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Effect of Device Structure on Electrical Conduction of Terphenyl-based Molecule

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1. Introduction

A recent study of phenylene-based molecular devices has revealed many intriguing features including molecular orbital gating [1]. However, the relationship between the structure and electrical properties of the devices is not well understood. In this report, a phenylene-based molecule with a large steric hindrance is selected, and the effect of device structure on electrical conduction is investigated using two types of nanogap electrodes; one obtained by electromigration of metal wire and the other by shadow evaporation.

2. Device Fabrication

Molecular devices were fabricated using two types of nanogap electrodes.

One type of nanogap (EM nanogap) was obtained by the electromigration of gold wire [2]. In the first step, a 120-nm-thick gate-insulating layer was obtained by thermally oxidizing a Si wafer. Then a 15 nm-thick, 100 nm-wide and 200 nm-long gold wire without a Ti underlayer was defined.

We employed terphenyldithiol (TPDT) as a phenylene molecule [Fig. 1(a)]. Self-assembled monolayers (SAMs) were formed on a gold surface by immersing the samples with gold patterns in TPDT solutions in an Ar atmosphere. After the immersion, electromigration and electrical measurements of the samples were performed in a vacuum.

Other nanogaps were obtained by shadow evaporation [3] (shadow-evaporated nanogaps). A 20-nm-thick gate-insulating layer was obtained by thermally oxidizing a Si wafer. The first metal layer (2.5 nm of Ti and 12.5 nm of Au) and the second metal layer (25 nm of Au) were deposited at 45° and -45° with respect to the substrate normal through the patterned mask. Some shorted contacts were converted to nanogap electrodes by the electromigration technique mentioned above. After obtaining the nanogaps, we formed SAMs by immersion.

3. Results

Figure 1(b) is a histogram of the resistances of nanogap electrodes with TPDT for $|V_d|$ = 0.5V with V_d of drain voltage at 20 K. As shown in Fig. 1(b), 25 of 39 nanogaps exhibit a resistance of 10^6~10^7 Ω. Figure 1(c) shows representative drain current-drain voltage (I_d-V_d) characteristics of EM nanogaps for gate voltages (V_g) of 0, +40 and -40 V. Although $|I_d|$ decreased slightly at V_g=+40 V, no clear gate effect was observed. The temperature dependence was evaluated to identify the effect of the molecules. Figure 2(a) is a set of temperature dependence (I_d-V_d) characteristics for V_d=-0.1~+0.1 V at several representative temperatures. Figure 2(b) is an Arrhenius plot (V_d=50 mV), and an activation energy of 0.21 eV is observed, which can be attributed to the hopping conduction. This value is comparable to those of other previously reported conjugated molecules [4], and could not be observed for EM nanogaps without molecules. On the other hand, the conductance did not exhibit large temperature dependence at low temperature. This temperature independence indicates that tunneling is the dominant conduction at low temperature.

To explore the origin of the activation energy, the *ab initio* molecular orbital was calculated with the density function method. Although TPDT has two stable conformers (helical and twisted structures) [Fig. 3(a)], the energy difference between them is negligible. To simplify the calculation, we adopted a twisted structure that has one variable rotation angle of the phenylene group. The most stable TPDT structure exhibited a rotation angle (θ) of 38°. From energy gaps of θ=38° and 0°, where the latter corresponds to the most conductive structure, the rotation barrier of the phenylene group was estimated to be 0.22 eV [Fig. 3(b)]. This value is in good agreement with the activation energy observed in Fig. 2(b), and it is considered that the rotation barrier of the phenylene group comprises the intramolecular hopping barrier and dominates the conduction at high temperature. It is worth noting that, in a certain class of molecules including TPDT [4], steric hindrance plays an important role in the electrical conduction.

With shadow-evaporated nanogaps, the conductance increased about four orders of magnitude after SAM formation [Fig. 4(a)]. Figure 4(b) is a representative Arrhenius plot (V_d=50 mV) of shadow-evaporated nanogaps. The activation energy was less than 38 meV. This value is clearly smaller than that of the EM nanogaps. The small activation energy may be related to the fabrication process and the resultant molecule-electrode configuration. The result could be the indirect connection of TPDT and nanogap electrodes via, for example, metallic dots in the nanogaps [3], or a larger contribution from the intermolecular conduction in the SAMs [5].

4. Conclusions

We investigated the relationship between the electrical characteristics and device structures of phenylene-based molecular devices. The activation energy of the electrical conduction was evaluated from an Arrhenius plot. This

energy is in agreement with the rotation barrier of the phenylene group in TPDT obtained from theoretical calculations. Shadow-evaporated nanogaps exhibited a small activation energy, and this may be attributed to the resultant molecule-electrode configuration with the indirect connection of TPDT to the nanogaps. Although TPDT-based devices did not exhibit a clear gate effect, improvement of the device structure may reveal some FET properties. This study encourages further investigation of the electrical conduction of molecules with a large steric hindrance, and its relationship to device structure.

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6. References

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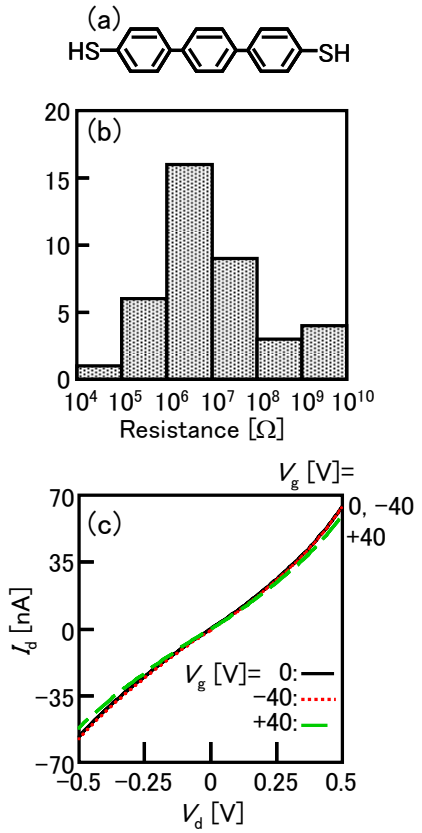

Fig. 1 (a) Structure of TPDT. (b) Histogram of the resistances of EM nanogaps for $|V_d|$=0.5 V. (c) I_d-V_d characteristics of EM nanogap for V_g=0, +40 and -40 V.

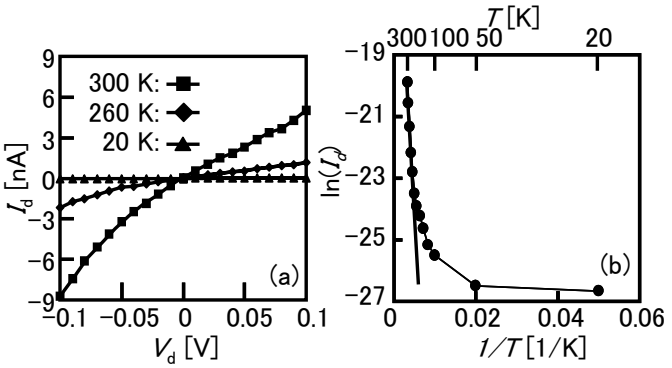

Fig. 2 (a) I_d-V_d characteristics of EM nanogap at several representative temperatures. (b) Arrhenius plots of EM nanogap.

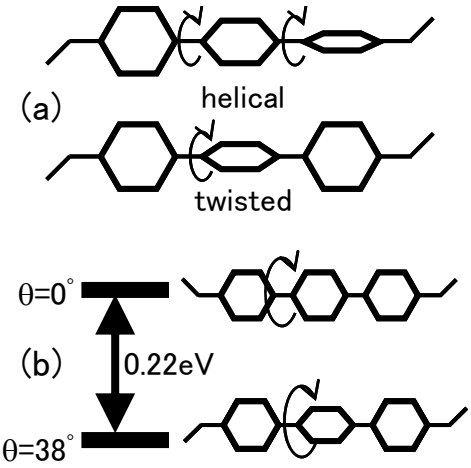

Fig. 3 (a) Helical and twisted conformers of TPDT. (b) Rotation barriers for θ=0° as the basis for the energy of most stable structure (θ=38°).

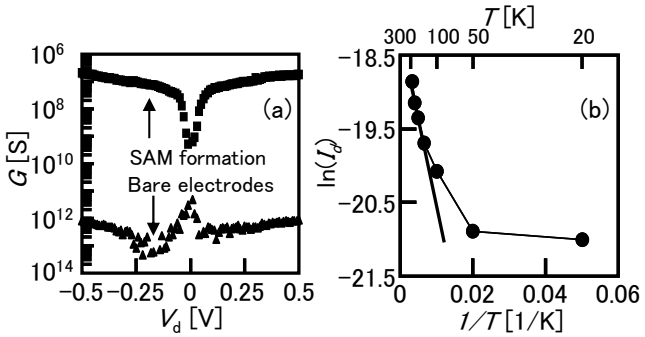

Fig. 4 (a) I_d-conductance (G) characteristics of nanogap electrodes fabricated by shadow evaporation of metals for bare electrodes and after SAM formation. (b) Arrhenius plots of shadow-evaporated nanogap.