NANO-SIZE MOLECULAR CONDUCTORS DIRECTLY FORMED ON SILICON SUBSTRATES


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1 INTRODUCTION

Recently, the physical properties of nano- and microcrystals of molecular conductors are attracting wide attention. Because molecular conductors exhibit a variety of conduction properties, such as photo-induced insulator-metal transition, humidity sensing behavior, superconductivity, ferroelectricity, and giant negative magnetoresistance, the size effect on these properties is interesting. For such studies, we have developed procedures that enable multi-probe measurement of nano-/microcrystals of molecular conductors on SiO₂/Si substrates at various temperatures. These procedures are based on direct crystal growth on a substrate, and are applicable to the study of not only the size effect on nanocrystals but also the gate field effect on these materials. The field effect is especially interesting in a highly correlated electron system, which is often observed in molecular conductors, because the physical properties of the system are very sensitive to the carrier concentration. Indeed, the transformation of an insulator into a superconductor by an electric field was reported in an inorganic material, whereas such kind of study in molecular conductors has yet to be conducted. In our previous paper, we reported the two-probe measurement of (DMe-DCNQI)₂Ag, (DMe-DCNQI-d⁷)₂Cu, (MeBr-DCNQI)₂Cu, (BEDT-TTF)₂I₃, (TMTSF)₂PF₆, (EDT-TTF)₂BrI₂(TIE)₂, and (EDO-TTF)₂PF₆, and the four-probe measurement of only (DMe-DCNQI-d⁷)₂Cu (DMe-DCNQI = 2,5-dimethyl-N,N'-dicynoquinonediimine; MeBr-DCNQI = 2-methyl-5-bromo-N,N'-dicynoquinonediimine; TIE = tetraiodoethylene; BEDT-TTF = bis(ethylendithio)tetrathiafulvalene; TMTSF = tetramethyltetraselenafulvalene; EDT-TTF = ethylenedithiotetrathiafulvalene; EDO-TTF = ethylenedioxidotetrathiafulvalene). Here we show the results of the four-probe measurement of α-(BEDT-TTF)₂I₃ as well as the gate field effect on this material. α-(BEDT-TTF)₂I₃ is known to exhibit very high mobility exceeding 10⁵ [cm² V⁻¹ s⁻¹], and therefore its behavior under an electric field is interesting.

2 METHODS AND RESULTS
2.1 Crystal Growth

Single crystals of $\alpha$-(BEDT-TTF)$_2$I$_3$ were grown by electrochemical reaction on a substrate. Ti (2 nm), Au (10 nm), and Pt (10 nm) were evaporated or sputtered onto SiO$_2$ (200 nm) doped-Si substrate to form an electrode. The electrode pattern was drawn by electron beam lithography using PMMA/MMA resist. Then, the substrate was placed in a glass cell containing 5 ml chlorobenzene solution of BEDT-TTF (ca. 2 mg) and tetrabutylammonium triiodide. An anodic probe was attached to the Ti/Au/Pt electrode. The cathodic probe was positioned approximately 1 mm above the electrode on the substrate. When a voltage of approximately 2 V was applied to the probes with 5 MΩ protect resistance, tiny plate-like crystals were formed on the electrode by the oxidation reaction on the anode. The crystal growth was observed with a microscope, and sufficient crystal size was achieved within 20 minutes. After the substrate was lifted out of the solution and dried, the electrodes were cut by laser ablation to form a circuit including the BEDT-TTF salt. The SEM image of $\alpha$-(BEDT-TTF)$_2$I$_3$ on a substrate is shown in Figure 1.

![SEM image of $\alpha$-(BEDT-TTF)$_2$I$_3$ crystal](image)

**Figure 1** Scanning electron microscope image of the $\alpha$-(BEDT-TTF)$_2$I$_3$ crystal whose resistance was measured by the four-probe method. The configuration of the measurement is shown as 'I+', 'V+', 'V-', and 'I-'.

2.2 Conductivity Measurements

Four-probe measurement was performed on the $\alpha$-(BEDT-TTF)$_2$I$_3$ single crystal, and the temperature dependence of the resistance is shown in Figure 2. The four probes were selected as shown in Figure 1. The bulk crystal of $\alpha$-(BEDT-TTF)$_2$I$_3$ is known to exhibit metal-insulator (M-I) transition at 135 K; however, the microcrystal showed M-I transition at approximately 150 K. This result was reproducible for several samples. Because the hard Si substrate tends to expand the soft organic crystal at low temperatures, this elevation of the transition temperature may have originated in the negative pressure produced by the difference in thermal expansion coefficient between the substrate and the microcrystal. However, the cell expansion seems to be not the only reason, because such elevation was not observed in $(\text{TMTSF})_2\text{PF}_6$ in our previous study² for example. The I-V characteristics at gate voltages of ±50 V were measured at 90 K. The source and drain electrodes for this measurement were 'V+' and 'V-' in the four-probe configuration. Because the insulator phase of $\alpha$-(BEDT-TTF)$_2$I$_3$ is known to be a charge order state, it is...
plausible to consider this material as an intrinsic semiconductor in a band picture. The numbers of electrons and holes are the same at zero gate voltage. Figure 3 shows that the source-drain current is increased at the positive gate voltage. This means that the mobility of electrons is higher than that of holes in this system. Further study focusing on the influence of gate field in the temperature range of the M-I transition is under way.

Figure 2  Temperature dependence of resistance measured by four-probe method for a-(BEDT-TTF)$_3$I$_3$ bulk and microcrystal. The data were obtained with the same instrument.

Figure 3  I-V characteristics of a-(BEDT-TTF)$_3$I$_3$ measured at 90 K and gate voltages of +50 V and -50 V. The source-drain current was changed by a factor of more than two according to the gate voltage.

3 CONCLUSIONS

The procedures we have developed to fabricate conductive molecular devices on silicon substrate are quite effective for the multi-probe measurement of micro-/nanocrystals of
molecular conductors. In this study, the change of the transition temperature of \( \alpha-(\text{BEDT-TTF})_2\text{I}_3 \) was revealed by the four-probe measurement. The device was also proved to be effective in applying the gate electric field to the molecular crystal.

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References