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Fowler-Nordheim Tunneling in Electromigrated Break Junctions with Porphyrin Derivatives

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1. Introduction

Electron transport mechanisms of single-molecular junctions have attracted much attention in the field of molecular electronics [1]. Many groups have investigated these junctions using various methods to clarify how the molecule contributes to the electron transport in the junctions. Many of the remarkable findings of these studies were made in observation of electron transport in single-molecule transistors (SMTs) fabricated using an electromigration method [2]. However, the molecular trapping in the nanogap electrodes of this method is a random process and the mechanisms have not been fully clarified. To understand the electron transport properties in the electromigrated break junctions, statistic data and control experiments are required.

We have measured the current-voltage (I-V) curves of 158 electromigrated break junctions with 5,15-bis(3,5-di-t-butylphenyl)-10,20-bis(4-mercaptophenyl)cobalt-porphyrin (CoBSTBPP) at a temperature of 11 K within the applied bias $\leq$ 1.0 V. As a control experiment, we have also measured the I-V curves of 163 junctions with no molecules. We found a contribution of the molecule to the electron conduction in the junctions with CoBSTBPP.

2. Experiment

Figure 1(a) shows the sample structure and the experimental setup. An Au continuous nano-wire (length: 150 nm, width: 80 nm, thickness: 15 nm) and the pad electrodes with 2 nm thick Ti adherent layer were fabricated on a doped Si substrate with 50 nm thick SiO_2 using a combination of electron beam and photo lithography and a liftoff process. Figure 1(b) shows the chemical structure of CoBSTBPP. The molecule was used in the form of a 0.5 mM solution in tetrahydrofuran (THF). The substrate, after being cleaned with acetone, ethanol, and oxygen plasma, was immersed in the solution at room temperature for 18 h. After the molecule adsorbed on the electrode, the substrates were rinsed with THF and ethanol and finally N_2 blow-dried. These molecular deposition procedures were performed in oxygen-free conditions. The electron transport properties were measured in a low temperature vacuum probe station. The electromigration process to form a break junction in the nanowire was performed at room temperature. The sample was then cooled to 11 K, and the I-V curves were measured.

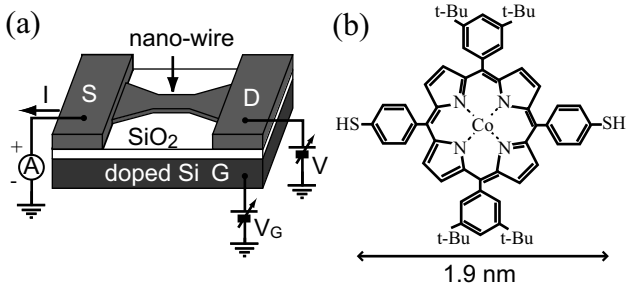

Figure 1: (a) Schematic illustration of the sample structure and the experimental setup for electron transport measurements. (b) Chemical structure of CoBSTBPP.

3. Results and Discussion

We measured the I-V curves of 158 junctions with CoBSTBPP and of 163 junctions with no molecules prepared by immersing bare-junctions in pure THF as the control samples. Four types of I-V curves were observed in these junctions (Table I), i.e., the current lower than 1 pA at the applied bias 1 V ("no current"), symmetry curves ("tunneling current"), the curves with staircase feature ("staircase"), and asymmetry curves ("others"). One can find a significant difference in the occurrence rate of "no current" and "tunneling current" in Table I. In addition, of the junctions with CoBSTBPP, we found the current higher than 100 pA at $|V| \leq 1.0$ V in 9.5 %, whereas only in 0.6 % of the junctions with no molecules. It is evident that the magnitude of the current in the junctions with CoBSTBPP tends to be higher than that of the junctions with no molecules, due to the presence of the molecules.

Table I. Statistics of the observed I-V curves.

Current type	CoBSTBPP % of junctions	No molecules % of junctions
No current	60.1	81.6
Tunneling current	18.4	1.8
Staircase	13.3	10.4
Others	8.2	6.1

Figure 2(a) shows the typical I-V curve of the tunneling current observed in the junction with CoBSTBPP.

Figure 2(b) is Fowler-Nordheim (FN) plot of Fig. 2(a). Figure 2(b) indicates that the mechanism of the electron transport in the junction at higher bias voltage ($|V| > 0.3$ V) was FN tunneling. Fowler-Nordheim tunneling is dominant when the junction satisfies $eV \geq \Phi$ [3]. Here, Φ is the tunneling barrier height. Thus the tunneling barrier formed in the junction is estimated to be lower than 0.3 eV. Most tunneling current observed in the junctions with CoBSTBPP showed FN transport behavior, and suggest $\Phi \leq 0.5$ eV.

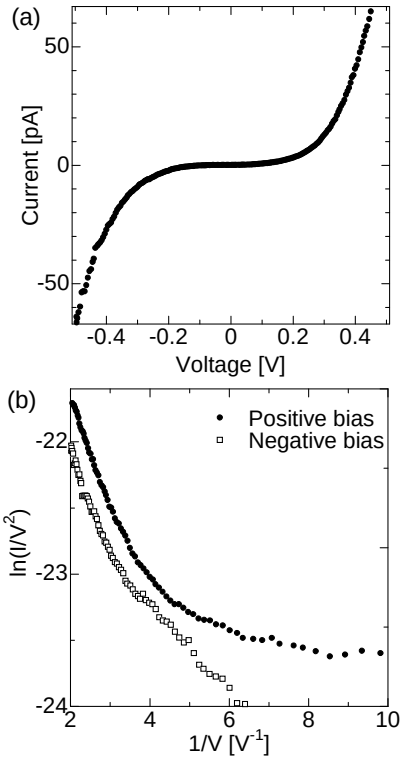

Figure 2: (a) A typical I-V curve of tunneling current observed in the junction with CoBSTBPP (b) Fowler-Nordheim plot of Fig.2(a)

The tunneling barrier height estimated by our experimental results are much lower than that previously reported on the junctions with alkanethiol monolayer with Au-S interface (1.39±0.01 eV) [3], and the junctions with no molecules (2.4±0.1 eV) [4]. The tunneling barrier height is determined by the relations between the Fermi level of the electrode surface and the energy gap of the tunneling layer, when assuming a simple rectangular tunneling barrier [5]. The lower tunneling barrier observed in our experiments may be due to the electrode-molecule interface effect, and the energy gap of the tunneling layer. The electrode-tunneling barrier interface is Au-S for the junction with CoBSTBPP or alkanethiol, and Au or Ti-SiO_2 for the junction with no molecules. The highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap is 3 eV for CoBSTBPP and 8 eV for alkanethiol, and the band gap of SiO_2 is larger than 8 eV. Although the energy alignment of these junctions is not clarified, the smaller energy gap of the tunneling layer forming the lower tunneling barrier in the junctions seems to be reasonable. We thus suggest that the tunneling barrier formed in the junctions with CoBSTBPP was lowered, consequently the conductance of the junctions was increased, by the molecule in the current path.

4. Conclusion

We have measured the I-V curves of 158 electromigrated break junctions with CoBSTBPP at 11 K, and 163 junctions with no molecules as a control experiment. The conductance of the junctions tended to be higher than that of the control junctions. Tunneling current was observed in 18.4 % of the junctions with CoBSTBPP and the most of these junctions showed FN tunneling behavior. The estimated tunneling barrier height was much lower than that of the junctions with alkanethiol monolayer, and the junctions with no molecules. This tunneling barrier lowering could be explained by taking into account the molecule in the current path.

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