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Phase transition induced by a gate electric field in (BEDT-TTF)(TCNQ) single crystalline field effect transistors

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1. Introduction

Among various organic charge transfer complexes, BEDT-TTF charge transfer complexes which exhibit superconductivity, Mott insulator and charge ordering phase originating from electron correlation have been well investigated. On the half-filled band of a material, if $U_{eff} >> 4t$ then the material is Mott insulator, where U_{eff} is effective Coulomb repulsion and t is intermolecular transfer energy. U_{eff} in organic materials is smaller than that in cuprate because molecular orbitals in organic materials are consist of *p*-electron, whose Coulomb repulsion is smaller than that of *d*-electron in transition metals. Therefore, Coulomb interaction in organic Mott insulator is comparable to other interaction, including electron-phonon interaction etc. As a result, a weak perturbation would be enough to cause phase transition, for example, photo induced metal-insulator transition[1] and gate electric field induced superconductivity[2] etc., which are matter of deep interest. In particular, a large response induced by a small external field is expected at around a phase boundaries of Mott insulator.

For the triclinic phase of (BEDT-TTF)(TCNQ) crystal, approximately 0.5 electrons transfer from BEDT-TTF to TCNQ, which should result in quarter-filling of BEDT-TTF HOMO band and TCNQ LUMO band. However, BEDT-TTF and TCNQ molecules form dimer band caused by the strong dimerization, each of half-filled hole and electron band which conduct in BEDT-TTF and TCNQ column respectively become Mott insulator. Hence the 2-dimensional hole band of BEDT-TTF and the 1-dimensional electron band of TCNQ are coexist in the (BEDT-TTF)(TCNQ) crystal. However, it is recognized that TCNQ band have little contribution to the bulk conductivity because of strong carrier locallization. In addition, observed metal-insulator transition temperature (T_{MI}) had been defined by the maximum of electrical conductivity as 330 K[3-5]. Also, it was observed that there was a peak in the logarithmic derivatives of electrical resistivity at 310 K. Further, it has been known that T_{MI} decrease by the application of hydrostatic pressure and phase diagram resembles that of the V_2O_5 [4].

2. Experimental details

A highly purified BEDT-TTF and TCNQ powder was provided by Nippon Steel Chemical Co., Ltd. A highly doped n-type Si wafer with thermally oxidized SiO_2 of 300 nm thickness was used as a substrate. Au/Cr source and drain electrodes were formed on the SiO_2 substrate by a standard vacuum evaporation techniques. The gap between these parallel source and drain electrodes was approximately 22 μm. A chloroform solution of BEDT-TTF and TCNQ was dropped on the substrate surface and slowly dried in a glove box. With vaporization of the solvent, many needlelike crystals of (BEDT-TTF)(TCNQ) grew on the substrate as seen in Fig.1. The typical dimensions of needlelike crystals were $0.8 \times 300 \times 0.1$ μm^3, although the number and the width of the grown crystals are variable by slow vaporization of the solvent. With the development of the crystallization method, the authors succeeded in growth of less number of wider crystals compared with our previous work[6]. The estimation of carrier mobilities were difficult in the previous work because of the difficulty in determination of effective channel width and length for many scattered crystals. This time, it is possible to count the crystals and determine the effective channel width. It is also possible to determine effective channel length by statistics. The long axis of the needlelike crystals which correspond to *c*-axis of triclinic phase directly bridge the source and drain electrodes. It also had been revealed by the X-ray diffraction that the high crystallinity and majority of triclinic phase, and spontaneous alignment of *a*-axis almost normal to the substrate surface[6].

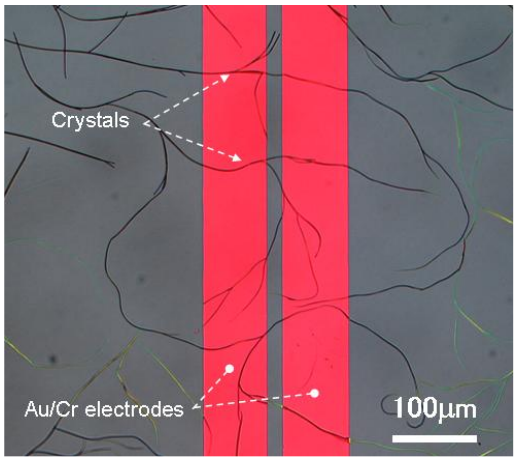

Fig.1. Optical micrograph of (BEDT-TTF) (TCNQ) crystals grown on the SiO_2/Si substrate. Many needle like crystals bridge the source and drain electrode.

3. Results and Discussion

As previously reported[6], obvious ambipolar FET

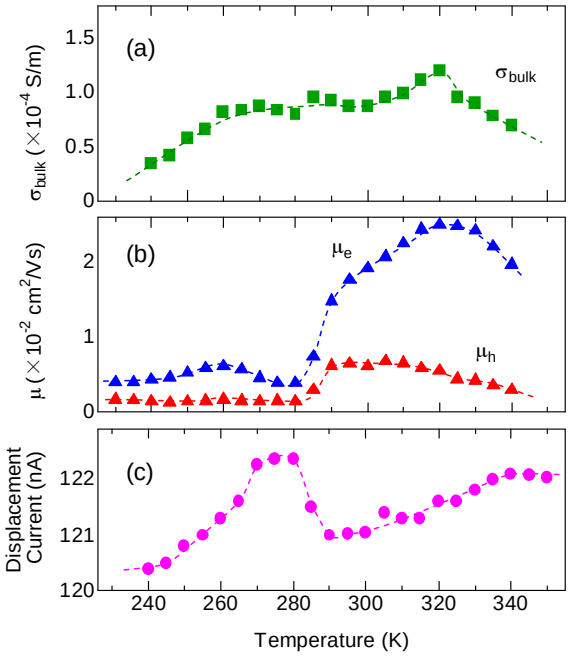

Fig.2. Temperature dependence of (a) electrical conductivity of bulk crystal, (b) field effect electron and hole mobility, and (c) total displacement current. Metal-insulator transition at 320 K, which is known in the prior art, is seen both in the electrical conductivity and electron mobility. Nobel phase transition at 280K is seen in electron and hole mobility, and total displacement current.

characteristics were observed for (BEDT-TTF)(TCNQ) crystalline FET. A precise analysis for ambipolar FET is not so easy because distribution of carriers and electric field in ambipolar FET is more complicated than that in unipolar FET. Therefore, gradual channel approximation for unipolar FET is not available for whole properties of ambipolar FET. However, low V_{DS} (<< V_{GS}) region is recognized as unipolar operation.

Figure 2(a) shows temperature dependence of bulk conductivity (σ_{bulk}). Metal-insulator transition, which is known in the prior art[3], is clearly seen at 320 K. Figure 2(b) shows temperature dependence of averaged field-effect mobility of electron (μ_e) and hole (μ_h) estimated in the linear region of the ambipolar FET characteristics. Electron mobility increases until 260K and have a local maximum at 260K, then decreases with increasing temperature from 260 to 280 K. However, μ_e abruptly begin to increase at 285 K and take a maximum at 320 K. On the other hand, μ_h exhibits similar temperature dependence until 290 K, and begin to decrease above 300 K. In addition, threshold voltage for electron and hole injection is not show significant shift at around 280 K. Temperature dependence of μ_e at 320 K indicate an obvious relation with metal-insulator transition observed in Fig.2(a). Therefore, it is concluded that the observed metal-insulator transition originate from the temperature dependence of electron mobility, which is common in the channel and bulk. On the other hand, there is no corresponding change in σ_{bulk} to the abrupt rise of μ_e at 285 K and the local maximum of μ_e at 260 K. Hence, the observed μ_e and μ_h in this temperature region reflect only the carrier conduction of the Mott insulator/ gate insulator interface, not in the bulk.

Figure 2(c) shows temperature dependence of displacement current $C \cdot dV_{GS}/dt$ at 20 V observed under the application of continuous triangular wave of gate voltage. The displacement current increase until 280 K and rapidly decrease at 285 K, then gradually increase with increasing temperature. This displacement current include the contribution of capacitance of gate insulator, carrier injection, and dielectric properties of (BEDT-TTF)(TCNQ) crystals. We have confirmed that the gate capacitance is almost constant in this temperature region. Since the contribution of carrier injection and dielectric properties cannot be distinguished experimentally, we tried to extract the peak component at around 275 K by calculating differential charge (ΔQ) to applied voltage ($\Delta Q - V$) cycles between two neighboring temperature. The obtained $\Delta Q - V$ curve, which corresponds to the polarization to electric field curve in the parallel capacitance configuration, exhibited ferroelectric-like hystelesis loop. By analogy with the case of TTF-QCl_4 [7], one possible explanation for this phenomena is excess charge transfer and lattice distortion induced by an applied gate electric field.

3. Conclusions

We have revealed that the metal-insulator transition originate from temperature dependence of electron mobility, not hole mobility and any other factor. We also have found anomaly on the temperature dependence of electron and hole mobility which is due to the interfacial phase possibly including ferroelectric-like phase at the FET channel of (BEDT-TTF)(TCNQ) crystalline FET.

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