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CHAPTER 3

Single electron tunneling organic devices

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1. Introduction

In recent years, many research studies have been done along with the rapid progress of nano-fabrication technology in the field of nano-electronics [1]. Until now, much effort has been done on the fabrication of novel devices based on physics of quantum mechanics, principally using the nano-fabrication technique developed in semiconductor device technology [2]. As a result, single electron tunneling (SET) devices using small particles in their systems have been successfully prepared. Nano-fabrication technology developed in the field of semiconductor device technology may lead to a new way to electronics and many novel electronic devices such as high-density memory devices, high-speed low-power switching devices, high-sensitive electrometer devices and others will be produced in the near future. As such, it is needless to say that the research along with this trend is important. However, this is not sufficient. The study of observing

specific functions of organic molecules and applying these functions to electronic and optical molecular devices is of crucial help, because one can realize novel functional devices only by using organic molecules, without using the maturing nano-fabrication technology in the field of semiconductor device technology. In this chapter, single electron tunneling (SET) devices using organic molecules prepared by the Langmuir–Blodgett (LB) technique is briefly introduced.

For the realization of SET devices, it is necessary to design the device system so that the one-electron charging energy of $e^2/2C$ is greater than the thermal energy kT [2]. In this sense, so-called small particles, whose size is less than several nm, must be introduced into the molecular systems to be used. However, there are many difficulties to do this, e.g., synthesis and others. Overcoming the difficulties, an attempt to use an organic mono-molecule as a so-called Coulomb island has been successfully made by the present authors [3–6]. In the following, single electron tunneling devices prepared using organic molecules is described.

2. Molecules and samples

2.1. Molecules

As the molecule used for fabricating the device, dendrimer molecules (Rh-G2), which have called much attention in the field of organic synthesis, were used as the Coulomb island. Polyimide LB film, which shows excellent insulating properties [7], was used as tunneling barrier in the device. The chemical structures of Rh-G2 and PI are shown in Fig. 1. The polyimide LB film functions as electron tunneling barrier, where the monomolecular film thickness of 0.4 nm can be controlled by the LB method. The dendrimer molecule Rh-G2 used as the Coulomb island has a spherical shell molecular structure, i.e. electrically insulating CH chains enclose rhodamine dye molecules [8]. That is, the dye molecules located at the center are electrically isolated from their surroundings. The use of such organic molecules facilitates the preparation of single electron tunnel devices.

2.2. Sample structure [3,4]

Fig. 2 shows the sample structure of a SET device prepared using rhodamine dendrimer (Rh-G2) molecules, where an Rh-G2 molecule is assumed to function as a Coulomb island. Au was evaporated on glass substrate with a thickness of about 100 nm, and the evaporated electrode was used as a bottom electrode of the SET device. Onto this evaporated electrode, 13 to 31 layers of polyimide LB film were deposited by the LB technique to form an electron tunneling layer, in the same manner as that in our previous study [7]. Then, polyimide LB film mixed with rhodamine dendrite molecules was deposited by mono-layer deposition to form a single layer working as a Coulomb island. The mixing ratio of PI : Rh-G2 was 500 : 1 in molar ratio. From the experimental surface pressure–area (F–A) isotherm of the mixture monolayer film, a number of about 1000 molecules of Rh-G2 was estimated to be present within an area of about

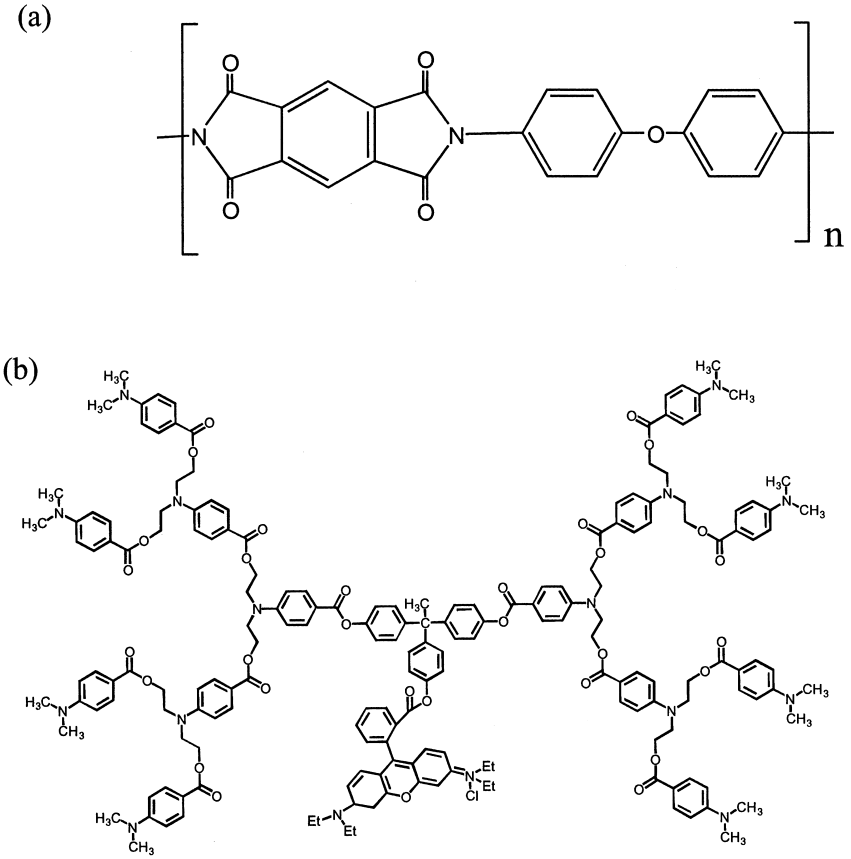

Fig. 1: Chemical structure of (a) polyimide (PI) and (b) dendrite polymer (Rh-G2).

1 μm^2. After the deposition of the mixing monolayer, 20–30 layers of polyimide LB films were again deposited as an upper electron tunneling layer. Finally, an Au electrode was evaporated with a thickness of 50–100 nm to form a top electrode. The working area of the resulting junction was about 50×100 μm (see Fig. 2). Furthermore, for the measurement of I–V characteristics under photoillumination, junctions with transparent indium–tin-oxide (ITO) electrodes were also fabricated.

2.3. I–V measurement

The electrical resistance of the prepared devices was several hundreds of MΩ to several tens of GΩ. Thus, current–voltage (I–V) measurement was performed using a 2-terminal method by applying a step voltage under constant temperature in a cryostat (Cryokelvin CG308SCPR; Nagase Electronics). The measurement temperature was between room temperature and 5 K.

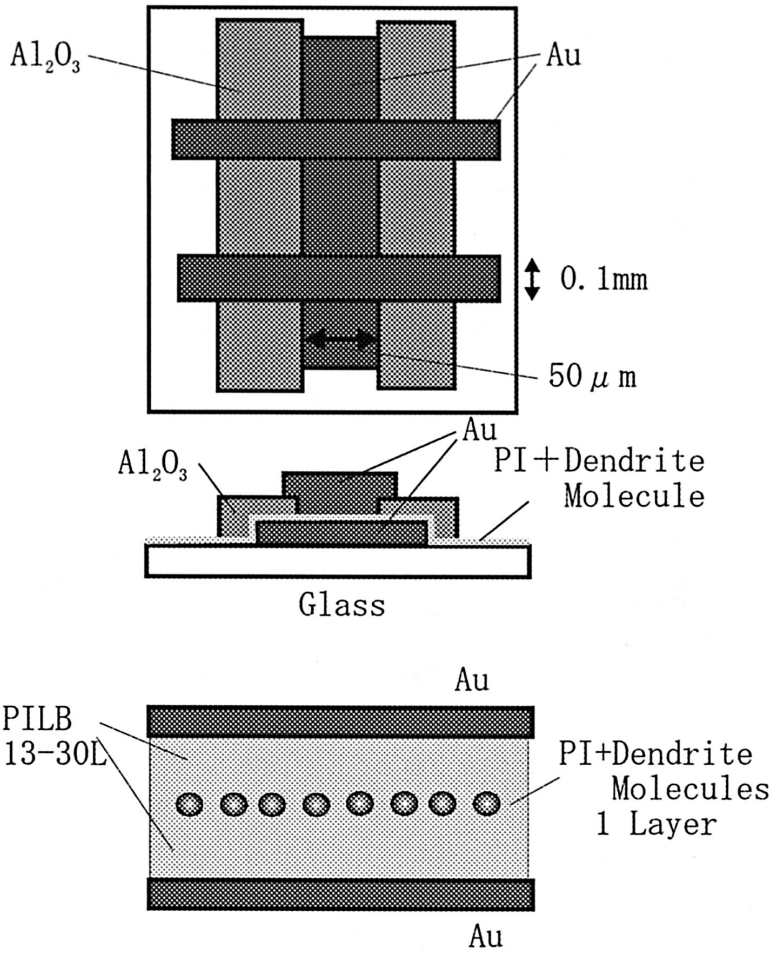

Fig. 2: Sample structure of a molecular single electron tunneling device.

3. Current–voltage characteristics

3.1. Single electron tunneling characteristic

Fig. 3(a) shows the I–V characteristics of an Au/PI25/PI+Rh-G2/PI30/Au device at a temperature of 5.2 K. The voltage step with constant spacing is clearly seen. This is the characteristic of SET devices, and the step spacing is given by e/C. Here C is the capacitance between the Coulomb island and the electrode [2]. The step spacing e/C is about 100 mV. In order to further clarify the step structure observed in the I–V characteristic, the $\mathrm{d}V/\mathrm{d}I$–V characteristic was plotted in Fig. 3(b). For both positive and negative voltage, peaks of $\mathrm{d}V/\mathrm{d}I$ are seen at 50, 150 and 250 mV with an equal step voltage spacing of 100 mV.

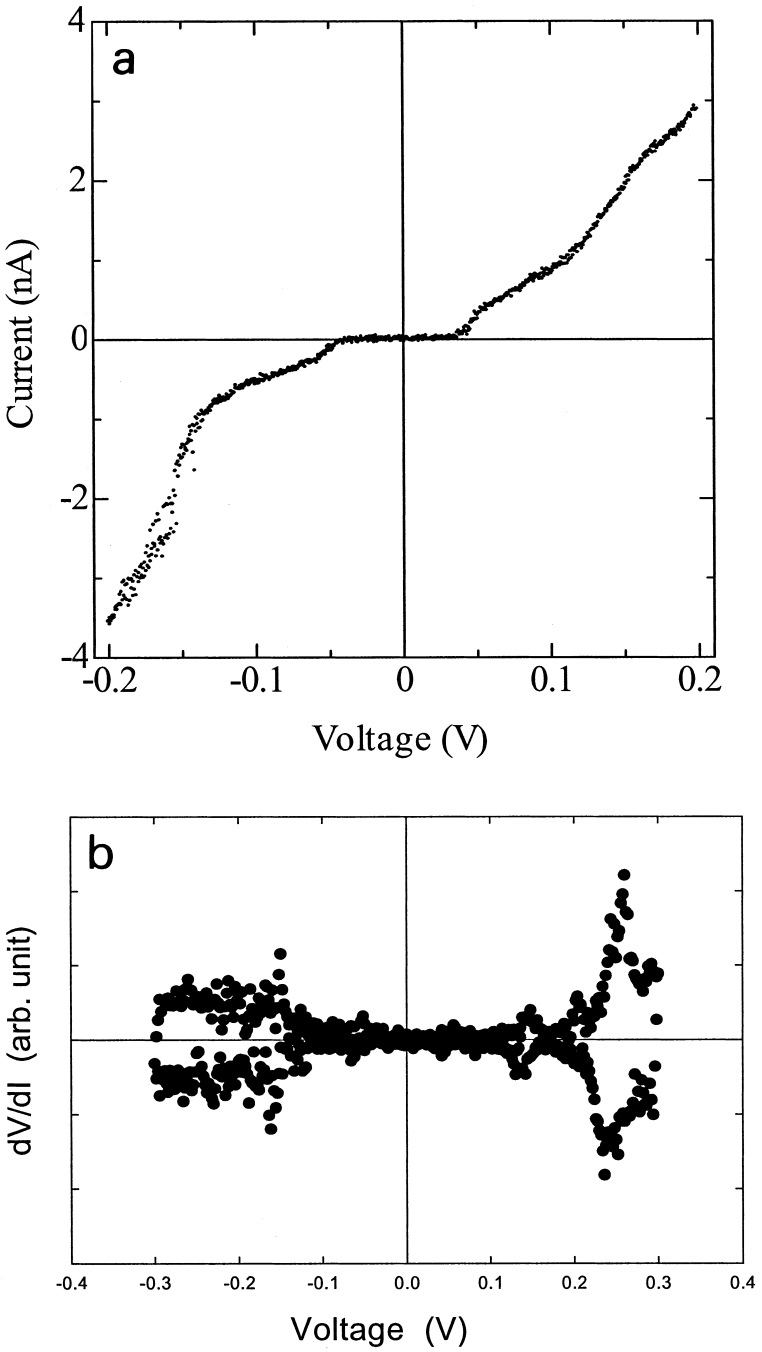

Fig. 3: (a) Typical I–V characteristics of metal/organic SET layer/metal junctions. (b) Typical $\mathrm{d}V/\mathrm{d}I$–V characteristics of metal/organic SET layer/metal junctions.

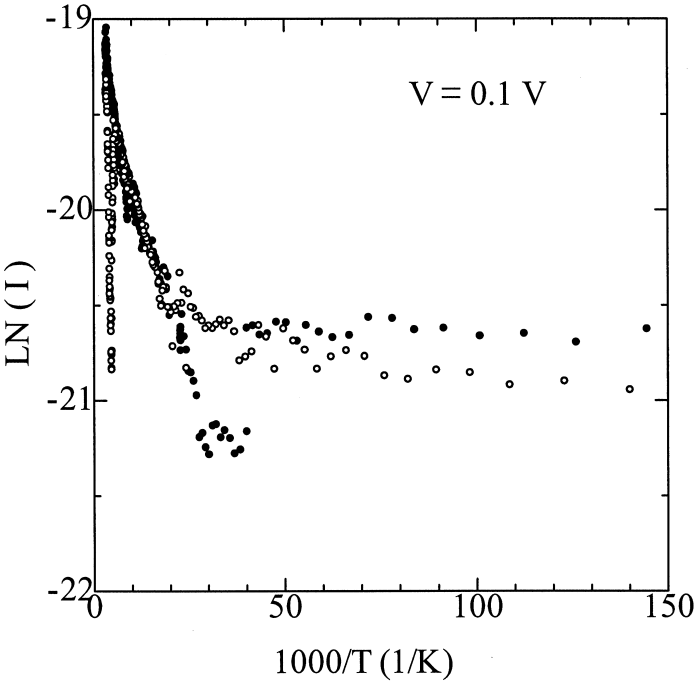

Fig. 4: Arrhenius plots (I–$1/T$ charcteristic) of an organic SET device.

Fig. 4 shows the temperature dependence of current flowing through the junction. The current flow decreases with the decrease of temperature in the region from room temperature to 50 K. This indicates that a thermally activated conduction type current flows through the junction. The thermal activation energy at a temperature higher than 50 K is estimated as less than 30 meV. On the other hand, the electrical current density is nearly constant at a temperature lower than 50 K. This indicates that a tunneling-conduction type current flows through the junction in this temperature region. These results reveal that both thermally activated conduction and tunneling-conduction currents are allowed to flow in this device. It is also suggested that the thermally activated conduction type current dominates at temperatures higher than room temperature, whereas this type of current decreases as temperature is getting lower and lower. Eventually, the tunneling-conduction type current becomes the main contributor. Of interest is that a single electron tunneling characteristic is found at lower temperature as shown in Fig. 3.

Fig. 5 shows the I–V characteristics at various temperatures. At a temperature lower than 50 K, tunneling-conduction type current is observed, and the step voltage can be seen. The voltage step width is the same as that observed at 5.2 K. The position of the step voltage is not dependent on the temperature. As described above, in the junctions using Rh-G2 dendrite molecules, single electron tunneling behavior is observed. From the theoretical side, the charging energy $e^2/2C$ associated with one electron tunneling must be greater than the thermal energy kT [2]. A voltage step due to single electron

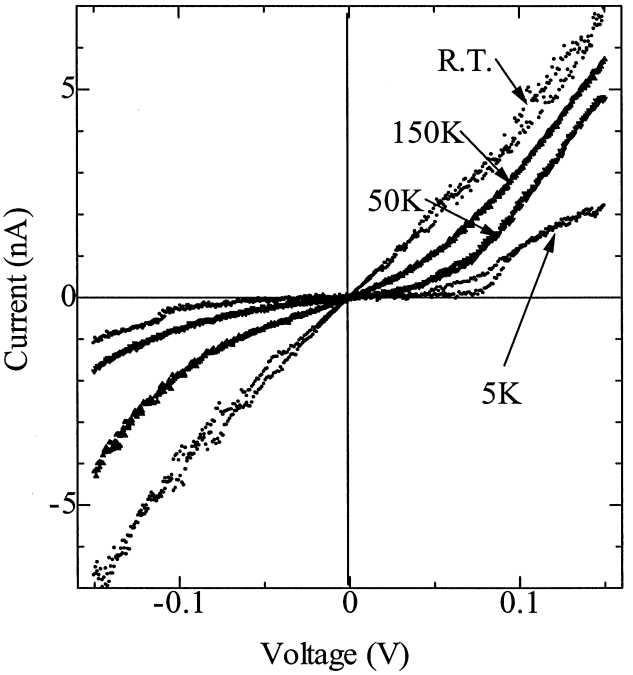

Fig. 5: Typical I–V characteristics of an organic SET device at various temperatures.

tunneling is about 50 meV for the device prepared here. We may expect that junctions showing a single electron tunneling characteristic is produced in the near future.

3.2. Organic molecule as Coulomb island

It is interesting here to discuss whether the Rh-G2 molecule introduced in the junction actually functions as a Coulomb island or not. For this purpose, the size of the Coulomb island is estimated. The size of the Coulomb island is a dominant factor to explain the I–V characteristic. The size can be estimated from the spacing of step voltage of e/C in the I–V characteristic. The capacitance C of a spherical conductor with radius r that is separated by a distance d from a planar electrode is given by

$$C = 4\pi\varepsilon_{\mathrm{r}}\varepsilon_0 F \quad \text{with} \quad F \approx (1/r - 1/2d)^{-1}, \tag{1}$$

under the assumption $r \ll d$. Therefore, assuming the observed voltage step spacing is given by ΔV, the radius r of the Coulomb island can be expressed as

$$r = \left(\frac{4\pi\varepsilon_{\mathrm{r}}\varepsilon_0}{e}\Delta V + \frac{1}{2d}\right)^{-1}. \tag{2}$$

Using this equation, the size r of the Coulomb island is estimated as 3.8 nm for $\Delta V = 100$ mV, $\varepsilon_{\mathrm{r}} = 3$ (polyimide), and $d = 10$ nm (25 layers of PI LB film). The size of an Rh-G2 molecule is speculated to be about 1–2 nm in radius from computer

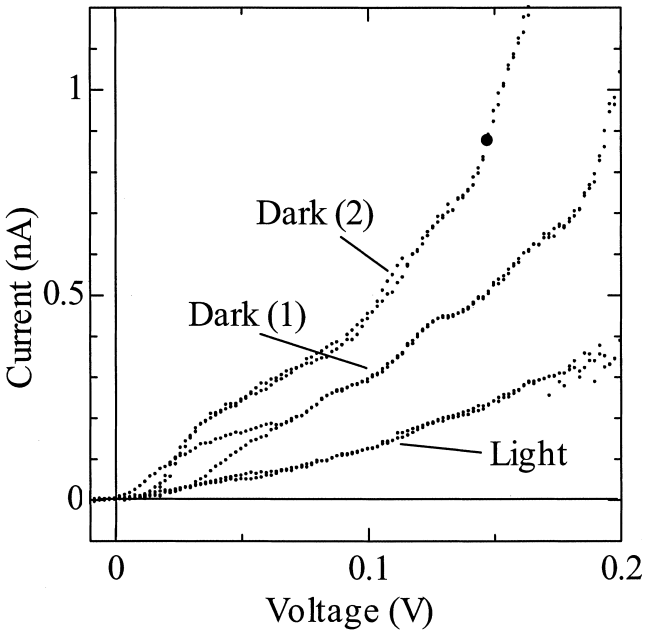

Fig. 6: Typical I–V characteristics of a SET device under photoillumination.

simulation and F–A isotherm measurement. There is a discrepancy between the size estimated from I–V characteristics and that from the computer simulation, possibly due to the assumptions made in the calculation. This discrepancy is within the constraints of our estimation. As mentioned above, using dendrite molecules designed by molecular ensemble, it is possible to prepare a SET device.

3.3. Light-irradiated single electron tunneling characteristics

When the fabricated samples are irradiated by light, electrons may be excited from the dye molecules and the single electron tunnel conduction mechanism may be changed. Further, the tunnel barrier height may be changed by the charge induced in the space charge layer. In other words, it is possible to control the single electron tunneling process by light illumination.

Fig. 6 shows the I–V characteristics of a SET device under white light irradiation. As shown in the figure, the current decreases, but no change is observed in the position and the spacing of step voltages. These are specific characteristics seen in the junctions using dendrimer molecules. These results suggest that the changes induced by light irradiation did not originate from the Rh-G2 molecules working as the Coulomb island but from the PI tunnel barrier [9].

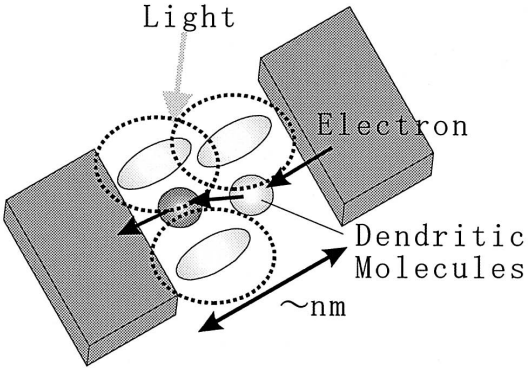

Fig. 7: Image of a double tunneling type molecular SET device.

4. Future prospect

By the use of core type dendrimer molecules created by molecular ensemble as Coulomb island, it is possible to fabricate SET devices. As has already been described, when organic molecules are used as the Coulomb island, the specific properties of the molecule will be added to the single electron tunnel characteristics. By choosing molecules, double type SET devices and others that can be used in e.g. detection of electromagnetic waves, light detection, etc. [10] will be produced. Furthermore, arranging the above double tunneling type device in another organic molecular matrix as shown in Fig. 7, the tunneling characteristics will be controllable by the field of the matrix with external stimuli, such as optical light or electrical field. As described above, by utilizing a molecular ensemble, building up organic electronics and molecular field control type electronics will be possible.

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