Field effect on organic charge-ordered/Mott insulators

Hiroshi M. Yamamoto*a,†, Mutsumi Hosoda a, Yoshitaka Kawasugi a,b, Kazuhiro Tsukagoshi c, Reizo Kato a,b

a RIKEN, Hirosawa, Wako, Saitama 351-0198, Japan
b Saitama Univ., Saitama, Saitama 338-8570, Japan
c AIST, Tsukuba, Ibaraki 305-8562, Japan

1. Introduction

Molecular conductor is an interesting material with its clear electronic structure and a strong electron correlation which is responsible for various electronic phases including charge-ordering, Mott-insulating, and superconducting [1–3]. Because the strength of electron correlation is sometimes severely dependent on the band filling, it is of intense interest how the electronic phases compete at different filling levels. The chemical doping to molecular conductors is, however, quite difficult since the disordered electric potential induced by the dopants destroys the intrinsic behavior of electrons. Therefore, electrostatic doping into molecular conductors by MIS (metal–insulator–semiconductor) structure is a hopeful candidate to inject carriers in order to control electronic phases without heavy potential disorder. Pioneering studies on such devices have been made by several groups, but those devices suffered poor gain, mobility, quality of the interfaces, and/or crystallinity, which has kept researchers from further discussions [4–6]. To improve the device quality, it is necessary to reduce the carrier number in unit area, and for this purpose we have been studying direct thin crystal growth on a substrate by electrochemical process in solution [7,8]. Although this direct method gives the field effect to some extent, we have recently noticed that a lamination method gives devices of better quality. In this paper, we report the conduction and FET (field effect transistor) properties of molecular conductor devices made in both methods, and compare them.

2. Results and discussion

2.1. α-ET2I3 grown by direct method

α-ET2I3 is known to exhibit MI (metal–insulator) transition at 135K, below which temperature it becomes a charge-ordered insulator (ET = bis(ethylenedithio)tetrathiafulvalene). The metallic phase of this material under high pressure is also known to possess linear band dispersion with zero-gap structure similar to that of a graphene [3,9]. Aim of our work is to survey the field effect on these interesting electronic states.

In chlorobenzene solution of ET and TBA·I3 (TBA = tetrabutylammonium), a thermally oxidized silicon substrate with platinum electrodes was immersed and a current was applied on the platinum to oxidize the ET molecules, after which crystalline cation radical salts of α-ET2I3 were grown directly on the electrode (Fig. 1). The self-assembling nature of the crystal growth makes the ET2I3/SiO2 interface quite smooth, although an incorporation of impurities such as ammonium cation might be expected. After the platinum electrode was separated by microscopic laser apparatus, the temperature dependence of the resistance for the α-ET2I3 microcrystal was measured by the four-probe method (Fig. 2). The result showed several differences from that of free bulk crystal. (1) The M–I transition temperature (Tc) that is observed at 135 K for bulk has been shifted to 150 K; (2) the transition has become broad; (3) the metallic behavior above the Tc has disappeared and the resistance has slightly increased as the sample was cooled down; and (4) the resistance below Tc has become lower than that of the bulk. Moreover, there was a moderate positive correlation between the broadness of the M–I transition and the crystal thickness. These behaviors can be understood as a negative pressure effect from the silicon substrate. Because the thermal expansion coefficient of silicon
Fig. 1. SEM image of α-ET$_2$I. White vertical lines are the platinum electrodes. S and D denotes source and drain electrodes for the FET measurement. The inset is the magnified image of the same crystal viewed from a tilted angle.

Fig. 2. Temperature dependence of the normalized resistance of a free bulk crystal (a), thin crystal on a silicon substrate (b), and a microcrystal on a silicon substrate (c) for α-ET$_2$I.

Fig. 3. Field effect gain of α-ET$_2$I microcrystal on a silicon substrate at $V_G = 70$V.

Fig. 4. Temperature dependence of the normalized resistance of several κ-ET$_2$Cu(N(CN)$_2$)Br microcrystals on silicon substrates. The inset shows $V_G$ dependence of the resistance of sample#1.

(2 ppm/K at r.t.) is far smaller than that of the molecular conductors (ca. 50 ppm/K), the crystal on the substrate will be expanded when the sample is cooled down. This will cause the increase of the $T_C$ and the disappearance of the metallic behavior because the increase of the intermolecular interaction due to the thermal contraction is prohibited on the substrate. In addition, because the upper side of the crystal contracts faster than the lower side as they are cooled down, there should be an inhomogeneity inside the crystal whose extent depends on the height from the substrate surface. This inhomogeneity should be the origin of the broad transition and decrease of the resistance at charge-ordered state.

The field effect on the charge-ordered phase of these microcrystals has been measured by applying gate voltage to the substrates. The source–drain current has been enhanced at positive gate voltage and decreased at negative gate voltage, which indicates that the dominant carrier is an electron. This result is consistent with thermoelectric measurement [10]. The temperature dependence of the current gain is plotted in Fig. 3. The value exhibit a peak of about 1.15 (15% increase) at 20–50 K depending on the sample, below which temperature the field effect suddenly diminished. This steep decrease of the gain seems to be related to the completion of the charge-ordering superlattice formation, although the details are not very clear as yet.

2.2. κ-ET$_2$Cu(N(CN)$_2$)Br grown by direct method

κ-ET$_2$Cu(N(CN)$_2$)Br is known to become superconducting at 11 K. Mott insulating phase is adjacent to this superconducting phase. Switching between these superconducting and insulating phases might be possible by the field effect [11].
The temperature dependence of the four-probe resistance is shown in Fig. 4. There was quite large sample dependence. Some samples exhibited partially metallic behavior while others showed insulating behaviors. It is likely that these behaviors come from the fact that the samples are on the phase boundary due to the negative pressure effect from the silicon substrates. On the phase boundary, this material is known to show phase separation between metallic (or superconducting) and Mott-insulating phases [12].

For the sample#1, we have succeeded in observing a field effect. The resistance drop around 11 K at $V_G = 0$ V has been enhanced at positive gate voltage while it has diminished at negative gate voltage. Since the $T_C$ of the superconducting transition for this material is 11 K, the resistance drop seems to be a percolative superconducting transition. If this assumption is correct, the fraction of superconducting phase in the sample has been increased by the positive gate and decreased at negative gate. This phenomena has been, however, observed only for sample#1, and therefore we need further study to obtain a conclusion.

2.3. $\alpha$-ET$_2$I$_3$ laminated on the substrate

To improve the device quality, it is important to reduce the inhomogeneity inside the crystal. In this sense, it should be effective to increase the width/thickness ratio of the crystal, in which case the crystal will be stretched much homogeneously. Experimentally, however, it is difficult to expect for the crystal of desirable shape to grow at desired position in desired orientation, as long as we employ the direct growth method. In order to improve the device quality, instead, we have tried a lamination method in ethanol. After $\alpha$-ET$_2$I$_3$ crystals were grown on a normal platinum electrode (0.4 mm diameter), a thin crystal (0.5 mm width, 1 μm thickness) was picked up by pipette and dispersed into ethanol. By transferring the crystal into the ethanol, it is possible to reduce the concentration of supporting electrolyte. Then a substrate with gold electrodes was immersed in the ethanol and the crystal was lead onto the substrate by a tip of hair. After the substrate was drawn off from the ethanol, the crystal was fixed as the ethanol dry out.

The result of four-probe resistance measurement is shown in Fig. 2 (curve b). The transition has become sharper and the resistance in the charge-ordered state has become higher than those of microcrystals (curve c), while the shift of the $T_C$ and the non-metallic behavior above $T_C$ has been kept almost the same. These facts mean that the inhomogeneity of the sample has been decreased by employing lamination method, while the negative pressure effect is still maintained.

The field effect for the laminated samples was also measured, of which results are shown in Fig. 5. The gain showed peak structure again at around 30 K, while the value was more than 2 (100% increase). This field effect is one order of magnitude larger than that of the direct growth. Therefore, it is clear that the FET quality of the lamination method is better. Above 150 K, the field effect exhibited ambipolar behavior, which may reflect the zero-gap linear dispersion of this material.

The results for $\alpha$-ET$_2$Cu[N(CN)$_2$]Br in lamination method has been published elsewhere [13].

![Fig. 5. Field effect gain of $\alpha$-ET$_2$I$_3$ crystal laminated on a silicon substrate measured at $V_G = 70$ V. The inset shows $V_C$ dependence of the gain.](image)

3. Conclusion

We have examined two methods for fabrication of FET devices based on molecular conductors. Although it is possible to measure the field effect on the samples grown by direct electrochemical growth, the lamination method gives better results.

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References
