Open up Future Electronics by Organic Molecules

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Education

1993	B.S. The University of Tokyo
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Professional Employment

1998	Research Associate, Gakushuin University
1999	Special Postdoctral Fellow, RIKEN
2000	Research Scientist, RIKEN
2007	Senior Research Scientist, RIKEN
2012	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2012	Visiting Professor, Tokyo Institue of Technology
2015	Visiting Professor, Tohoku University

Awards

2009	RSC Publishing CrystEngComm Prize
2009	Young Scientist Awards, Japan Society for Molecular Science

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Keywords Molecular Conductors, Organic Superconducting Transistors, Supramolecular Nanowires

Organic molecules are attracting recent attention as new ingredients of electronic circuits. Their functionalities have been developed considerably, but are still to be explored and advanced. Our group focuses on a development of organic electronics in the next era by providing new mechanism and concepts of the device operation and fabrication. For example, an electronic phase transition is utilized for the ON/OFF switching of our field-effect-transistor (FET). This special FET is called an organic Mott-FET, where the conduction electrons in the organic semiconductor are solidified at the OFF state because of Coulomb repulsion among carriers. However, these solidified electrons can be melted by applying a gate voltage, and show an insulator-to-metal transition so-called Mott-transition to be switched to the ON state. Because of this phase transition, a large response of the device can be achieved, resulting in the highest device mobility ever observed for organic FETs. At the same time, Mott-transition is known for its relevance to superconductivity. Not only in organic materials but also in inorganic materials such as cuprates, Mott-transition is frequently associated with superconducting phase at low temperature. Indeed, our organic FET shows an electric-field-induced superconducting transition at low temperature.

Another approach to the future electronics is a three-dimensional (3D) patterning of molecular devices using crystal engineering. Because each molecule can be designed to show different functionalities, it should be attractive to construct nano-structured devices by self-assembly. We are especially focusing on a development of supramolecular nanowires that allow 3D periodic wiring in nano-scale. By encapsulating a 1D array of conducting molecules in a channel formed inside 3D supramolecular network, it is possible to construct a sheathed nanowires aligned in a periodic order as shown in Figure 1.

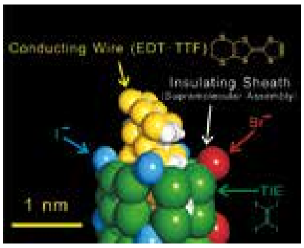

Figure 1. Crystal structure of supramolecular nanowire.

Selected Publications

- Y. Kawasugi, K. Seki, Y. Edagawa, Y. Sato, J. Pu, T. Takenobu, S. Yunoki, H. M. Yamamoto and R. Kato, "Electron–Hole Doping Asymmetry of Fermi Surface Reconstructed in a Simple Mott Insulator," *Nat. Commun.* **7**, 12356 (8 pages) (2016).
- M. Suda, R. Kato and H. M. Yamamoto, "Light-Induced Superconductivity Using a Photo-Active Electric Double Layer," *Science* **347**, 743–746 (2015).
- H. M. Yamamoto, M. Nakano, M. Suda, Y. Iwasa, M. Kawasaki and R. Kato, "A Strained Organic Field-Effect Transistor with a Gate-Tunable Superconducting Channel," *Nat. Commun.* **4**, 2379 (7 pages) (2013).
- H. M. Yamamoto, "Sheathed Nanowires Aligned by Crystallographic Periodicity: A Possibility of Cross-Bar Wiring in Three-Dimensional Space," *CrystEngComm* **16**, 2857–2868 (2014).

1. Light-Induced Superconductivity in an Organic Mott-FET[1,2]

κ-(BEDT-TTF)Cu[N(CN)$_2$]Br (κ-Br) is an organic Mott-insulator at room-temperature, but turns into metallic and superconducting states at low temperature. (BEDT-TTF = bis(ethyelenedithio)tetrathiafulvalene) In our previous works, a tensile strain from FET substrate altered κ-Br's ground state into a Mott-insulating state, when its thin (*ca.* 100 nm) crystal was laminated on top of SiO$_2$/Si^{++} substrate and cooled down to low temperature. In those experiments the electronic state at low temperature became completely insulating because of the large tensile strain that originates in mismatching of thermal expansion coefficients between κ-Br (30 ppm/K) and Si (2 ppm/K). However, one can anticipate from the *T–P* (temperature *vs.* pressure) phase diagram that mixed electronic state between superconducting and Mott-insulating states will be realized when the tensile strain is much weaker. To achieve such a mixed state (or, percolate-superconducting state), Nb-doped SrTiO$_3$ is used 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 to form a FET device structure. With this type of FET substrate, we have achieved an electric-field-induced superconductivity in κ-Br.

Recently, we have inserted a photochromic self-assembled monolayer (SAM layer: Figure 2, right panel) into this device in order to make it photo-active. We have employed a photochromic molecule 'spiropyran' whose UV-converted isomer 'merocyanin' is known to exhibit zwitter-ionic structure. Because the photochromic molecules are aligned in the same direction in the SAM, a strong electric field can be generated by photo-irradiation, when the spiropyran is converted into the merocyanin form. Thus, excess carriers can be injected to the FET interface due to the strong dipole moment of merocyanin.

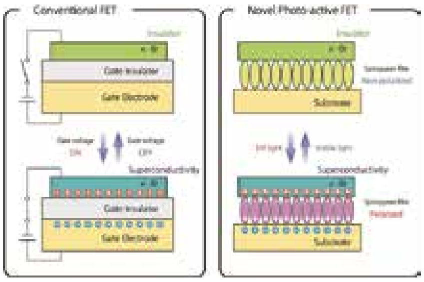

Figure 2. Device schematic for conventional superconducting FET (left) and our photo-active FET (right).
This figure shows p-type doping by molecular dipole-moment.

A κ-Br thin crystal is mounted on the SAM/Al$_2$O$_3$/Nb-SrTiO$_3$ substrate, and cooled down to low temperature. The resistance of the device showed weakly insulating temperature dependence, suggesting a percolate-superconducting state. Upon irradiation of UV-light, the resistivity at 5 K went down quickly and low-resistance state was observed after 180 sec. Temperature dependence of resistivity showed sudden drop around 7 K, confirming superconducting transition after the UV-light irradiation. Reverse photo-reaction by visible light led the phase transition back to the insulating state again. The switching of this device seems to originate from the light-induced formation of internal dipole moment in the SAM-layer, which resulted in a hole-doping at the FET interface. This speculation was confirmed by dual-gate experiment of this device, where gate-induced hole carriers worked cooperatively with the light-induced carriers. This result is the first example of light-induced superconductivity in FET devices, and allows remote control of superconducting device without direct wiring.

One can invert the direction of the molecule and its related electric field by designing a photochromic SAM molecule with different geometry. By such a strategy, we were able to achieve n-type light-induced superconductivity as shown in Figure 3. In this device, the threshold gate voltage for superconducting transition was shifted in the negative direction, as the UV irradiation proceeded. This implies that the light-induced carrier is an electron. These photo-active devices pave the way for new type of photo-electronics.

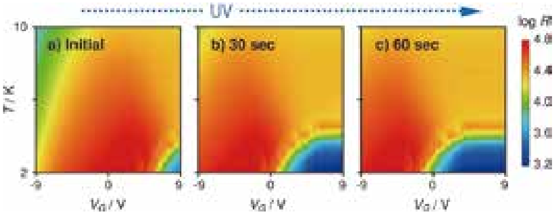

Figure 3. Emergence of n-type superconductivity by UV-irradiation. At the initial state (a), the device shows a normal ambipolar transistor behavior. After the UV-irradiation, superconducting region (blue) appears from electron-doped side (panels b and c).

References

1) M. Suda, R. Kato and H. M. Yamamoto, *Science* **347**, 743–746 (2015).
2) M. Suda, N. Takashina, S. Namuangruk, N. Kungwan, H. Sakurai and H. M. Yamamoto, *Adv. Mater.* **29**, 1606833 (2017).

Awards

SUDA, Masayuki; Young Scientist Awards, Japan Society for Molecular Science (2016).
SUDA, Masayuki; Ishida Prize, Nagoya University (2016).
SUDA, Masayuki; CSJ Award for Young Chemists, Chemical Society of Japan (2017).
SUDA, Masayuki; The 6th Young Scientist Award of National Institutes of Natural Sciences (2017).
SUDA, Masayuki; Morino Foundation for Molecular Science, Morino Foundation (2017).

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* IMS International Internship Program

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