ELSEVIER

Synthetic Metals 103 (1999) 2105–2106

SYNTHETIC METALS

Anomalous Structural Transition of the β-(BEDT-TTF)$_2$PF$_6$ Surface Observed by Scanning Tunneling Microscopy

M. Ishida[1, 2], T. Mori[3] and H. Shigekawa*[1, 2]

[1]*Institute of Materials Science, University of Tsukuba, Tsukuba 305-8573, Japan*

[2]*CREST, Japan Science and Technology Corporation (JST)*

[3]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152-8552, Japan*

Abstract

In a unit cell of the crystal *a-c* plane of the β-(BEDT-TTF)$_2$PF$_6$ crystal surface, four BEDT-TTF molecules form two dimers. Since the alternate molecular rows consisting of the dimers are observed to be bright by scanning tunneling microscopy (STM) along the crystal *a*-axis, the surface molecular structure is considered to have a periodic modulation. From the analysis of the STM images, the modulated surface structure was found to fluctuate in an anomalous manner. The two dimers are known to have a similar conformation in the crystal, and one of the BEDT-TTF molecules in each dimer is located about 0.2 nm to the surface. Despite the difference in the distance from the surface, molecules that are farther from the surface were observed to be brighter by STM.

Keywords: STM, Structural Phase Transition, Organic conductor based on radical cation and/or anion salts

1. Introduction

On the surfaces of inorganic materials, structural instability due to symmetry disruption is known to be reduced by surface reconstruction, which has been extensively studied by scanning tunneling microscopy (STM). Recently, a structural modulation involving a drastic change in the molecular arrangement was observed to occur on the surface of β-(BEDT-TTF)$_2$PF$_6$, an organic material, [1]. A surface with a PF$_6$ top layer was observed to be formed by the alternate missing rows of PF$_6$ molecules, and another periodic modulation formed by the combination of molecular and electronic structural changes in the surface layers was observed on a surface with a BEDT-TTF top layer. Since structural modulation influences the physical characteristics of materials, such as charge density wave (CDW), it is important to clarify the observed surface superstructures in greater detail. Through examinations by STM and atomic force microscopy (AFM), the observed phenomena were comprehensively explained by the charge compensation model[2,3], i.e., charge and molecular rearrangements reduce the charge imbalance in the surface layers. For the PF$_6$ surface, each surface PF$_6$ molecule can have one electron through the alternate desorption of PF$_6$ molecules. On the other hand, for the BEDT-TTF surface, charge transfer is induced by the BEDT-TTF molecular rearrangement on the surface instead of molecular desorption. However, since charge compensation is incomplete for the latter case, its structure is considered still to be unstable at finite temperatures. In fact, structural fluctuation has recently been observed on this surface[4].

In this paper, we present results of the structural fluctuation of this surface studied by STM on an atomic scale.

*Corresponding author.

hidemi@ims.tsukuba.ac.jp (http://dora.ims.tsukuba.ac.jp)

2. Experimental

Single crystals of β-(BEDT-TTF)$_2$PF$_6$[5,6] were grown by the standard electrochemical oxidation method and fixed to metallic plates with conductive silver epoxy. STM measurements were performed over the crystal *a-c* plane under ambient temperature and pressure conditions using a mechanically sharpened Pt/Ir tip.

3. Result and discussion

Figure 1 shows an STM image of the *a-c* plane of a BEDT-TTF surface. Likewise, molecular arrangements in the *a-c* and *a-b* plane are schematically shown in Fig. 1. The surface unit cell includes four BEDT-TTF molecules forming dimers A-B and C-D, as shown in Fig. 1. If the surface has an ideal structure, upper molecules of each of the tow dimers, A and C in Fig. 1, should be observed with the same brightness by STM because they have the same distance from the STM tip. However, only one molecule in a unit cell (A or

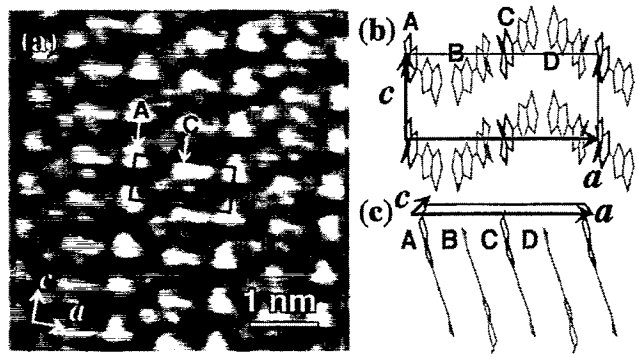

Fig. 1. (a) STM image of the *a-c* plane of β-(BEDT-TTF)$_2$PF$_6$. 5×5 nm^2, V_s = -30 mV, I_t = 0.45 nA. Schematics of molecular arrangement in (a)*a-c* plane and (c)*a-b* plane.

PII: S0379-6779(98)00460-3

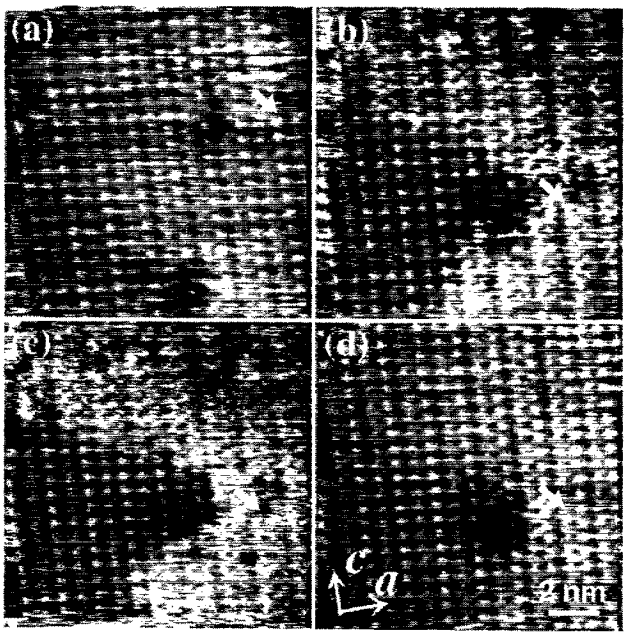

Fig. 2. A series of STM images observed over the *a-c* plane of β-(BEDT-TTF)$_2$PF$_6$, 12×12 nm^2, V_s = -30 mV, I_t = 0.76 nA.

C) is brightly imaged as shown in Fig. 1, resulting in the observed modulation, i.e., the contrast of the dimer rows alternates along the crystal *c*-axis. Since the two dimers have similar conformation in the crystal, two phases are possible for the modulation, i.e., each of the rows consisting of A-B or C-D dimers can be bright or dark.

As shown in Fig. 2, the modulated structure was observed to fluctuate with time. Here it took about 15 sec. to take each image. The surface in (a) is covered by one phase. However, another phase merged from the right side as shown in (b). In (c), the new phase seemed to be pinned by the defect existing around the center of the figures, but disappeared again in (d). The fluctuation seems to be the change in the brightness between the two dimer rows consisting of A-B and C-D dimers in Fig. 1. However, the observed fluctuation was more complex and anomalous.

Figure 3(a) shows an STM image in which two phases coexist. For convenience, four BEDT-TTF molecules are labeled A, B, C, and D, respectively. In order to clarify the details, magnified images of the two phases in Fig. 3(a) are shown in Figs. 3(b) and 3(d) with their cross sections, respectively. These cross sections were obtained through the averaging of the cross sections acquired in the unit cells. As is shown clearly in Fig. 3(b), row A is most brightly imaged. If the fluctuation is due to the change in brightness between A-B and C-D dimer rows, row C is expected to be bright in another phase. However, rows B and D are brightly imaged in Fig. 3(c). Since these molecules are farther from the surface, some new mechanism is necessary to explain the observed phenomenon.

The ethylene groups attached on both edges of BEDT-TTF are flexible and the existence of several metastable conformations is possible, which may be a factor contributing to the observed fluctuation. In such case, some long-range interactions between the groups may occur. Further analysis is necessary to clarify the mechanism in detail. Since structural modulation is expected to influence the physical characteristic of the surface, an important and urgent requirement is to clarify the observed structural change.

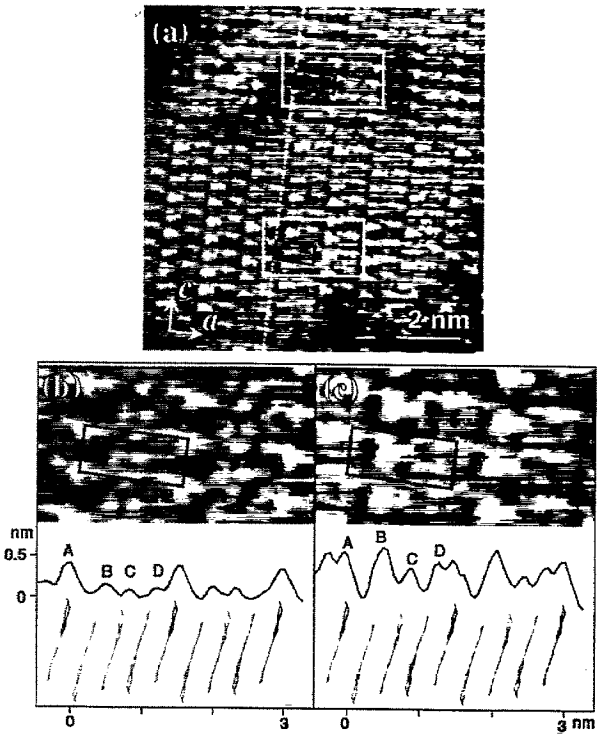

Fig. 3 (a) STM image obtained over the *a-c* plane of β-(BEDT-TTF)$_2$PF$_6$, 12×12 nm^2, V_s = 30 mV, I_t = 0.45 nA. (b) (c) magnified images of the squared areas in the upper and lower parts in (a), and averaged cross sections along the *a*-axis.

4. Conclusion

An anomalous structural transition was observed on a β-(BEDT-TTF)$_2$PF$_6$ crystal surface with a (BEDT-TTF) molecular top layer. In the fluctuation, the molecules located farther from the surface are brighter than other molecules in one phase as observed by STM. Some long-range interaction may contribute to the occurrence of the observed phenomenon.

Acknowledgments

This work was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan. One of the authors (M.I.) was financially supported by the Japan Society for the Promotion of Science (JSPS) Fellowships for Japanese Junior Scientists.

Reference

[1] M. Ishida, K. Hata, T. Mori, and H. Shigekawa, Phys. Rev. B 55 (1997) 6773.
[2] R.W. Nosker and P. Mark, Surf. Sci. 19 (1970) 291.
[3] M. Tsukada and T. Hoshino, J. Phys. Soc. Jpn. 51 (1982) 2562.
[4] M. Ishida, K. Hata, T. Mori, K. Nakamoto, M. Iwatsuki, R. Yoshizaki, and H. Shigekawa, Jpn. J. Appl. Phys. 36 (1997) 3894.
[5] T. Mori, A. Kobayashi, Y. Sasaki, R. Kato, and H. Kobayashi, Solid State Commun. 53 (1985) 627.
[6] H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, Chem. Lett. 1983 (1983) 759.