Heteroacene-based organic single crystal transistors under high pressure

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Abstract

Carrier transport properties of heteroacene-based organic field effect transistors are investigated under the application of hydrostatic pressure. In contrast to monotonic and moderate increase in carrier mobility for inorganic semiconductors, present organic devices exhibit anomalous and giant pressure dependent mobility. These performances are revealed by the combination with x-ray structural analysis; it is suggested that electronic properties of hetero elements and molecular rearrangement in accordance with pressurization play key roles for the realization of such pressure responses.

1. Introduction

Molecular solids such as organic semiconductors are constructed by weak van der Waals interaction, resulting in the mechanical flexibility being absent in inorganic materials formed by well-defined covalent bonds. In microscopic scale, the application of the external force induces the ease reorientation of relative molecular arrangement which governs various properties of molecular solids. This should be paid much attention in that performance of organic semiconducting devices are also tunable by applying external pressure and practical organic devices are subjected to mechanical force causing significant pressure by bending, in the prospect of establishing a flexible and soft printed electronics industry. In this presentation we introduce current progress about the pressure effect of organic semiconductors from the viewpoint of charge transport and crystal structure especially focusing on compounds possessing hetero elements peculiar molecular shape.

2. Experimental

Pressure effects of DNTT and newly-designed V-shaped organic semiconductors, DAT-V and DAF-V [thiophene and furan, respectively. See Fig. 1(a)], are employed as channel materials for FET. Organic single crystals are grown by PVT method with Ar gas flow condition. Expect for gold electrodes, the FET are fabricated with polymer materials possessing comparable compressibility with those of typical organic crystals, in order to realize homogeneous compression on whole devices. Then devices are completely coated with STYCASTTM to give devices mechanical stability [Fig. 1(b)]. Hydrostatic pressure is applied to devices through pressure medium (Flourinert FC70/77) and carrier mobility is measured by 4-terminas method at each pressure point. In order to have idea of the variation of crystal structure, x-ray structural analysis were carried out with single crystal.

3. Results and discussion

Pressure dependence of the carrier mobility in individual FETs is shown in Fig. 3. Pressure coefficient $d\mu/dP$ of DNTT, DAT-V and DAF-Vis evaluated to be up to about 3.8 GPa⁻¹, 0.75 GPa⁻¹, and 0.20 GPa⁻¹, respectively. Compounds including sulfur atoms are more sensitive against applied pressure than that of oxygen-including materials. This is attributed to difference in spatial distribution of atomic orbital on sulfur and oxygen atoms; $3p_z$ orbital on sulfur atom is largely spread in space than $2p_z$ on oxygen atom. Especially pressure coefficient of DNTT is found to be extremely large as compared to those for other two materials, and previously reported organic semiconductors such as rubrene which is already one order of magnitude larger than typical values for inorganic semiconductors [1]. Furthermore overall pressure dependence of carrier mobility on DNTT-FET exhibits non-monotonic behavior whereas carrier transports of other materials are lineally improved with increasing pressure. These two features of DNTT observed on pressure response, giant and anomalous pressure effect, are well discussed with the structural change induced by pressurization. According to observation of change in unit cell by x-ray structural analysis, it is deduced that such two intriguing pressure effect on DNTT-FET, giant and anomalous pressure effects, are brought about by the molecular rearrangement in order to suppress Coulomb interaction between sulfur atoms on nearest neighbor sites because of their electro-negative nature [2].

Unlike DNTT with planar molecular framework V-shaped organic semiconductors have bending shape in solid state. From crystal structure analysis, additional force by compression makes molecular shape deformed towards linear shape. In addition to this, molecular rearrangement is responsible for the change in carrier transport property, from anisotropic to isotropic behavior. Details concerned with relationship between charge transport and geometric structure will be discussed.

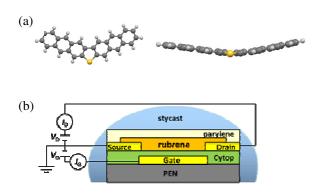


Fig. 1 Molecular shape of V-shaped materials. Central site on five membered ring is sulfur for DAT-V and oxygen for DAF-V, respectively. Left and right pictures are front and side views of molecular shape. (b) Schematic image of FET structure designed for carrier transport measurement under high pressure.

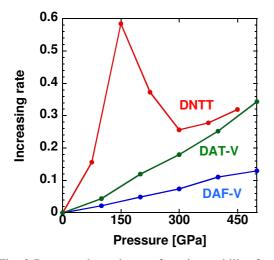


Fig. 2 Pressure dependence of carrier mobility for three organic semiconductor devices. Increasing rate is defined on the basis of mobility measured in ambient condition.

References

[1] Y. Okada and K. Sakai et al., Phys. Rev. B. **84** (2011) 245308.

[2] K. Sakai et al., Phys. Rev. Lett. **100** (2013) 096603.