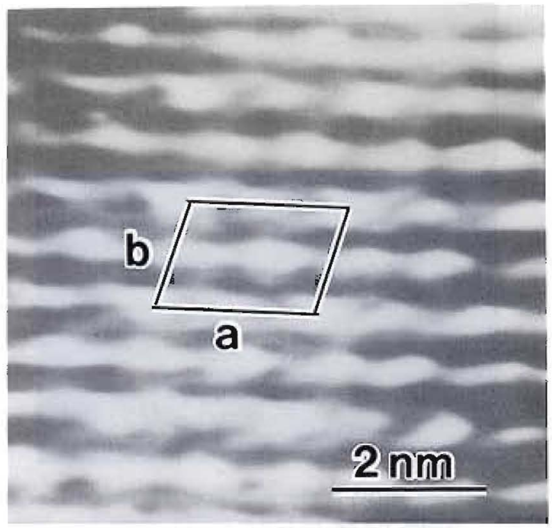

Fig. 4. Current image of the as-grown film obtained at the sample voltage of −57.7 mV (7.0×7.0 nm^2). Unit cell is drawn for reference.

the surface of the single crystal of β-(BEDT-TTF)$_2$I$_3$ [3], there are defects consisting of voids of BEDT-TTF molecules, which is considered to indicate the instability of this surface.

Fig. 4 shows a current image obtained in another part of the as-grown sample. The sample voltage to the tip was −57.7 mV. Four kinds of protrusions can be seen clearly. However, the size of the unit cell is $\sim 2.1 \times 1.4$ nm^2 ($a \times b$); about two times longer in the direction of the a-axis than that of the bulk crystal (0.92 nm).

Although it is not clear at this point how the electronic and the geometric structures are modified spatially, it is certain that two different structures exist in the same sample. The conductance behavior of the α-(BEDT-TTF)$_2$I$_3$ thin films was reported to the different from that of the single crystals; the former shows the gradual drop of conductance around 160 K, while an abrupt metal–insulator transition can be observed at 135 K for the latter [4]. Our results may indicate the premonitory symptoms of the metal–insulator transition appearing in some parts of the thin films even at the normal temperature; the new structure appearing in the films in addition to the normal structure may be responsible for the peculiar gradual transition behavior which appears at a somewhat higher temperature.

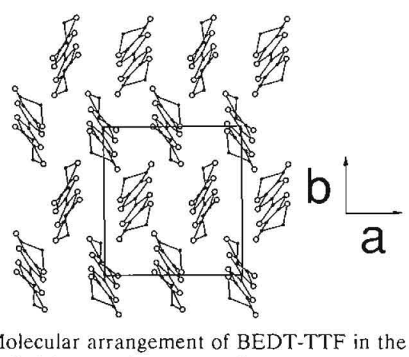

Fig. 3. Molecular arrangement of BEDT-TTF in the ab-plane of the α-(BEDT-TTF)$_2$I$_3$ crystal (a = 0.92 nm, b = 1.09 nm).

Fig. 5 shows the image observed for the annealed sample. The sample voltage to the tip was 17.4 mV. The periodical stripe structure can be seen; however, every row has the same image and individual molecules are not resolved. This poor resolution is considered to be caused by the poor conditions of this surface. Despite the fact that the annealed α-phase crystal is known to have the α_t-phase from X-ray diffraction, the periodicity of the rows observed here is ~ 2.1 nm, which

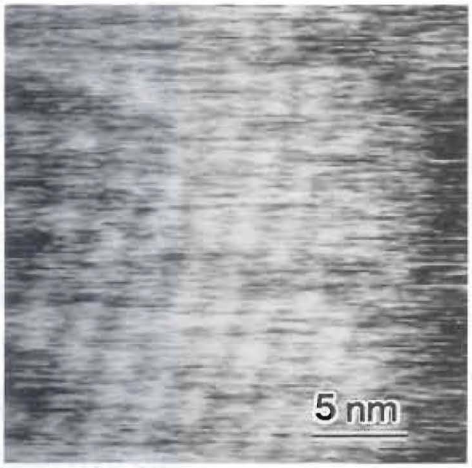

Fig. 5. Current image of the annealed film obtained at the sample voltage of 17.4 mV (25×25 nm^2).

is almost two times as large as that of the crystal value along the a-axis of the α_t-phase (0.924 nm).

Superconductivity of thin films of α_t-phase is verified by magnetization measurements [5]. However, the change in the conductivity for this transition is not so sharp, which has been inferred by the existence of the disordered structure around the grain boundary. In consideration of these results, the new structure observed for the annealed α_t-phase thin films may correspond to the structure observed for the as-grown α-phase thin films, which is considered to cause the metal–insulator transition. The new phase in the annealed films may be emphasized because of the peculiar condition of the thin films. Further experiments are necessary to clarify this point.

4. Conclusions

The surface structures of thin films of BEDT-TTF iodide were studied by STM. Films of α-(BEDT-TTF) iodide were observed to show a new structure in addition to its normal crystal structure; the periodicity in the direction of the a-axis is about two times as large as that of its crystal value. The appearance of this new structure is considered to be responsible for the anomalous metal–insulator transition reported by Kawabata et al. Similar structures were also observed for thin films of α_t-BEDT-TTF iodide.

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