Temperature dependence of the lattice parameters in (BEDT-TTF)(TCNQ) microcrystals grown on a SiO₂/Si substrate

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Introduction

(BEDT-TTF)(TCNQ) is an organic charge transfer complex composed of a donor molecule bis(ethylene dithio)tetrathiafulvalene (BEDT-TTF) and an acceptor molecule tetracyanoquinodimethane (TCNQ). Among the known three polymorphism on (BEDT-TTF)(TCNQ), triclinic phase crystal is known as an organic Mott insulator[1,2].

We have investigated the electrical properties of (BEDT-TTF)(TCNQ) crystalline field effect transistors (FET) and have found strange electrical properties on field effect mobility of electron and hole, ferroelectric-like dielectric response, pyroelectric current etc.[3,4] These phenomena had not been reported in the electrical properties of bulk crystal. To investigate this novel phenomena from the viewpoint of the crystal structure, our experiments were proposed.

Experimental

(BEDT-TTF)(TCNQ) microcrystals directly grown on a Si substrate were prepared by the solution cast method from a chloroform solution of BEDT-TTF and TCNQ. Typical dimensions of the obtained microcrystals were 0.8×300×0.4 μm³. The microcrystal was not detachable from the Si substrate without breaking them. In addition, novel phenomena mentioned above was observed only in the FET structure. Hence we carried out our experiments by as-grown microcrystals.

Results and Discussion

Figure 2 is a diffraction pattern of the microcrystals grown on the Si substrate. Intensity of the diffraction were not sufficient for precise analysis of the crystal structure because of the small volume of the crystals, but was sufficient for the estimation of the lattice parameters. The assigned diffraction pattern indicated that the a-axis of the microcrystals was normal to the substrate surface. The major diffractions were assigned as a triclinic phase. And residual diffractions were also well assigned as a monoclinic phase. However, temperature dependence of these assigned diffractions did not agree with the temperature dependence measured with a triclinic single crystal. For example, d(2-10) decrease with decreasing temperature in free-standing single crystal. However in microcrystal sample, d(210) increase with decreasing temperature as shown in Fig.3. These difference between a single crystal and microcrystals are explained by the thermal expansion of the Si substrate. Thermal expansion coefficient of Si is approximately 3×10⁻⁶ K⁻¹ at around room temperature. On the other hand, thermal expansion coefficient of organic charge transfer complex is in the range of 20-40×10⁻⁶ K⁻¹. Due to the large difference of thermal expansion coefficient and elasticity of organic crystals, the organic microcrystals are practically “expanded” compared to the natural contraction by lowering temperature as reported in ref.[5]. If the ferroelectric-like dielectric response found in our sample is caused by this negative pressure effect, the negative or positive practical pressure effect caused in an interface or by embedding will be available for the modulation of the electronic state of organic crystals.

References


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