X-ray Irradiation-induced Carrier Doping in Organic Mott Insulators

Modulation of the band-filling in the Mott insulator could produce the novel interesting strongly correlated electronic states like as High-Tc superconductors and non-Fermi liquid states. X-ray irradiation for the molecular materials could be a new way of the carrier-doping into the Mott insulating state.

X-ray irradiation usually induces disorders in a crystal, for example, displacement of the atomic position. In the case of molecular materials, the irradiation produces the molecular defects, which are radiolysed by ionizing radiation. This kind of molecular defect permanently remains, while the irradiation damage in inorganic materials in general is only due to atomic displacements which can be restored by a proper heat treatment. These defects and disorders make the electrical conductivity worse because of increasing the electron scattering [1]. Increase of the conductivity by X-ray irradiation, however, has been found in organic Mott insulators [2]. The irradiation-induced defects expected at the donor molecule sites might cause a local imbalance of the charge-transfer in the crystal. Such local modulation of the charge-transfer comes into being the effective doping of carriers into the half-filled Mott insulators.

Figure 1 shows a schematic crystal structure of κ-type BEDT-TTF molecule based organic conductor. The anion and donor molecule layers are stacked alternatively. Charge transfer between donor and anion molecules introduces a hole carrier for a BEDT-TTF dimer. In the case of the Mott insulating state that the band width W is smaller than the effective on-site Coulomb energy U, the hole is localized at the dimer site. When the sample is irradiated by X-ray, some molecular defects could be introduced into the donor layer. The expected defects at donor molecule sites might cause a local imbalance of the charge transfer between BEDT-TTF donor and anion molecules. Such molecular defects result in the effective carrier doping into the half-filled dimer-Mott insulators.

As shown in Figure 2, the in-plane resistivity of the organic Mott insulator κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl decreases drastically by X-ray irradiation with the tungsten tube (40kV, 20mA). It is noted, moreover, that a metal-like temperature dependence appears with rather small irradiation dose. These large changes of the transport properties may indicate that the carrier-doping by X-ray irradiation breaks down of the Mott insulating state due to small shift from half-filling of the conduction band. By controlling the molecular defects by X-ray irradiation, we could tune the carrier doping continuously for the Mott insulator, which has not been possible for the organic system by chemical substitution and other methods. This new way of carrier-doping technique will be useful not only for studying the Mott physics but also for molecular device fabrications.
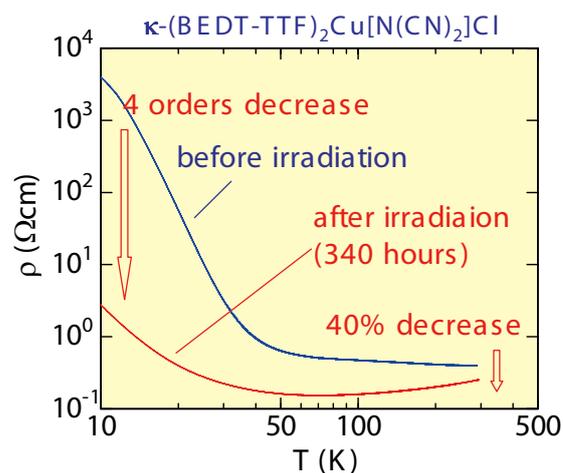
Fig.2 Temperature dependence of the resistivity of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl before and after X-ray irradiation at room temperature. After irradiation, the resistivity drastically decreases by about 40 % at room temperature and four orders of magnitude at low temperatures in comparison to the resistivity before irradiation. Moreover the resistivity shows a metallic temperature dependence above 50 K.

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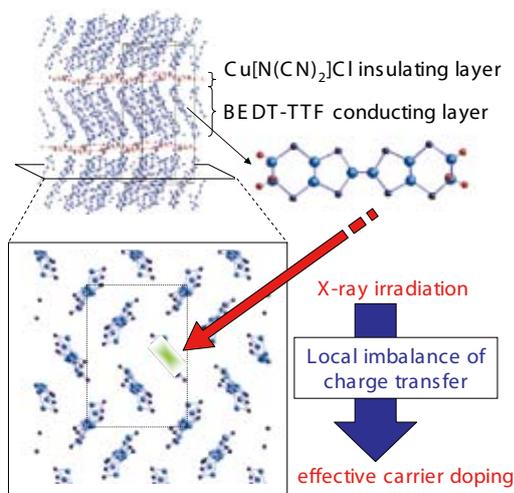
Fig.1 Schematic crystal structure of organic dimer-Mott insulator κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. X-ray irradiation produces molecular defects in the BEDT-TTF layer. The molecular defects will act as a carrier-doping site due to local imbalance of charge transfer.

Organic Light Emitting Transistor

Organic transistor is one of the key devices in organic electronics, which has a function of the electrical current switch. Here we demonstrate a new function of organic transistor, the first single crystal ambipolar light emitting transistor (LET), which is capable of carrying high current density, providing a novel opportunity of challenge to realize current-driven organic lasers.

2007 was an epoch-making year for organic electronics, since OLED-TV (television set using organic light-emitting diodes) has come to the market. This achievement is accelerating the research on the other organic electronic devices, such as transistors and solar cells. Particularly, organic field effect transistors (OFETs) are attracting a growing interest, since the mobility in OFETs are now higher than that in amorphous Si, and hence the application of OFETs to flexible, low-cost and environmental-friendly electronic devices are becoming more and more realistic.

A unique feature of organic FETs that has been uncovered by fundamental research is that the polarity of the device, *i. e.* the sign of carriers can be simply changed by the sign of gate voltages. In 2006, we found poly(methylmethacrylate) (PMMA) is a very good insulator to promote electron conduction, and realized a first ambipolar FET of organic single crystals using rubrene in an anaerobic atmosphere [1].

Using the ambipolar nature of OFETs, one is able to inject both electron and holes from source and drain electrodes. Injected charges meet at the center of the transistor channel, forming a kind of electric field-induced PN junctions, where charge recombination takes place to emit light. This light emitting device, which is called light emitting transistor (LET) provides a novel possibility of organic materials, which is a realization of current-driven organic laser. The conventional organic light emitting device, OLED, is a sandwich structure of hole-transport, light-emitting, and electron-transport layers (Fig.1 (a)). Injected electron and holes are transferred through the corresponding transporting layers to the light-emitting layer. One of the crucial requirements for realizing a current-driven organic laser is a large current density, higher than 10^3 A/cm^2. However, in the
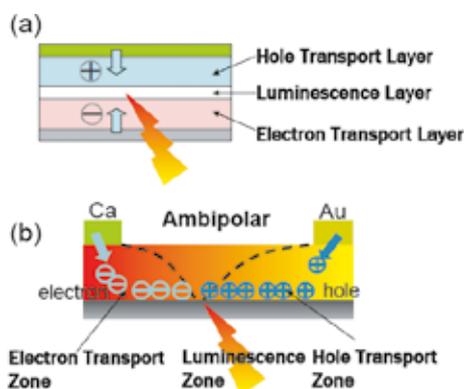
Fig.1 Comparison of organic light emitting devices: (a) Light emitting diodes, where carriers are transported in a vertical direction. (b) Light emitting transistors, where lateral carrier transport is occurring.
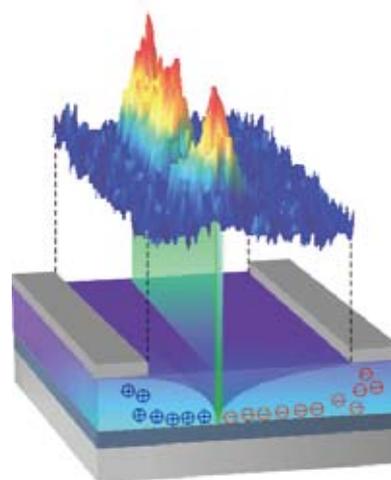
Fig.2 LET using an organic single crystal: (bottom) Schematic device structure and the carrier density distribution of tetracene single crystal LETs. (Top) Emission intensity distribution map.

conventional OLED structures, the highest current density has been so far limited to 10 A/cm^2. This is basically because the resistivity of both carrier transport layers are too high to carry such a large current density, because these transport layers have been made of basically insulating materials.

The lateral structure of LET devices (Fig. 1(b)), on the other hand, is disadvantageous because the carrier paths are extremely long in length comparing to that in the LED structure. However, since the carrier transport zones in LETs are doped by the gate electric field, the resistivity of these zones is dramatically low comparing to the carrier transport layer of OLEDs. Particularly, since we are utilizing organic single crystals, the mobility is two or three orders of magnitude larger, and thus the electrical current in LET using single crystals are as high as 10^2-10^3 A/cm^2 [2].

Using tetracene and rubrene single crystals, we succeeded in realizing a first organic LET device using tetracene single crystals (Fig. 2)[3], where carrier density has reached 10^3 A/cm^2, which is nothing but what is required for current-driven organic lasers. These findings might pave ways for ambipolar LETs based upon organic single crystals as a possible route for pursuing the realization of an electrically-driven laser oscillation from organic materials.

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Ab initio Simulation Study on the Control of Electron Transport in Molecular Device

We present the controlling factors of the electron transport in the molecular junctions through the deep understanding of the electronic and transport processes at the single molecular level. In parallel, we show that the designed junctions with single-molecule or low-dimensional carbon allotropes open the door to the design of nanogadgetry embodied with interesting device characteristics, namely "Computer-Aided Nanodesign".

"Molecular electronics" has emerged as a next-generation technology because of the fact that useful devices can be built on the basis of individual molecules. Since the advent of molecular electronics, an abundance of organic functional molecules have been designed and investigated as components in electronic devices such as molecular wires, rectifiers, and switches. Accompanied with the synthesis of functional organic molecules, the advancement of techniques for characterizing and manipulating individual molecules and the availability of first-principles methods to describe electron tunneling through atomic chains or single molecules, make it possible to realize molecular electronic devices.

In this work, a series of theoretical analyses were devoted to the designed molecular devices with single molecule or molecular strands in order to have the basic physics in the molecular electronic devices and to determine the factors controlling the electron transport. The important feature emerging from this work is that the individual features of electron transport characteristics originate from the distinct alignment of molecular levels to the Fermi level according to the molecule-contact coupling and applied bias voltage. In addition, the alignment of molecular levels is closely related to the intrinsic nature of molecule. In this work, we propose four controlling factors of the electron transport: *1) aromaticity, 2) π-conjugated framework, 3) doping, and 4) dipole moment.*

The incorporation of different types of aromatic components induces unique electron transport characteristics through the distinct electronic structure and the response to the molecule-contact coupling and applied bias.[1] In the multiporphyrinic systems, we showed that the distinct arrangement of π-conjugated framework gives the switching behavior as a single-molecule switch.[2] And we could know that the tunneling barrier can be controlled by the strength of dipole moment and the rectifying behavior as a Schottky-like
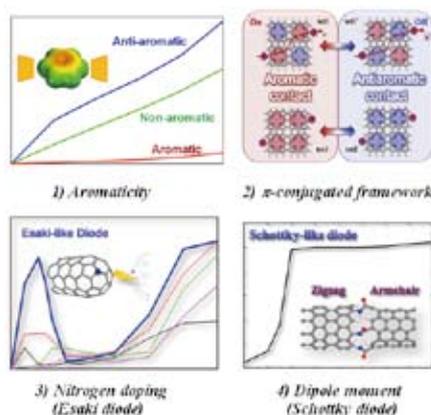
diode can be improved by incorporating the peptide linkages to the metallic/semiconducting CNT junctions, where the direction of the dipole moment plays an important role in the determination of the rectifying behavior.[3,4] Finally, we showed that the doped nitrogen atoms modify the molecular orbitals so as to generate a conducting channel in the designed CNT junctions by inducing a negative differential resistance (NDR) behavior, which is a characteristic feature of the Esaki-like diode, *i.e.* tunneling diode.

In parallel, we showed that the designed junctions with single-molecule and low-dimensional carbon allotropes (namely fullerene, CNT, and recently graphene) open the door to the design of nanogadgetry embodied with interesting device characteristics, namely "*Computer-Aided Nanodesign*". When we inserted Zn metal layers within metallic CNT electrodes thereby providing 1D heterojunctions that can act as a wire-like, NDR, or varistor-type nanoscale device.[5]

In general, the preceded theoretical investigations allow us to avoid starting costly experiments by choosing preferentially the way which has no serious objections from a theoretical point of view. Therefore, we believe that our results will give an insight into the design and implementation of various electronic logic functions for applications in the field of nanoelectronics.
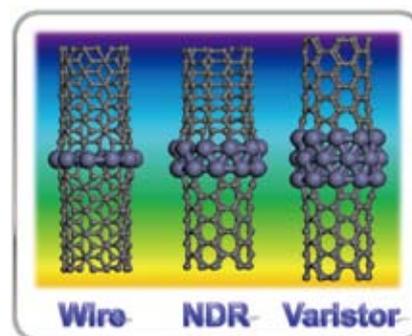
Fig. 2 Designed nanogadgetry using carbon nanotube with Zn metal layers

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Fig. 1 Controlling factors of electron transport at the molecular device

Conducting Polymer / ZnO Schottky Junction Toward Transparent Oxide Electronics

An oxide semiconductor ZnO is one of the promising semiconductors for future electronics. In this study, high quality Schottky junctions were realized on a ZnO (0001) bulk single crystal simply by spin-coating a commercial conducting polymer as the metal electrode. This polymer electrode can be used for implementations of various functional oxide electronic devices.

A wide-gap semiconductor zinc oxide (ZnO) is one of the promising compounds for realizing transparent oxide electronics. Recently, the light emission of ZnO *p-n* homojunction and the observation of quantum Hall effect in ZnO heterostructure were realized [1,2]. In order to advance the ZnO-based electronics further, it is indispensable to implement high quality electrode contact on ZnO for the perfect control of carrier dynamics in well-designed energy band structures. For example, a metal / semiconductor Schottky junction is very useful not only for evaluating the electronic states of semiconductor, but also for practical applications such as photodetector and field-effect transistor. Many groups have tried to develop ZnO Schottky junction using various noble metals such as Au and Pt, however, high device performance is difficult to be achieved mainly because of the poor interface quality. Recently, we realized a high quality ZnO Schottky junction by using a commercial conducting polymer, poly(3,4-ethylenedioxy- thiophene) poly(styrenesulfonate) (PEDOT:PSS), as a metal electrode [3]. Simple spin-coating process of the polymer in air at room temperature is sufficient to make a good Schottky contact. From this Schottky junction, it is possible to demonstrate the field effect transistor, the solar/visible-blind photodetector and the carrier profiling in two-dimensional electron gas in ZnO heterostructures.

Figure 1 shows a schematic energy band profile of PEDOT: PSS/ZnO Schottky junction. ZnO is *n*-type semiconductor and its electron carriers are depleted at the interface leading to the upward band bending that serves as a Shottky barrier for the electron flow. The chemical structure of PEDOT:PSS is shown in bottom of Fig. 1. When raising the Fermi level of ZnO by applying bias voltage (forward bias), the Schottky barrier decreases exponentially hence the electron flow from ZnO to PEDOT:PSS increases according to thermionic emission model expressed as $J \propto T^2 \exp(-\varphi_b / k_B T) \exp(q V/(n k_B T))$. J is current density, T temperature, φ_b Schottky barrier height, k_B Boltzman constant, V bias voltage, and n ideality factor representing a deviation from the ideal model. For reverse bias, the electron flow is significantly suppressed, and the interface can serve as a gate capacitor. The capacitance C is a function of the bias voltage: $1/C^2 \propto V_{bi} - V$, where V_{bi} is built-in potential (see Fig. 1).

Figure 2 shows bias voltage dependence of current density and inverse square of capacitance. The current density at positive bias is much larger than that at negative bias, representing very high rectification ratio of the Schottky junction. The ideality factor n is close to an ideal value 1, that is one of the smallest values among the existing reports. The $1/C^2$ vs. V relation shows very high linearity without the frequency dependence up to 1 MHz. Both J vs. V and $1/C^2$ vs. V curves show no hysteresis suggesting high quality of the interface between ZnO and PEDOT:PSS. It is noted that these ideal Schottky behaviors are achieved by simple spin-coating method with mild conditions, and such easy-to-use approach without any damage of the interface enables us to obtain the reproducible junction performance among large area production. It is expected that this PEDOT:PSS electrode can be applied to various functional oxides toward realization of next-generation transparent oxide electronics.
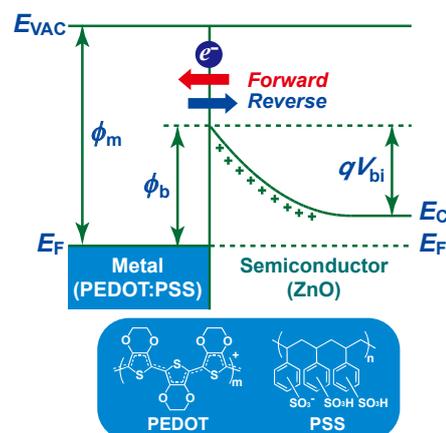
Fig. 1. A band profile of Schottky junction (upper panel). Electrons flow from semiconductor to metal under forward bias and vice versa. E_{VAC}, E_F, φ_m, φ_b, E_C, and qV_{bi} are vacuum level, Fermi energy, work function of metal, Schottky barrier height, conduction band bottom of semiconductor, and built-in potential, respectively. Bottom panel shows chemical structure of a conducting polymer, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS), used as a Schottky metal in this study. This Schottky metal can be formed on oxide semiconductors just by spin-coating method.
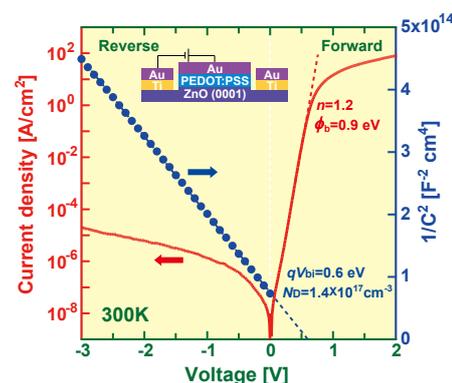
Fig. 2. The current density (J)–voltage (V) and the $1/C^2$ (C: capacitance)-V relations at 500 kHz for a PEDOT:PSS/ZnO Schottky junction. The ideality factor (n) and the Schottky barrier height (φ_b) deduced from the J-V curve, the built-in potential (V_{bi}) and the ionized donor concentration in depletion layer (N_D) deduced from the $1/C^2$-V curve are also shown.

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