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Epitaxial Growth of BEDT-TTF Thin Films on KCl and Mica

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Dibis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) was vacuum-deposited onto KCl {001} and mica {001}. The molecular orientation in thin films and surface morphology were characterized using transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray diffraction (XRD). On the KCl substrates, BEDT-TTF crystals were oriented epitaxially in the relation of (10-2) $[020]_{BEDT\text{-}TTF}$ // $(001)[001]_{KCl} \pm 5°$. Two types of orientations were found in the films on the mica substrates. Coexisting with the orientation found in the films on KCl, $(2\text{-}21)_{BEDT\text{-}TTF}$ // $(001)_{mica}$ was found in the films formed on the mica substrate. However, the two-dimensional epitaxial relationship was not observed in the BEDT-TTF films formed on the mica surface.

Keywords: BEDT-TTF; thin film; vacuum deposition, molecular orientation, transmission electron microscopy

INTRODUCTION

Dibis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is an organic donor molecule which constitutes principal organic superconductors such as $(BEDT\text{-}TTF)_2I_3$ and $(BEDT\text{-}TTF)_2Cu(NCS)_2$ [1,2]. Although the physical properties of these organic superconductors have been intensively investigated using bulk crystals, only a few studies have been carried out on the thin film states [3-5]. This is due to the difficulty in the preparation of thin films of organic superconductors. To obtain the well controled organic superconducting thin films, information of crystal

growth and thin film structure of the constituent molecules is necessary. In this study, we have newly determined the orientations of the thin films of BEDT-TTF formed on the KCl and mica substrates.

EXPERIMENTAL

BEDT-TTF powder was sublimated in a pressure of 4 x 10^{-8} Pa from K-cell type crucible kept at 80°C. The substrates used were air-cleaved (001) planes of KCl and mica maintained at 20 °C after baked at 200 °C for 1 hour. The deposition rate and final film thickness were 0.17 nm/min and 20 nm, respectively. The as-prepared thin films were observed using an AFM in air, and the lattice spacing normal to the substrate plane was measured using a high-resolution XRD. Other films were reinforced with evaporated carbon film. The films covered with amorphous carbon film were stripped off from the substrates on a water surface and placed on electron microscopic grids. A gold film on the grid was used as a standard calibration material for lattice spacing measurements.

RESULTS AND DISCUSSION

Figure 1 shows the TEM images (a) and electron diffraction (ED) pattern (b) of the BEDT-TTF thin films formed on the KCl substrate. The thin film consists of rhombohedral-shaped crystals having interplanar angles of 77 ° and 102°. Electron diffraction through these crystals displayed four-fold symmetry with the diffraction spots corresponding to lattice spacings of 0.70 and 0.29 nm as shown in Fig.1 (b). The lattice parameter of a bulk single crystal of BEDT-TTF is monoclinic, space group is $P2_1/c$, a=0.6614 nm, b=1.3985 nm, c=1.6646 nm and b=109.55° [6]. On comparison of

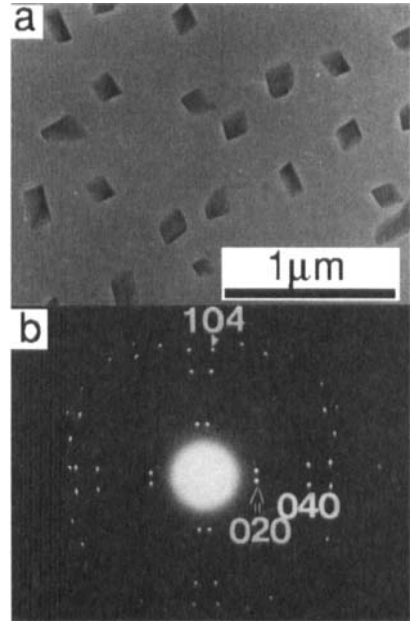

FIGURE 1 TEM images (a) and electron diffraction pattern (b) of the BEDT-TTF thin films formed on the KCl substrate.

the observed lattice spacings and the calculated ones, the ED spots in Fig. 1(b) can be indexed by (020) and (104). A consistent result was obtained in XRD measurement, in which two remarkable peaks corresponding to (10-2) and (20-4) lattice spacings were appeared. From these facts, it was determined that the (10-2) face of BEDT-TTF is located in parallel with the (001) face of KCl. Furthermore, the epitaxial relationship was analyzed from an AFM image as shown in Fig. 2. The lateral faces of the crystals in the films consist of the {011} and {01-1}. From the morphology, it was determined that directions <010> and <103> of BEDT-TTF crystal which run parallel to (10-2) were oriented in the directions tilted by ±5° from the <100> on KCl (001). Consequently, this analysis is consistent with the ED pattern shown in Fig. 1(b).

Figure 3 shows TEM images (a), and ED patterns (b) and (c) of the BEDT-TTF thin films formed on the mica substrate. The film consists of crystals having two kinds of morphology. The one appeared as rhombohedral shape which has the same crystal habits observed in the films on KCl, and the other appeared as triangular shape. Electron diffraction through the triangular-shaped crystal displayed single crystal patterns with the diffrac-

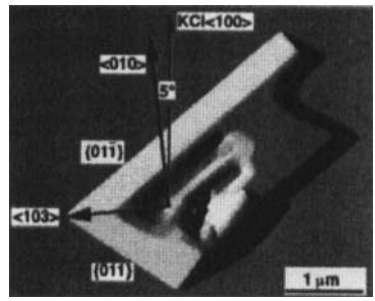

FIGURE 2 AFM image of BEDT-TTF thin film.

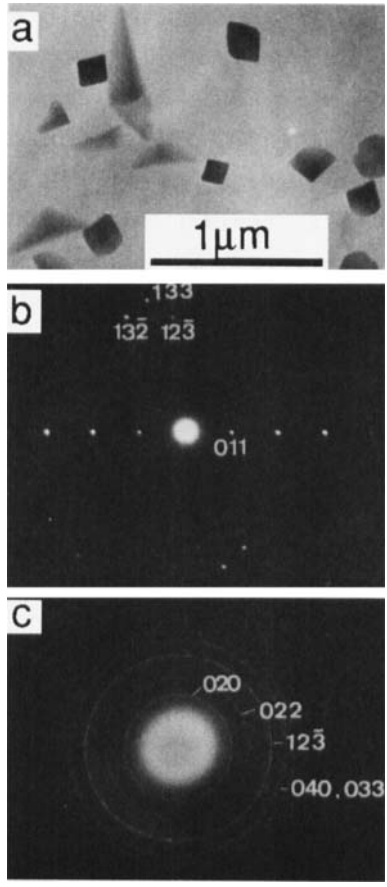

FIGURE 3 TEM images (a) and ED patterns (b) and (c) of the BEDT-TTF thin films formed on mica.

tion spots corresponding to lattice spacings of 1.04, 0.40, 0.37 and 0.34 nm, as is shown in Fig.3(b). From the lattice spacings and the angles between spots, the spots can be indexed by (011), (12-3), (13-2) and (13-3). This means that the (2-21) face of BEDT-TTF runs parallel to (001) of mica. As the electron diffraction though rhombohedral-shaped crystals displayed the same pattern that from the films on KCl, the orientation in this crystals are regarded as the same one in the films on KCl. Electron diffraction through wider region of this film displayed a ring pattern including diffractions from two types of orientations as shown in Fig.3(c). Therefore, the two-dimensional epitaxial relationship with the substrate was not observed in the films formed on the mica surface.

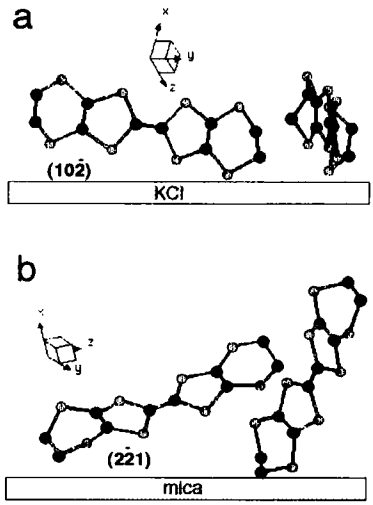

FIGURE 4 Two types of molecular orientations $(10\text{-}2)_{\text{BEDT-TTF}}$ // $(001)_{\text{KCl}}$ (a) and $(2\text{-}21)_{\text{BEDT-TTF}}$ // $(001)_{\text{mica}}$(b).

Figure 4 summarizes the molecular orientations of BEDT-TTF thin films revealed in this study. On the KCl substrate, The BEDT-TTF crystal was oriented in the relation of (10-2) $[020]_{\text{BEDT-TTF}}$ // $(001)[001]_{\text{KCl}} \pm 5°$. Two types of orientation coexists on the mica substrate. The relations of the orientations were determined as $(10\text{-}2)_{\text{BEDT-TTF}}$ // $(001)_{\text{mica}}$ and $(2\text{-}21)_{\text{BEDT-TTF}}$ // $(001)_{\text{mica}}$.

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