

Studies of Field-Effect-Transistor Based on Highly-Correlated Molecular Materials

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems



YAMAMOTO, Hiroshi
Professor

LE GOFF, Florian
SHIMIZU, Atsuko



SUDA, Masayuki
Assistant Professor

Visiting Scientist*
Secretary



URUICHI, Mikio
Technical Associate

Field effect transistors (FETs) with organic channel materials are under intense studies because of the possibilities of application in flexible, printable, and large-area electronic devices. Despite single-component neutral molecules like pentacene and rubrene are mainly investigated to pursue high performance (*ex. high mobility etc.*) organic FETs, few studies are known for FETs based on compound-type organic semiconductors. We have been exploiting FET devices with charge-transfer salts of organic molecules, namely cation-radical salts of electron-donating molecules (donors) such as BEDT-TTF and anion-radical salts of electron accepting molecules (acceptors) such as Ni(dmit)₂. Among these materials, our focus concentrates in Mott-insulators in which Coulomb interaction among carriers blocks metallic transport. In this highly correlated situation of charge carriers, Mott insulator stays in a fragile semiconducting state, where carrier injection, chemical and/or physical pressure (or strain), and thermal fluctuation can drive it into a metallic state by phase transition (*i.e.* Mott transition: Figure 1). One can expect an abrupt change of the conductivity of device due to phase transition that is induced

by very small external stimuli. More specifically, it is anticipated that the Mott-insulating state can be switched to a metallic state by a field effect, since the carrier density (bandfilling) of a FET interface can be finely modulated by an electrostatic field from the gate electrode. Indeed, our previous work showed such an insulator-to-metal transition in terms of the band structure, and these results provide not only a possibility of application use of organic Mott-FET but also a significant insight into the mechanism of Mott transition itself. We are now expanding our research target both to the superconducting transition of Mott-FET and to its room-temperature operation.

(BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene,
dmit = 1,3-dithiole-2-thione-4,5-dithiolate)

1. Field-Induced Superconductivity in an Organic Mott-FET

κ -(BEDT-TTF)Cu[N(CN)₂]Br (κ -Br) is an organic super-

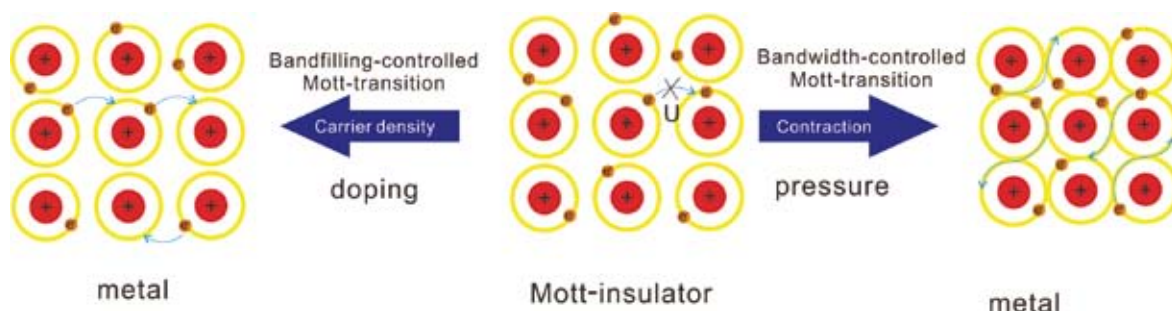


Figure 1. Concept of a Mott-insulator (center) along with its bandfilling-controlled (left) and bandwidth-controlled (right) Mott transitions. When the band is half-filled and band energy is small, the carriers are localized because of on-site Coulomb interaction (U). This situation is broken down either by changing the carrier concentration or by compressing the lattice. In many cases, the Mott transitions are associated with superconductivity at the boundary between metallic and insulating phases.

conductor whose electronic state is Mott-insulating at room-temperature but turns into metallic at low temperature through a crossover around 50–100 K, possibly because of an increase of bandwidth upon thermal contraction. In our previous works, a tensile strain altered its ground state into a Mott-insulating state, when its thin (100–300 nm) crystal is laminated on top of $\text{SiO}_2/\text{Si}^{++}$ substrate and cooled down to low temperature. Although the electronic state at low temperature became completely insulating in this experiment because of the very small thermal expansion coefficient of Si substrate (2 ppm/K), one can anticipate from the T - P (temperature vs. pressure) phase diagram that mixed electronic state between superconducting and Mott-insulating states can be realized when the tensile strain is much weaker. To achieve such a mixed state (or, percolate-superconducting state) in the device, where phase-separation occurs between superconducting and Mott-insulating states, we have chosen Nb-doped SrTiO_3 as a back-gate substrate because of its larger thermal expansion coefficient (*ca.* 10 ppm/K) than Si. An aluminum oxide layer was grown by atomic layer deposition technique to form a gate dielectric on the substrate. After lamination of κ -Br on the substrate, the Mott-FET device which showed a weakly insulating behavior at low temperature was fabricated (Figure 2).

Upon applying a positive gate voltage, the resistivity went down and weakly metallic behavior was observed at $V_G > 2$ V. By further increasing the gate voltage up to 8 V, the device showed a sudden drop of resistivity around 5 K, which can be attributed to superconductivity. Taking into account of bistable I - V characteristics observed in the low resistance region, the above transition can be understood as a percolation transition of superconducting islands that is induced by the electrostatic doping of electrons. The transition temperature increased as the gate voltage rose and saturated around $V_G = 11$ V. The above result is the first example of field-induced superconductivity in organic materials, and can be utilized for uncovering a phase diagram of organic Mott system in the simultaneous control of band filling and band width.¹⁾

2. Operation of Organic Mott-FET at Higher Temperature

In order to operate the organic Mott-FET at higher temperature, hopefully at room temperature, it is necessary to realize much larger Mott gap energy and thinner crystal thickness. For this purpose, we are examining several strategies in parallel.

κ -(BEDT-TTF) $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ (κ -Cl) is a Mott-insulator with larger Mott gap than κ -Br and is therefore suitable for examining the influence of an increase in Mott-gap energy on the device performance. For example, it has higher resistance than κ -Br and exhibit better ON/OFF ratio. In addition, it always shows ambipolar behavior, probably because of its clean surface. This situation allows us to analyze the critical exponents of filling-controlled Mott transition, which will give

us important information about ON/OFF efficiency of the device (Figure 3).²⁾ Because it is also possible to control the Mott gap energy by applying a mechanical strain, κ -Cl device provides an ideal platform to expand Mott-FET strategy to higher temperature.

Another candidate of the channel material for Mott-FET that can be used at room temperature is (BEDT-TTF)(TCNQ). We are exploiting this material both in a crystalline and amorphous form to find a better FET setup for simple but highly efficient device operatable at room temperature. (TCNQ = tetracyanoquinodimethane)

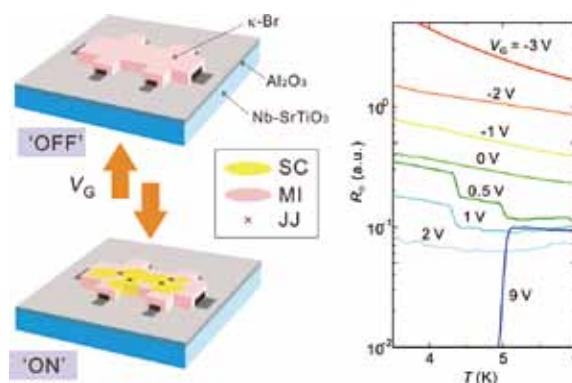


Figure 2. The device structure and temperature dependency of device resistance under various gate voltages. The device comprises κ -Br thin-layer single crystal and $\text{Al}_2\text{O}_3/\text{SrTiO}_3$ substrate. By applying a positive gate voltage, the resistance of the device starts decreasing, while a negative gate voltage results in an increase of the resistance. Although superconducting (SC) and Mott-insulating (MI) phases are separated in the device, the four-terminal resistance drops to zero when the Josephson junction (JJ) network forms a pathway to shunt the voltage terminals. This kind of percolation transition is clearly observed in the right panel, where the resistance drops at 5 K with a gate voltage of 9 V.

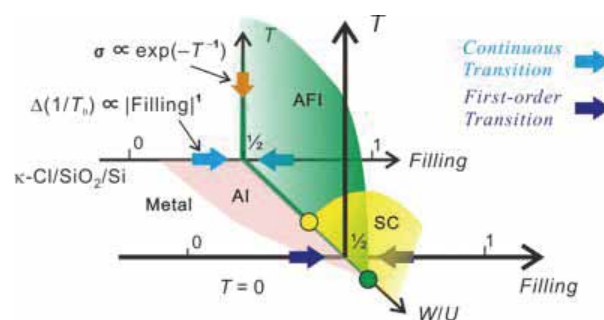


Figure 3. Universal phase diagram based on the experimental results obtained by organic Mott-FETs.

References

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