PROGRESS REVIEWS

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To cite this article: Hiroshi M. Yamamoto et al 2018 Jpn. J. Appl. Phys. 57 03EA02

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Organic phase-transition transistor with strongly correlated electrons

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Received August 7, 2017; accepted September 14, 2017; published online January 24, 2018

Phase transitions show large responses in physical properties including electrical conductivity changes caused by thermodynamic parameter control or by external stimuli. Thus, an element that shows electronic phase changes in response to input signal may help to provide efficient electronic devices. Strongly correlated electron systems such as Mott insulators are promising candidates for this purpose because they exhibit a large number of electronic phase transitions. Recently, much progress has been made in phase-transition transistors based on organic Mott insulators. In this paper, we review organic transistors that exhibit an insulator-to-metal or an insulator-to-superconductor transition induced by external stimuli such as electric fields, strain, and light. © 2018 The Japan Society of Applied Physics

1. Introduction

The past half-century has witnessed the miniaturization of transistors and the associated increases in computational speed and data capacity that scale inversely with the size of the elements. However, the metal oxide semiconductor field-effect transistor (MOS-FET) has several obstacles preventing further improvement, including dopant number fluctuation and subthreshold swing limited by thermodynamic requirements. To overcome these problems for next-generation computing, many device concepts and architectures should be tested. Newns and coworkers at IBM have proposed a phase-switching transistor based on Mott insulators. This “Mott-FET” can switch its conductance owing to a phase transition by the electrostatic control of carrier density. In the first paper published in 1997,\textsuperscript{1} they described field-effect devices based on organic charge transfer salts (Fig. 1). This is a kind of serial connection of single-electron transistors whose Coulomb blockade occurs at each molecule. Although this idea has been tested in oxide-based Mott-FETs,\textsuperscript{2} performances exceeding those of silicon-based transistors have not yet been obtained. Another interesting feature of the Mott-FET is its potential to become a superconducting field-effect transistor.\textsuperscript{3} Because some Mott insulators, including high-$T_c$ cuprates,\textsuperscript{4} bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) cation radical salts,\textsuperscript{5,9} and fullerene anion radical salts,\textsuperscript{10} exhibit superconductivity in the vicinity of a Mott transition, it might be possible to induce superconductivity at low temperatures at the Mott-FET interface. Indeed, recent advances in ferroelectric-gate transistors\textsuperscript{11} and electric-double-layer transistors (EDLTs)\textsuperscript{12} allow the switching of high-$T_c$ cuprates’ superconductivity by electrostatic doping, although the latter’s phase switching is only possible above the freezing point of ionic liquid, which is approximately 200 K.

With this background in mind, we have started the construction of an organic Mott-FET based on BEDT-TTF cation radical salts. In this review, a brief summary of our recent achievements is provided.

2. Phase-transition transistor based on organic charge-transfer salts

2.1 Mott-FETs based on BEDT-TTF salts

Early trials to realize Mott-FETs based on molecular materials were conducted by two independent groups lead by Kudo\textsuperscript{13} and Hasegawa.\textsuperscript{14} Kudo et al. reported the FET performance of drop-casted (BEDT-TTF)(TCNQ) on a silicon substrate with an oxide layer (TCNQ = tetracyanoquinodimethane). As expected for a Mott-FET, this device showed an ambipolar field effect. Because this charge-transfer complex is believed to show Mott transition at approximately room temperature, they reported the temperature dependence of conductance in the range of 100–300 K as a measure of metallicity after phase transition. Indeed, they succeeded in obtaining metallic behavior, or a positive $d\rho/dT$ slope, after the application of a highly positive gate voltage, although its metallic temperature range is only limited to approximately around 250–300 K. The field-effect efficiency was also moderate and resulted in a device mobility on the order of $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ and an ON/OFF ratio of 100 at maximum. Hasegawa et al. reported FETs fabricated on top of (BEDT-TTF)(F$_2$TCNQ) single crystals (F$_2$TCNQ = 2.5-difluorotetracyanoquinodimethane). Again, ambipolar characteristics were obtained, but the device mobility and ON/OFF ratio were even lower than those reported by Kudo et al. Some of the possible reasons for these low performances include low interface quality and a robust Mott insulating state far from the Mott transition in their pressure-temperature phase diagram.

To improve the performance of organic Mott-FETs, we have developed a method of fabricating a FET using a thin-layer single crystal of $\kappa$-type BEDT-TTF salt, whose phase diagram is shown in Fig. 2(a). By this method, it has become possible to obtain a Mott insulating state very close to the metallic/superconducting phase in a crystal of $\kappa$-Br...
Various values of band...surrounded by a superconducting phase, although this is not yet...cooled, respectively. (b) Phase diagram of...rarement. It seems that the thin crystal...the SiO2 surface by van der Waals or dipole forces, thus sustaining the tight lamination, resulting in an effectively negative pressure in the two-dimensional conduction layer of κ-Br. This strain effect is again confirmed in the case of a polystyrene substrate, where the superconducting (SC) transition temperature slightly decreases (Fig. 3, inset) owing to the compressive strain from the substrate resin whose thermal expansion coefficient is about 80 ppm/K. [Note that the phase boundary slope in this situation is negative in Fig. 2(a)].

2.2 Phase transition at Mott-FET interface

A Mott insulating FET channel formed by the above process allows field-effect experiments at low temperatures. Figure 4 shows the structure of the device, and with a gate electric field from the back-gate substrate, the device shows n-type switching of conductivity. The device mobility estimated from the slope of transfer characteristics was about 100 cm² V⁻¹ s⁻¹ in our first report, and it now exceeds 200 cm² V⁻¹ s⁻¹ for a FET based on a sister compound, κ-CI \{κ-(BEDT-TTF)₂Cu[N(CN)₂]Br\}. This is the highest value ever observed for an organic FET. The latter FET clearly shows metallic behavior in conductivity, or a negative \(d\sigma/dT\) at low temperatures and high gate voltages \(V_G\), although there is an Anderson localization regime at very low temperatures. It is also possible to apply a scaling plot on both metallic and insulating sides of the transition, as shown in Fig. 5. This is clear evidence of a filling-controlled insulator-to-metal transition in an organic Mott insulator.
Besides the conductivity, Hall-effect measurement also provides important evidence of phase transition. Since the Hall coefficient \( R_H \) has a direct relationship with the carrier density \( n \) as \( R_H = -1/(ne) \), the change in interface carrier number can be detected by magnetotransport measurements. The sign of the carrier measured by this method was always positive, and exhibited a steep jump from the OFF state to the ON state, as shown in Fig. 6. In the ON state, the carrier number approached a half-filled condition with a narrow interpretation, the negative Seebeck coefficient is known to re-appear in an insulator-to-metal phase transition at the interface through conductivity, Hall-effect, and Seebeck-effect measurements in our Mott-FET device.

2.3 Particle–hole asymmetry at Mott-FET interface

Although the polarity of the FET performance is dominated by n-type behavior, it is also possible to observe ambipolar switching when the sample quality is good enough. It seems that \( \kappa \)-Cl has better surface quality than \( \kappa \)-Br because of chemical stability, and it more easily shows an ambipolar behavior, as observed in our \( \kappa \)-Cl device. This negative Seebeck coefficient is known to reflect the topology of the Fermi surface expected for the metallic phase of \( \kappa \)-Br. In total, we found evidence of an insulator-to-metal phase transition at the interface through conductivity, Hall-effect, and Seebeck-effect measurements in our Mott-FET device.
underlying this asymmetry has been clearly uncovered by experiments using EDLT.\cite{21,22} From the Hall-effect measurements and theoretical calculation (cluster perturbation theory), it turned out that the carrier number in the p-type region is about one-third of the expected carrier number for the metallic state because of pseudogap formation (Fig. 7). This can be understood by considering the original band structure of \( \kappa \)-type BEDT-TTF salts: electron doping decreases the density of states at the Fermi level while hole doping increases it. Since the density of states is a measure of carrier mass, the carriers in the p-type region show enhanced correlation and heavier carrier mass, especially at several points near the van Hove singularity, to form a \( k \)-dependent pseudogap. This pseudogap also gives rise to a simultaneous increase in conductivity and Seebeck coefficient, resulting in a high power factor for a thermoelectric material.\cite{22}

3. Mott-FET with superconducting channel

3.1 Electric-field-induced superconductivity

The concept of electric-field-induced phase transition can be extended to a superconducting transition at the FET interface. Compared with the high-\( T_c \) cuprates, there are two advantages in using molecular Mott-FETs as an active material for field-induced superconductivity switching. One is their low carrier density \((2 \times 10^{14} \text{ cm}^{-2})\), which is less than one-third of that for cuprates \((7 \times 10^{15} \text{ cm}^{-2})\). Owing to this, the extent of controllability over band filling is more than three times larger for organic Mott insulators, as long as the same gate dielectric is employed. Another advantage is its flexible lattice that allows tuning of the bandwidth over a wide range upon application of a small pressure or strain. This situation provides fine tuning of the effective on-site Coulomb interaction \((U/W)\), where \( U \) is the on-site Coulomb energy and \( W \) is the bandwidth) through substrate bending, for example. Note that both \( U \) and \( W \) are modified by pressure and/or strain in \( \kappa \)-type BEDT-TTF salts, but \( W \) is more sensitive to the lattice constant. The above-mentioned high controllability of the system makes the molecular Mott insulator attractive to realize both a real-time switching device of superconductivity and a tool to investigate the unknown phase diagram of the Mott insulating material. Note that the electric-field-induced switching of high-\( T_c \) cuprates is normally carried out using EDLT, where the switching of the phase is limited at a higher temperature than the glass transition temperature of ionic liquid (FETs with high-\( T_c \) cuprates operate only at depletion mode). The pressure-induced superconductivity of nondoped cuprates ("pure" Mott insulators) is also impossible because of their hard lattices.

The first example of a superconducting FET with a molecular conductor was fabricated by employing \( \kappa \)-Br on a Nb-doped SrTiO\(_3\) (Nb-STO) substrate.\cite{23} STO shows a rather larger thermal expansion coefficient, ca. 10 ppm/K, at room temperature, than silicon, and guides the \( \kappa \)-Br crystal into a percolated superconducting region, as shown in Fig. 2. In this situation, field-induced carriers can alter the band filling to reduce the electron correlation and induce superconductivity at the interface. Figure 8 shows the operation of one of the devices, clearly indicating the superconducting transition at 5 K when a \( V_C \) of 9 V is applied. This is the first example of an organic FET with a superconducting channel. Note that the operation temperature of this organic device is above the liquid helium temperature. On the basis of the ambipolar nature of Mott-FETs, it should also be possible to find an ambipolar superconducting action in these devices. Such a device has not been found yet, but clues have been found in an ambipolar device described in Ref. 24.

3.2 Strain-induced superconductivity

Another method to switch superconductivity is the use of one-dimensional strain through substrate bending.\cite{25} When a \( \kappa \)-Cl crystal is laminated on a poly(\( p \)-xylylene)/Au/poly- (ethylene napthalate) substrate, it shows superconductivity at about 12 K owing to the compressive strain from the substrate. This superconductivity can be suppressed when a one-dimensional tensile strain is applied to the crystal by pushing the substrate from the back surface (Fig. 9). We found that the \( \kappa \)-Cl crystal switched into a completely insulating state with a tensile strain of only 0.3%, with a conductivity change of ten orders of magnitude. This type of efficient response can potentially be used for highly sensitive sensors at low temperatures. This device also showed an electric-field-induced superconducting phase transition, as determined by gate-voltage scanning in the percolated superconductivity region.

3.3 Light-induced superconductivity

The last example of superconducting transition at an organic interface is light-induced superconductivity.\cite{26} Figure 10 shows the structure of a device where a photochromic molecular layer is formed as a self-assembled monolayer between the \( \kappa \)-Br crystal and the back-gate substrate. The photochromic spiropyran is aligned in a unidirectional manner, because it is covalently connected to the substrate at specific positions of the molecule. Therefore, after UV light irradiation, the photochemical reaction generates a large interface dipole owing to the zwitter-ionic structure of the merocyanin dye, which is a product of the photochromic reaction. This kind of interface dipole moment is known to induce excess carriers at the organic FET channel, and thus can potentially switch the superconductivity.

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**Fig. 7.** (Color online) Gate-voltage dependence of \( 1/eR_H \) for \( \kappa \)-Cl EDLT devices at 30 K. Data from three different samples are shown. The blue and red solid lines denote the \( 1/eR_H \) estimated from the area surrounded by the noninteracting large Fermi surface \((\beta \text{ orbit})\) and the one surrounded by the small lens like Fermi surface \((\alpha \text{ orbit})\), respectively.
We have tested this process at 5 K, as shown in Fig. 11. Initially, the device is in a high-resistance state because of previously mentioned tensile strain. Then, UV light is shone on the device, which results in a rapid decrease in resistance. The low-resistance state obtained after 3 min can be maintained even after the UV light is switched off, because the photoreaction product does not undergo the reverse reaction at low temperature unless visible light irradiation is applied.

Indeed, after visible-light irradiation, a sudden increase in resistance is observed, and the original high resistance is restored within 3 min. To confirm that this low-resistance state is associated with superconductivity, the light irradiation was stopped every 30 s to check the temperature dependence of the resistance. At an irradiation time of 180 s, a clear drop in resistance was observed at 7.3 K, indicating a percolative superconducting transition induced by light. This was also confirmed by magnetization measurement.

Since this device has a bottom gate structure as well as the phototunable dipole layer, a dual gate sweep was performed. The results shown in Fig. 12 clearly indicate that the photoinduced p-type carriers act cooperatively with the electric-field-induced p-type carriers. Therefore, the present photoinduced electric double layer is a continuous and remote switch for a superconducting device. Since the photo manipulation does not require any electric wiring, this kind of device may find new applications in future superconducting electronics. At the same time, the electric field generated by the light can help find unknown electronic phases in the...
molecular interface owing to its large carrier injection capability. Recently, an n-type carrier injection has also been accomplished with a different design of photochromic molecular layer.27)

4. Conclusions

It has been shown that two kinds of phase transitions, an insulator-to-metal and an insulator-to-superconductor transition, are possible at a molecular interface with strongly correlated electrons. A new concept and the possibility of high performance are clearly shown, although an actual device is yet to be fabricated. For example, a κ-Br Mott-FET cannot be operated at room temperature because of the small Mott gap and the shunting effect from the bulk crystal. Superconducting devices show high contact resistance that prevents the transport of supercurrent between connected devices. A fabrication process without large sample dependence is also necessary. To address these issues, we are now developing a new type of Mott-FET based on SAM technology.28) On the other hand, a study of fundamental physics underlying the strongly correlated electrons can be performed using the present devices. Our measurements will provide much information that can be compared with the theoretical calculations.29–31) Owing to its soft lattice and low carrier density, the organic Mott-FET provides an indispensible opportunity to complete the phase diagram around a two-dimensional Mott insulator as a function of $T$, $U/W$, and band filling.

Acknowledgments

The authors are deeply thankful to their collaborators: Drs. R. Kato, Y. Sato, N. Tajima, K. Seki, T. Fukunaga, T. Minari, K. Tsukagoshi, J. Pu, T. Takenobu, S. Yunoki, M. Nakano, Y. Iwasa, S. Namuangruk, and H. Sakurai. The authors also acknowledge the financial support from RIKEN, IMS, JSPS [Grant-in-Aid for Young Scientists (A) (No. 16H06058), Grant-in-Aid for Scientific Research (B) (No. 16H04140), (S) (No. 16H06346), Grant-in-Aid for Scientific Research on Innovative Areas (No. 15H01005)], and JST (PRESTO and ERATO Grant Number JPMJER1301). Part of the work was conducted in the Equipment Development Center (Institute for Molecular Science), supported by the Nanotechnology Platform Program (Molecule and Material Synthesis) of the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

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