

# Structural studies of tetrathiafulvalene–tetracyanoquinodimethane thin films by scanning tunneling microscopy

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Thin films of tetrathiafulvalene–tetracyanoquinodimethane (TTF-TCNQ) grown on mica substrates by vacuum deposition were studied by scanning tunneling microscopy (STM). STM images displayed the usual arrangement of alternative TTF and TCNQ columns aligned parallel to the crystal *b* axis. However, in addition to the same phase as that of a TTF-TCNQ bulk crystal, a new phase is observed. In this new phase the tilt angles the TCNQ and TTF molecular planes make with the  $\mathbf{a} \times \mathbf{b}$  axis are different from those observed in the normal phase. This new phase can be explained by the introduction of a stacking fault on the surface. © 1995 American Institute of Physics.

Organic materials are highly designable on a molecular level, especially with regards to their electronic properties. For this reason molecular electronic devices which use molecular films have been considered as strong candidates to succeed semiconductors as the next generation of electronic devices.<sup>1</sup> In order to utilize the high potentiality of organic materials, thin films structures must be designed to produce ideal or new functions. However, because the properties of organic films strongly depend on their molecular structure, characterization of an organic thin film's molecular or electronic structures on an atomic scale is very important from both a practical and fundamental standpoint.

Scanning tunneling microscope (STM) has recently been used to characterize the organic materials. In particular, STM molecular images can be compared with the theoretical models.<sup>2–6</sup>

In this letter, we present the results of an STM study of thin films of the organic molecular metal, tetrathiafulvalene–tetracyanoquinodimethane (TTF-TCNQ), grown on mica substrates by vacuum deposition.

Figure 1(a) shows the crystal structure of TTF-TCNQ determined by x-ray diffraction.<sup>7</sup> The crystal is monoclinic with lattice constants:  $a=1.2298$  nm,  $b=0.3819$  nm,  $c=1.8468$  nm, and  $\beta=104.46^\circ$ . Since the molecules form homologous columns along the *b* axis and molecular orbitals between adjacent molecules in each column overlap along this direction, the crystal shows one-dimensional electronic conductivity along the *b* axis. TTF and TCNQ molecular planes are set at an angle of  $58.5^\circ$  to one another. They are oppositely directed by  $24.5^\circ$  and  $34.0^\circ$ , respectively, relative to the axis  $\mathbf{c}^*=\mathbf{a} \times \mathbf{b}$ , as shown in Fig. 1(b).

Mica substrates were cleaved in air and were cleaned by heating at 373 K in a vacuum of  $3 \times 10^{-4}$  Pa for 1 h. TTF-TCNQ was deposited in high vacuum of  $1 \times 10^{-4}$  Pa on the mica substrate at room temperature by heating a quartz crucible containing TTF-TCNQ crystals. The deposition rate was 10 nm/min and the thickness of the films grown was about 100 nm. STM measurements were performed in air at room temperature by the constant height mode using a

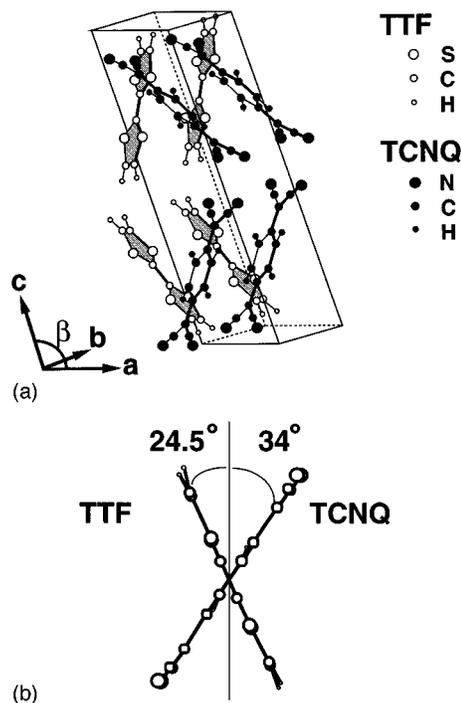
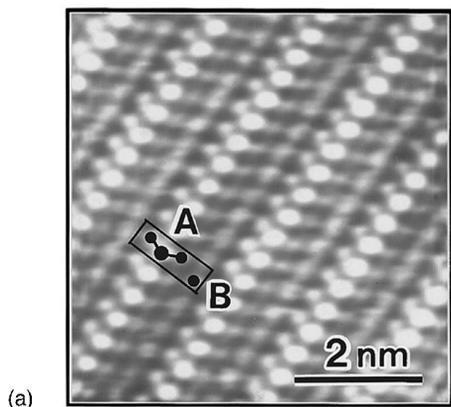
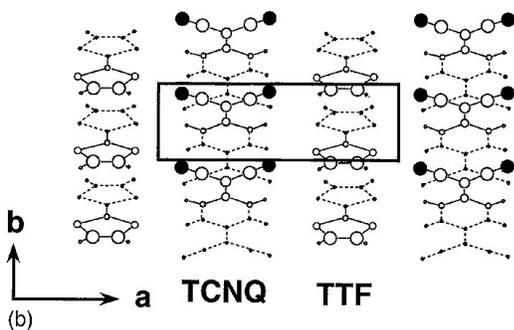


FIG. 1. (a) Crystal structure of TTF-TCNQ determined by x-ray diffraction. (b) Angular relation between TTF and TCNQ molecules.

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(a)



(b)

FIG. 2. (a) A  $6.0 \times 6.0 \text{ nm}^2$  image of a TTF-TCNQ film on a mica substrate obtained over the  $ab$  plane at a tip bias of  $V_t = -4.9 \text{ mV}$  and an average tunneling current  $I_t = 0.42 \text{ nA}$ . (b) Upper half and lower half of the molecules are drawn by solid and broken lines, respectively.

NanoScope II (Digital Instruments, Inc., Santa Barbara, CA) with 80% Pt/20% Ir tips. The STM images presented here are filtered to remove higher frequency noise with the low-pass filter.

Figure 2(a) shows an STM image obtained at the tip bias voltage  $V_t$  of  $-4.9 \text{ mV}$  and average tunneling current  $I_t$  of  $0.42 \text{ nA}$ . Figure 2(b) shows the molecular arrangement of the crystal, which was determined by x-ray diffraction,<sup>7</sup> projected onto the  $ab$  plane. The measured size of the unit cell indicated in Fig. 2(a) is  $1.23 \text{ nm} \times 0.40 \text{ nm}$  and this agrees well with an  $ab$  plane x-ray measurement of a bulk crystal, which yielded  $1.2298 \text{ nm} \times 0.3819 \text{ nm}$  [Fig. 2(b)]. Two kinds of columns appear alternately in Fig. 2(a); one type of column consists of triplet protrusions, indicated by "A," and the other type of column consists of columns of single protrusions, indicated by "B." The triplets have a chevron shape and the center balls in the triplets are brighter than the outer ones. This image is similar to the STM image of the surface of a TTF-TCNQ single crystal  $ab$  plane obtained by Sleator and Tycko.<sup>2</sup> According to their assignment, the triplets correspond to the TCNQ molecules and the single balls correspond to the TTF molecules. These results indicate that the TTF-TCNQ thin film was grown with its  $ab$  plane parallel to the mica substrate.

Figure 3 shows an STM image taken under the same scanning conditions as Fig. 2(a). The STM images of TCNQ molecules on the left-hand side (region II) of the boundary, indicated by the arrows, are quite different from those on the right-hand side (region I). In numerous such studies, we have

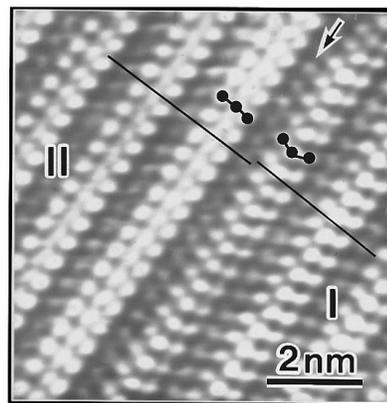


FIG. 3. A  $6.8 \times 6.8 \text{ nm}^2$  image showing the domain structure at a tip bias of  $V_t = -4.9 \text{ mV}$  and an average tunneling current  $I_t = 0.42 \text{ nA}$ .

found that there exist only two such types of images. Because the STM images in region I are very similar to those of Fig. 2(a) as well as those of a single crystal surface obtained by Sleator and Tycko<sup>2</sup> and these two types of STM images coexist in a single picture, we believe the image in region II is not an artifact. The differences of the images in these two regions originate not from a difference of measurement conditions, such as different tip shapes, but from a difference in the surface structures. It is reasonable to think that a packing structure different from that of bulk is formed under the non-equilibrium conditions which occur during vacuum deposition. This new packing structure has not been reported yet in the bulk. Such a structure must be specific to the film. The main differences between the images in the two regions are as follows: (1) the TCNQ triplets are oppositely directed in the two regions; (2) the central angle of the triplet in region II,  $156^\circ \pm 8^\circ$ , is larger than that in region I,  $145^\circ \pm 10^\circ$ ; (3) the center ball in the triplet in region I is brighter than the outer ones, but in region II they have almost the same intensity or the center one is darker than the outer ones; and (4) there is a displacement between the two lines drawn on the TTF molecules along the  $a$  axis in regions I and II as shown in Fig. 3.

Difference (1) is the most striking one and can be understood to be the result of two neighboring domains in which TCNQ molecules are oppositely directed, relative to the  $c^*$  axis. We cannot conclude that the region II is a new phase only from the difference of the STM image because STM images sometimes depend strongly on the direction of a scan. Namely, it is possible that the two domains are simple twins and the differences between their images originate from the direction dependence of a scan. However, the STM images for a scan from the right-hand side to the left-hand side had the similar characteristics as those for a scan with the opposite direction and the characteristics of STM images did not depend on the direction of a scan. Since the angle of TTF molecular plane relative to the axis  $c^* = a \times b$  is different from that of TCNQ molecular plane, simple twins in which molecules are oppositely tilted must not be able to exist. Therefore, it is concluded that two domains are not simple twins and the region II is a new phase specific to thin film. This new phase did not disappear with time and was ob-

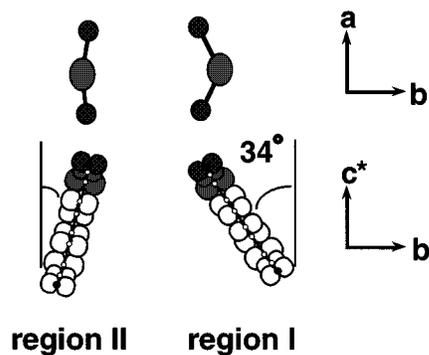


FIG. 4. TCNQ molecules with two different tilt angles (balls show the electron distribution of TCNQ LUMOs) and the expected change of the projections of a TCNQ triplet onto the  $ab$  plane.

served on the sample after annealing at 50 °C for 10 min.

Differences (2) and (3) can be interpreted as follows: When the tilt angle a TCNQ molecular plane makes with the  $c^*$  axis becomes smaller, their projection of the TCNQ triplets onto the  $ab$  plane will change, as is shown in Fig. 4, and the central angle of the TCNQ triplet becomes larger. When the tilt angle of the TCNQ molecular plane becomes smaller, the distances from the center robe and outer ones of the TCNQ triplet to the STM tip become larger and smaller, respectively. Tunneling current strongly depends on the distance between a tip and a substrate surface. Therefore, the image of the center ball of the triplet becomes darker, and the outer balls become brighter.

In this study these two STM images were often simultaneously observed at many places on the sample surface. We have also observed similar images in STM studies of TTF-TCNQ films on alkali halide substrates. The frequent coexistence of these two phases suggests that these two phases differ only slightly in energy. Therefore, the TTF and TCNQ molecules also in region II must be oppositely directed, relative to the  $c^*$  axis, as those in region I. The TTF molecules at the boundary indicated by the arrow in Fig. 3 belong to region II because those are on the line drawn on the TTF molecules in region II. These boundary TTF molecules must be parallel to the TCNQ molecules in the adjacent column in region I to decrease the strain at the boundary, while the tilt angle a TTF molecular plane makes with the  $c^*$  axis are

different from that of a TCNQ molecular plane in a normal phase. This is why no particular distortion and no change in the  $a$ -axis lattice constant in the image were observed around the boundary, as can be seen in Fig. 3. This boundary effect results in the displacement of the TTF balls in the different regions [difference (4)], and the change in the angular orientation of the molecular planes. Further studies on the origin of such a domain structure are in progress.

In conclusion, TTF-TCNQ thin films grown on mica substrates were found to consist of two types of domains; in addition to the normal phase with STM images similar to those previously reported for TTF-TCNQ crystals, a new phase was observed. This new phase can be explained by the introduction of a stacking fault formed in the thin films. In this new phase the tilt angles the TCNQ and TTF planes make to the  $c^*$  axis are different from those in the normal phase. This study shows that organic thin films can have different structures in surfaces from those in bulks. Such structural differences must be clearly understood before the thin films are applied to molecular electronic devices. Therefore, STM is essential to understand the structures or electronic properties of the surfaces of organic conductors on an atomic scale.

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