Strain-Tunable Superconducting Field-Effect Transistor with an Organic Strongly-Correlated Electron System

Masayuki Suda,* Yoshitaka Kawasugi, Takeo Minari, Kazuhito Tsukagoshi, Reizo Kato, and Hiroshi M. Yamamoto*

An electric field-induced tuning of the interface carrier density through field-effect transistor (FET) structures has long been a key technology in modern electronic industry. [1–3] Especially, in the past half century, field-induced superconductivity in condensed matter has been one of the main subjects in this field. [4] Recent advances in the electrostatic carrier-doping concepts such as electric-double-layer (EDL) transistor configuration realized an accumulation of extremely high carrier density and field-induced superconductivity in inorganic (highly correlated) materials. [5–7] However, EDL-induced superconductivity has not been realized in organic materials because the application method of EDL transistor technique to organic materials has been well-established only at room temperature. [8–9]

Recently, we have demonstrated the first field-induced superconductivity in the organic-based FET. [10] We used a thin single crystal of \( \kappa \)-(BEDT-TTF)\( \_2 \)Cu[N(CN)\( \_2 \)]Cl (\( \kappa \)-Br) laminated on Nb-doped SrTiO\( \_3 \) (STO) (BEDT-TTF = bis(ethylenedithio) tetraethylvalene). Novel concept of this device was to take advantage of the soft lattice of organics to tune the intermolecular interaction by strain effects from the substrates. Bulk \( \kappa \)-Br is a strongly-correlated molecular superconductor (\( T_C = 11.6 \) K) [11] that neighbors Mott-insulating phase. [12] The ground state of \( \kappa \)-Br on this device was tuned in the vicinity of a band-width-controlled Mott transition by tensile strain from the relatively harder substrate. As a result, field-induced superconductivity was realized by electrostatic carrier doping into \( \kappa \)-Br near the band-width-controlled Mott transition. However, substrate-exchange is needed to control the strain effects, that is, the strain effects in this device is not able to be controlled continuously.

In this study, we fabricated a novel type of organic FET, in which strain effects can be finely tuned continuously. The device has a bottom-gate FET configuration where a thin single crystal of \( \kappa \)-(BEDT-TTF)\( \_2 \)Cu[N(CN)\( \_2 \)]Cl (here after denoted as \( \kappa \)-Cl) is used as a channel (Figure 1a, b). The substrates are flexible polyethylene naphtalate (PEN) sheets with thermally evaporated Au gate-electrodes and parylene gate-dielectric. In this device, desired strain effects can be induced by bending the substrate from the back side of the substrate (Figure 1c). Hence, this device enabled coregulation of “bandwidth” and “band-filling” in \( \kappa \)-Cl by combination of the field-effects and the strain-effects.

Figure 2 shows the temperature dependence of the four-probe resistance for the \( \kappa \)-Cl device and bulk crystal without any substrate. The \( \kappa \)-Cl device exhibited a superconducting behavior below 11.8 K (blue plot) despite the Mott insulating character for the bulk crystal (orange plot). The superconducting transition temperature of 11.8 K is in good agreement with that of the \( \kappa \)-Br crystals (11.6 K), when one considers the strain effect in the following discussion: Generally, the ground state of \( \kappa \)-type BEDT-TTF family can be finely tuned by physical or chemical pressure. The \( \kappa \)-Cl, which lies next to \( \kappa \)-Br in the phase diagram, becomes a superconductor by application of low pressure (−300 bar). [13] It is likely that a slightly compressive strain from the substrate corresponds to a similar shift in the phase diagram, because thermal expansion coefficients are different between a PEN and a \( \kappa \)-Cl crystal along the a axis (−35 ppm/K and 20−30 ppm/K at room temperature, respectively). Similar positive strain effect was also observed in a grease-coated \( \kappa \)-Cl crystal [14] and a \( \kappa \)-Br crystal laminated on a polystyrene substrate. [17] On the other hand, two-dimensional tensile strain effects were also observed in \( \kappa \)-Br crystals laminated on STO [10] or SiO\( \_2 \)/Si substrates, [18] those crystals of which were guided into Mott insulating state at low temperature.

A tunable tensile strain was applied to the \( \kappa \)-Cl devices by providing the mechanical pressure from the back side of the substrate. The strain is a kind of uniaxial strain, in which the direction of the tensile force is applied parallel to the substrate bending. The current direction was set parallel to the crystal a axis (Figure 1b). The magnitude of the strain was defined as \( S \) (%: percentage of the extended length in the substrate).

Figure 3a shows temperature dependence of the resistance under the various strain values. The initial superconducting transition temperature was slightly increased from 11.8 K to 12.3 K with increasing the strain until \( S = 0.67\% \). When the strain reached \( S = 0.78\% \), the \( \kappa \)-Cl device showed insulating behavior below 20 K and it showed a small resistance drop at 12.4 K. This behavior indicates that separation between a superconducting state and a Mott insulator state occurs in the device with \( S = 0.78\% \). Finally, the \( \kappa \)-Cl device became a insulator at \( S = 1.11\% \). This phenomena can be well-understood by considering on the pressure-temperature (P-T) phase diagram of \( \kappa \)-Cl investigated using He gas pressure by Lefebvre et al. [19] and Kagawa et al. [20] (Figure 3c). According to this phase diagram,
κ−Cl is an antiferromagnetic Mott-insulator at ambient pressure. When κ−Cl is pressurized, it becomes metallic and undergoes a superconducting transition at $T_C = \sim 13.1$ K under a pressure of 30 MPa. It is considered that pressure induces the Mott transition. When one reviews current strain-induced transition based on these phase diagrams, the lower-strain ($S = 0$) region for the κ−Cl device seem to correspond to the higher-pressure region (superconductor or metal region) of the phase diagram, while the higher-strain region correspond to the lower-pressure region (Mott insulator region). In other words, the strain effects seem to be working as negative pressure-like effects. In Figure 3c, the temperature trajectories of the κ−Cl device with the corresponding strain-effects of 0.00, 0.78 and 1.11%, respectively, are expressed as orange, green and blue arrows on the P-T phase diagram.

Isothermal resistance as a function of the strain for the κ−Cl devices was also investigated (Figure 3b). Above ca. 40 K, the resistance variation against the strain can be regarded as crossover between metal and insulator, because the resistance gradually increased with increasing the strain without any

Figure 1. a) Schematic illustration for the device configuration without (upper) and with (lower) strain effects. b) Optical microscope image of the κ−Cl single crystal laminated on the substrate; scale bar = 200 µm. c) Optical image of the stepper-positioner installed in a probing insert designed for PPMS (left) and the detailed dimensions of the substrate and the sample holder. The magnitude of the strain-effects was defined as $S = (\Delta L/L) \times 100$ (%) (right).

Figure 2. Plot of resistance $R$ versus temperature $T$ for bulk κ−Cl crystal (orange plot) and the κ−Cl device (blue plot).
anomaly and hysteresis for this temperature region. On the other hand, for the lower temperatures, clear resistance jump was observed by increasing the strain. This means that the thermodynamic crossover is changed into the first-order transition. The first-order transition was also evidenced by the existence of hysteresis (not shown here). The band-width-controlled Mott transition in a $\kappa^\text{−}\text{Cl}$ has been well-investigated by He gas pressure.\[19−22]\ The resistivity measurements under continuously controllable He gas pressure unveiled the Mott phase diagram, where the first-order transition line dividing the insulating and metallic phases has an endpoint around 40 K.

The one-to-one relationship between the hydrostatic pressure $P$ and unidirectional strain $S$ can be also found in a two-dimensional phase diagram of the present device. Figure 4 shows the contour resistance mapping representing a strain-temperature ($S$-$T$) phase diagram for the $\kappa^\text{−}\text{Cl}$ device. The resistance values are those from Figure 3b. The transition line (narrow yellow region) in the $S$-$T$ phase diagram has a kink around 30 K. Similar kink around 30 K can be also seen in the $P$-$T$ phase diagram, which was interpreted as the relief of spin entropy due to magnetic ordering around 30 K.\[12]\ The current system...
seems to be reproducing such a hydrostatic pressure-induced phenomena despite the uniaxial feature of the strain-effects. The kink in the strain-induced transition line can be reasonably understood by interpretations of the strain as a negative pressure effect. Therefore, observed metal(superconductor)-insulator transition in the current system must be the bandwidth-controlled Mott transition by the strain-effects that produce similar influence as a negative pressure. Judging from the analogy between these two phase diagrams, the tunable range of insulator transition in the current system must be the band-width-controlled Mott transition by the strain-effects that produce similar influence as a negative pressure. The kink in the strain-induced transition line can be reasonably understood by interpretations of the strain as a negative pressure. 

Successively, we tried electrostatic doping into the \( \kappa \)-Cl device under various strains. By applying a gate voltage \( V_{g} \) at low temperature (below 12 K), the field-effect was found for Mott insulating phase \( (S = 0.89\%) \) with n-type polarity (Figure 5a). The \( V_{g} \)-dependent variation of the four-probe resistance is reversible without significant hysteresis. The field-effect mobility is given by \( \mu_{FE} = (1/C_{i})(d\sigma_{i}/dV_{g}) \), where \( C_{i} \) is the normalized capacitance of the gate insulator and \( \sigma_{i} \) is the sheet conductivity. The \( \mu_{FE} \) value derived from the transfer curve was 3.78 cm\(^2\)/Vs at 12 K (Figure S4a). The field-effect is reproducible in many samples although the field-effect polarity is sample dependent as shown in supporting information (device 2–4). The ambipolar \( \mu \)-type field-effect transfer-curves were also found in other samples (shown in supporting information), indicating that present \( \kappa \)-Cl device is intrinsically ambipolar as expected for Mott insulators.\(^{[23]} \) The observed sample dependence of the field-effect polarity would be due to changes in the surface (interface) conditions of the crystals during the fabrication process. We speculate that this polarity variation is depending on whether the outermost surface (interface) layer of the \( \kappa \)-Cl crystals is cation-rich or anion-rich. For example, cation-rich-interface would show n-type polarity and anion-rich-interface would show p-type polarity.

Most important nature of present \( \kappa \)-Cl device is abnormal field-effects found in the Mott insulator/superconductor mixed phase (Figure 5b). By applying a gate voltage, n-type field-effect was observed with \( S = 0.78\% \) below 12 K (the Mott insulator/superconductor mixed phase) while almost no field-effect was found over 13 K (metallic phase). The \( V_{g} \) dependence of the sheet conductance at 12 K (Figure S4b) showed strong non-linearity until 50 V–V\(_{g}\). Although the ON/OFF ratio was only ca. 1.1, a remarkable device mobility, ca. 5900 cm\(^2\)/Vs, was obtained in this phase when we selected a linear-fit range of 40–50 V–V\(_{g}\), which is the highest mobility ever reported for an organic FET (the average device mobility between 0–50 V–V\(_{g}\) is 1740 cm\(^2\)/Vs). Similar device mobility values of 4340 and 4550 cm\(^2\)/Vs (2500 and 4000 cm\(^2\)/Vs in average) were also obtained in device 3 and 4 (see Figure S2 and S3). Hence, we believe these remarkable mobility are universal features for this type of device configuration. In the present device, the system would have inhomogeneous islands-like partially superconducting phases in the Mott insulating phase. Such a situation was already visualized by infrared spectroscopy mapping\(^{[24]} \) for bulk crystals of partially deuterated \( \kappa \)-Br. These phase separation is considered to originate from the bistability of the free energy between a Mott insulating phase and a superconductor. The significant field-effects in a mixed phase suggests that the superconducting fraction emerges (expands) by electrostatic doping into the insulating phase that can reduce the Coulomb repulsion among charge carriers. To confirm this hypothesis, we investigated the field-effects in the mixed state under strong magnetic fields at 11 K (device 4). As shown in Figure 6a, magnitude of the field-effects in the mixed state were successively suppressed by increasing the magnetic field and finally, ca. 90\% of the field-effect was suppressed with magnetic field of 7 T. Such magnetic field-dependent effects were not observed for the field-effects in the Mott insulating phase. This result clearly elucidate that the field-induced phase in the mixed state was not metallic phase but the superconducting phase, which could be destroyed by strong magnetic fields. A schematic image of field-induced emergence of the superconducting phase is shown in Figure 6b. As mentioned above, our previous work realized field-induced superconductivity in the \( \kappa \)-Br device by choosing the appropriate substrate whose strain guided it into the vicinity of a band-width-controlled Mott transition.

Figure 5. a) Plot of resistance \( R \) versus applying gate voltage \( V_{g} \) for the \( \kappa \)-Cl device at 2 – 12 K with \( S = 1.00\% \). b) Plot of resistance \( R \) versus applied gate voltage \( V_{g} \) for the \( \kappa \)-Cl device at 7 – 12 K with \( S = 0.78\% \).
Corresponding field-induced superconductivity must have occurred also in the current κ−Cl devices utilizing the combination of continuous strain effects and field-effects.

In summary, we have realized a strain-tunable organic FET with a flexible substrate. In this novel device structure, electronic phases could be controlled both by “band-filling” and by “band-width” continuously. Co-regulation of “band-filling” and “band-width” in the strongly-correlated organic material, that is κ−Cl, realized field-induced emergence of superconducting fractions at low temperature. Furthermore, this novel strategy will be useful for not only current material but also any other organic/inorganic materials to explore undiscovered electronic phases.

Experimental Section

An unoriented isotropic polyethylene naphthalene (PEN) sheet (Theonex, Teijin Chemicals) cut into 4 × 18 mm rectangular dimensions was used as a substrate. A 50 nm-thick Au bottom gate-electrode was thermally evaporated on the substrate. Subsequently, a 400 nm-thick parylene C (Poly-(chloro-p-xylene)) gate dielectric films are deposited by thermally evaporated on the substrate. A 400 nm-thick Au bottom gate-electrode was used as a substrate. A 50 nm-thick Au bottom gate-electrode was electrochemically in a similar manner with a previous report. [10] In this current case, BEDT-TTF, TPP[N(CN)2], CuCl and TPP-CI were used as starting materials (TPP = tetraohenylphosphonium). After crystals were formed, thin crystal was selected and pipetted into pure ethanol for rinsing two times. Subsequently, the crystal was pipetted again and casted on the substrate to be laminated after the evaporation of ethanol.

After the lamination process, gold wires (15 µm φ) were attached on the crystals with carbon paste (Figure 1b). Standard four-probe measurement was done under reduced He pressure in Physical Property Measurement System (PPMS) (Quantum Design). To apply the strain effects, the substrate was bended by applying a mechanical force from the backside of the substrate using a Stepper-positioner (attocube) installed in a probing insert originally-desiged for a PPMS (Figure 1c). We investigated 4 devices (device 1–4) which showed both strain-effects and field-effects. Although the magnitude of strain-effects and field-effects were sample dependent, the results were reproducible for each sample from a qualitative perspective. In this manuscript, we refer to the results of device 1 unless otherwise noted. The other important results of device 2–4 are shown in Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Financial support for this work was provided by Grants-in-Aid for Scientific Research (S) (No. 22224006) from the Japan Society for the Promotion of Science (JSPS).

Figure 6. a) Plot of Normalized resistance versus applied gate voltage \(V_g\) for the κ−Cl device 4 at 11 K with \(S = 0.67\%\). Blue, green, orange and black plots show the field-effects under external magnetic field of 0 T, 1 T, 5 T and 7 T, respectively. (b) Schematic illustrations for representing \(V_g\) OFF and \(V_g\) ON states of the κ−Cl device. When gate voltage is applied, the ratio of the superconducting fraction increases.

Received: November 24, 2013
Revised: January 31, 2014
Published online: March 24, 2014


