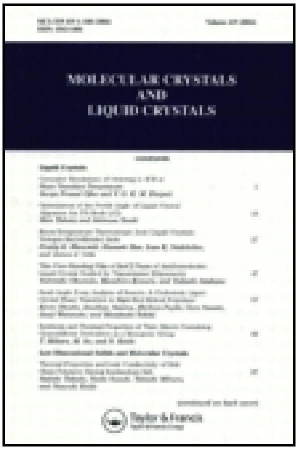

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Highly Oriented TTF-TCNQ Crystal Growth Using an Electric-Field Induced Evaporation Technique

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Highly oriented TTF-TCNQ grains were prepared by applying an electric field during the evaporation. We were able to clarify the orientation process of TTF-TCNQ grains and the electrical property corresponding to the long axis of the crystal grain.

Keywords: TTF; TCNQ; charge transfer complex; electric field; orientation

INTRODUCTION

Organic molecules are interesting materials with potential for use in next-generation optical and electronic devices. Since the optical and electronic properties of organic films strongly depend on their molecular orientation, it is important to prepare thin films with controlled molecular orientation.

The organic compound tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) has been widely studied due to its quasi-one-dimensional conductivity. It consists of homologous stacks of cations (TTF) and anions (TCNQ) along the *b* axis and shows one-dimensional metallic conductivity due to a charge transfer between the two different types of molecules. In our previous study, it was found that the molecular orientation of TTF-TCNQ charge-transfer (CT) complex films could be controlled using the co-evaporation technique with an applied electric field [1]. However, the precise mechanism of the TTF-TCNQ orientation by applying electric field has not yet been clarified.

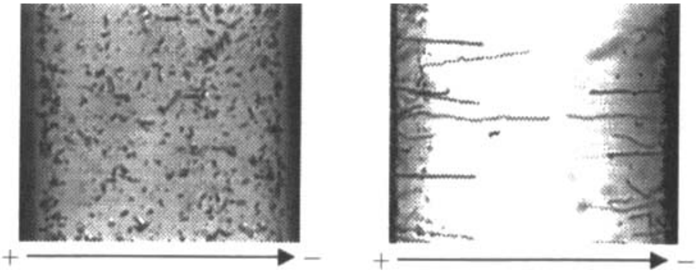
In this paper, we investigated the orientation mechanism of TTF-TCNQ films and the characterization of TTF-TCNQ grains by electric measurement.

EXPERIMENTAL PROCEDURE

TTF-TCNQ orientated grains were prepared on glass substrates, with 100 μm spaced Au electrodes in plane, and an electric field was applied between the electrodes during the evaporation process. TTF-TCNQ grains were prepared by a conventional evaporation technique with a one-source (TTF-TCNQ) and a co-evaporation technique with two separate sources (TTF and TCNQ). The TTF-TCNQ complex was initiated by mixing two solutions of TTF and TCNQ in acetonitrile. TTF, TCNQ, and TTF-TCNQ powder samples were put into crucibles and they were sublimed by heating up to 55℃, 110℃, and 120℃, respectively at a pressure of 10^{-6} Torr (10^{-3} Pa). The substrate temperature was maintained between 40 and 43℃. The electric field between the electrodes was varied from 0 to 35 kV/cm. The morphology of the TTF-TCNQ grains on the substrates was observed using an optical microscope. Electrical characterization was performed by an I-V measurement of the space between the Au electrodes.

RESULTS AND DISCUSSION

To study how to electric field affects on the molecules (TTF, TCNQ, and TTF-TCNQ) we investigated the growth processes of TTF-TCNQ crystals prepared by using the one-source (CT) evaporation and co-evaporation techniques. Figures 1 (a) and (b) show the surface morphologies of the TTF-TCNQ grains prepared by one-source (CT) evaporation and co-evaporation, respectively. Both evaporated films contain needle-like crystal grains. Although the orientation of the grains prepared from the CT complex was random, the long axis of co-evaporated grains aligned parallel to the applied electric field. These results demonstrate that the electric field is more effective when using the co-evaporation technique. It seems that TTF was attracted to the negative electrodes and TCNQ was attracted to the positive electrodes because TTF was a cation and TCNQ was an anion. Yase et al. reported that TTF and TCNQ molecules sublimed individually



(a) CT complex evaporation
Electric field = 35 kV/cm
(T_S = 35℃)
(about 40℃ : no deposition)

(b) Co-evaporation
Electric field = 35 kV/cm
(T_S = 43℃)

FIGURE 1 Morphology of TTF-TCNQ films

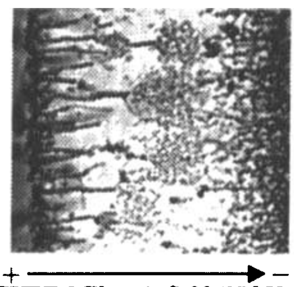


FIGURE 2 Electric field (35 kV/cm) around the tip of needle-like grains (T_S = 40℃)

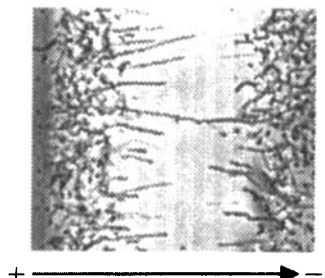


FIGURE 3 Electric field = 10 kV/cm (T_S = 43℃)

and recombined again on the substrate surface at the TTF-TCNQ source temperature of 200℃ [2]. Therefore, both of these morphologies (Figs. 1 (a) (b)) should be similar to each other. Although the difference of the morphologies due to the evaporation techniques (one source and co-evaporation) has not been clear, the evaporation condition, such as the flux ratio, substrate temperature, and evaporation source temperature may affect the surface morphologies.

Figure 2 shows the effect of electric field during the growth of needle-like grains. Small grains are distributed along the line of electric force between the tip of the needle-like grains and electrodes. These results indicate that the applications of electric field enhance the growth of the needle-like grains along the line of electric force. When a large electric field is applied (Fig. 1 (b)), longer needle-like grains grow from the edge of the electrodes but these grains do not reach to the opposite side grains. Under a small electric field (Fig. 3), however, random grains are distributed around the edge of electrodes and some needle-like grains contact through the gap. Higher voltages applied to the electrode cause higher Joule's heat and may prevent the grains from reaching toward the opposite side.

TABLE 1. Conductivity of Sample and Single Crystal

	Conductivity(S / cm)
Samples (average)	1.8×10^2
Single crystals (b-axis)	5.0×10^2

Table 1 summarizes the conductivity of samples (along long axis) and single crystals (b-axis). The measured electric conductivity of the TTF-TCNQ grains showed a slightly smaller value than that of the b-axis of the single crystal. This result indicates that TTF-TCNQ crystal growth occurs with the b-axis parallel to the electric field, but the crystal grains have many defects. These crystal structures were already examined by STM analysis [1][3].

CONCLUSION

We investigated the growth process of TTF-TCNQ grains with an applied electric field and evaluated their electrical properties. It was found that the application of electric field enhanced the growth of the needle-like orientated grains only when using the co-evaporation technique, and the grains contacted the opposite side grains under a small voltage condition. The experimental results indicated that TTF-TCNQ crystal growth occurred along the b-axis parallel to the electric field.

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