Dependence of Stretch Length on Electrical Conductance and Electronic Structure of the Benzenedithiol Single Molecular Junction

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We have investigated the current-voltage (I-V) curves of the benzenedithiol (BDT) single molecular junction as a function of stretch length of the junction. The BDT single molecular junction was prepared with the nano fabricated Au electrodes using the mechanically controllable break junction (MCBJ). The conductance of the BDT single molecular junction gradually decreased with the stretching length of the junction. We analyzed the obtained I-V curves based on the two different models; the single channel model and the field emission model. Based on the single channel model, it was revealed that the decrease in conductance was mainly caused by the decreases in the metal-molecule coupling and that the HOMO approached to the Fermi level with the decrease in the electrode separation. The energy shift of the HOMO was supported by the analysis based on the field emission model. [DOI: 10.1380/ejssnt.2018.145]

Keywords: Single molecular junction; Electron transport; Electronic structure; Break junction

I. INTRODUCTION

Single molecular junctions have been envisioned as components for miniaturized electronic circuits since the first theoretical proposal of a molecular diode [1]. The introduction and refinement of scanning tunneling microscopy break junction (STM-BJ) and mechanically controllable break junction (MCBJ) techniques establish single molecular junctions in a systematic and robust fashion [2–5]. Currently, single molecular diodes, transistors, switches and other functional devices are realized with the single molecular junctions [6–11]. One of the intrinsic properties of a single molecule measurement is the large temporal fluctuation. In contrast to the ensemble averaged bulk measurement, the signal from a single molecule fluctuates with time. The electric conductance of the single molecular junction also temporally fluctuates [12]. The conductance fluctuation is an interesting topic in fundamental science, but it inhibits the fabrication of reliable electronic devices. The single molecular junction is prepared by breaking a metal contact in the presence of molecules [2, 3]. The junction conductance changes upon the stretching process. Conductance jump, gradual change, and steps are observed in the conductance traces [13]. The conductance fluctuation of the single molecular junction is explained by the transition between the molecular adosrtion sites, change in molecular orientation and metal-molecule distance by theoretical calculations [14–17]. Nara et al. calculated the conductance of a single benzenedithiol (BDT) molecule sandwiched between Au(111), and showed that the conductance changed by factor of 10 depending on the molecular adsorption site (bridge, hollow, and atop) [14]. The effect of molecular orientation on molecular conductance was theoretically investigated by Kornilovitch et al. The conductance of BDT single molecular junction changed by more than an order of magnitude with angle between the molecular axis and the normal to the electrode [15]. Andrews et al. revealed that low bias conductance of the BDT single molecular junction changed by up to a factor of 30 upon Au-S bond lengthening [16]. Although the origin of the conductance fluctuations of the single molecular junction has been investigated by theoretical investigations, there are little experimental studies on this issue. Most of experimental studies have measured the conductance at fixed bias voltage, and discussed the conductance fluctuations based on the theoretical calculation results [18]. It is essential to experimentally study the change of conductance and electronic structure of the single molecular junction during the formation process, in order to govern the conductance fluctuations of the single molecular junction.

There are several experimental techniques to study the electronic structure of the single molecular junction. Thermopower, current-voltage (I-V) characteristic, and shot noise measurements have been developed [19]. The thermopower measurement determines whether the charge carriers are holes or electrons, that is, whether conduction orbital is the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) [19, 20]. The I-V measurements provides the information of the energy difference between the conduction orbital and the Fermi level of the metal electrodes, and the strength of the electronic coupling between the metal and molecule [20–24]. The simultaneous shot noise and conductance measurement give information on the number of conductance channels and the transmission probability of each channel [25–27].

In this study, we have investigated the conductance and electronic structure of the BDT single molecular junction as a function of stretching length of the junction. The high stability of the junction is required for the stretch-
In length dependence measurement. The stability of the MCBJ device and the single molecular junction depends on the length of the free-standing nano bridge part of the Au electrodes [4, 28]. Therefore, the Au electrodes were fabricated with the nano fabrication techniques. The electronic structure was investigated by the current-voltage (I-V) characteristics. We analyzed the obtained I-V curves based on two different models; single channel model and field emission model (transmission voltage spectroscopy) [21–23]. The conductance of the BDT single molecular junction gradually decreased with the stretching length of the junction. The decrease in conductance was mainly caused by the decreases in the metal-molecule coupling. We also revealed the decrease in energy level of the HOMO with the stretching length.

II. EXPERIMENTAL

Figure 1 shows the experimental setup of the DC-conductance and I-V characteristic measurement for the single molecular junction. The Au nano-MCBJ sample was prepared with the following process [28]. A polyimide film (thickness: 0.2 mm) was deposited with spin-coating on the polished phosphor bronze substrate (thickness 0.5 mm). The nano-sized Au electrode was prepared using electron beam lithography and lift-off process. The size of the narrowest constriction was 150 nm × 130 nm. The Cr and Au films (Cr: 3.5 nm, Au: 130 nm) were thermally evaporated on the polyimide-coated substrate. Subsequently, the polyimide underneath the Au electrode was etched by isotropic reactive ion etching using O₂ plasma (80 W). A free-standing Au nano bridge (length ∼2 μm) was prepared. Figure 1(b) shows the scanning electron microscope (SEM) image of the nano-MCBJ sample. The Au nano-MCBJ sample was mounted on a MCBJ setup, consisting of a stacked piezo-element (piezoelectric constant: 0.116 μm/V; NEC tokin) and two fixed counter supports. A drop of a BDT solution (0.97 mM in EtOH) was dropped on the Au electrode. A self-assembled monolayer (SAM) film was formed on the surface of the Au electrode. The free-standing Au nano bridge was mechanically broken by bending the substrate using a piezoelectric push-rod. By retracting the push-rod, the substrate bending was reduced. The two point DC-conductance and I-V curves were measured as a function of stretching length. For stretching length dependence of I-V curves, a series of 18 curves were sequentially measured with two seconds interval between each measurement.

III. RESULTS AND DISCUSSION

Figure 2 shows the typical DC-conductance trace of the Au junction during the breaking process. The conductance trace showed a step around 1 G₀ (2e²/h), corresponding to the Au atomic junction [4, 11]. The 0.01 G₀ step appears after the 1 G₀ step. The previously reported STM-BJ measurement showed that the conductance of the BDT single molecular junction was 0.01 G₀ [17, 19, 29]. The step at 0.01 G₀ suggested the formation of the BDT single molecular junction. Finally, the conductance decreased to low value (< 10⁻³ G₀), indicating the breaking the junction. Figure 3 shows the example
FIG. 4. (a) Examples of I-V curves of the BDT single molecular junctions with different stretch length. Each I-V curve is shifted in the vertical direction with different value. The change in (b) energy difference between conduction orbital and Fermi level of the metal electrode, (c) strength of the metal-molecule coupling, and (d) conductance, as a function of the stretch length. The distribution was obtained by 11,088 I-V curves.

of the I-V curve of the BDT single molecular junction. Non-linear I-V curves were observed. In the single channel symmetric model, the I-V curve is represented by

\[
I(V) = \frac{2e}{h} \Gamma \left[ \tan^{-1} \left( \frac{eV - 2\varepsilon_0}{2\Gamma} \right) + \tan^{-1} \left( \frac{eV + 2\varepsilon_0}{2\Gamma} \right) \right]
\]

(1)

where \( \varepsilon_0 \) and \( \Gamma \) are the energy difference and coupling strength between molecular orbital and metal orbital [17, 23]. By fitting the experimental result with Eq. (1), \( \varepsilon_0 \) and \( \Gamma \) were determined to be \( \varepsilon_0 = 0.74 \) eV, \( \Gamma = 0.074 \) eV, respectively. The obtained values were close to the previously reported results of the BDT single molecular junction [17].

We then continuously measured the I-V curves of the BDT single molecular junction by stretching the junction (\( \Delta d \)). In the MCBJ configuration, the reduction factor \( r \), defined as a ratio between \( \Delta d \) and the displacement of the piezoactuator (\( \Delta z \)), is represented by \( r = \Delta d / \Delta z = 3ut/L^2 \), where \( L \), \( u \), and \( t \) are distance between the counter supports, length of the free-standing nano bridge, and thickness of the substrate, respectively [4]. In our sample, \( L = 15 \) mm, \( u = 2 \) mm, and \( t = 0.55 \) mm. Therefore, the reduction factor was \( 1.5 \times 10^{-5} \). By considering the reduction factor, the stretch length of the junction was calculated with \( \Delta z \), which was controlled by the voltage applied to the piezoactuator. The resolution of \( d \) was 10 pm. In order to statistically analyze the I-V curves of the BDT single molecular junction, we defined \( \Delta d = 0 \) as the stretch length where the junction conductance was \( 5.0 \times 10^{-4} \) G_0.

For each I-V curve, the conductance \( (G) \) was obtained by the average conductance around zero bias (-0.1 V–0.1 V), \( \varepsilon_0 \) and \( \Gamma \) were obtained by fitting the I-V curve with Eq. (1). We then averaged \( \varepsilon_0 \), \( \Gamma \), and \( G \) values at each \( \Delta d \) for 18 samples. Figure 4(b–d) is the average conductance, \( \varepsilon_0 \) and \( \Gamma \) as a function of \( \Delta d \). The conductance decreased with \( \Delta d \). \( \Gamma \) also decreased with \( \Delta d \), while \( \varepsilon_0 \) slightly increased with \( \Delta d \), although the change was quite small for the \( \varepsilon_0 \). In order to reveal the relationship between \( G \) and \( \Gamma \), and between \( G \) and \( \varepsilon_0 \), we obtained the correlation coefficient.

\[
r = \frac{\Sigma(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\Sigma(x_i - \bar{x})^2 \Sigma(y_i - \bar{y})^2}}
\]

(2)

where \( x_i \) was conductance of \( i \)-th I-V curve, \( \bar{x} \) was the average conductance, \( y_i \) was \( \varepsilon_0 \) or \( \Gamma \) of \( i \)-th I-V curve, and \( \bar{y} \) was the average of \( y \). The correlation coefficient was obtained by 11,088 data sets. The correlation coefficient between \( G \) and \( \Gamma \) was 0.71, while the correlation coefficient between \( G \) and \( \varepsilon_0 \) was -0.049. Therefore, the present experimental result clearly showed that the conductance change was caused by the change in \( \Gamma \), that is the degree of the hybridization of the metal and the molecular orbital.

Here, we compare our experimental results with previously reported results. Diez-Perez et al. studied the conductance of single ladder-type pentaphenylene molecule bridging Au electrodes as a function of stretch length [30]. The conductance decreased with the stretch length. With an increase in stretch length, the angle of the molecule changed from a highly tilted state to an orientation nearly perpendicular to the electrodes, which decreased the molecular \( \pi \)-orbital coupling to a metal electrode.
Therefore, the conductance of the single molecular junction decreased with the stretch length, which agreed with the present study. Kim et al. studied the conductance of alkanedithiol single molecular junction as a function of stretch length [18]. They observed both conductance increase and decrease with the stretch length. Using the theoretical calculation, they revealed that the stretching-induced conductance variation trend was strongly correlated with the S–Au coordination number. The conductance decreased with stretching when the coordination number was one, while the conductance increased when the coordination number was two or three. In their experiment, the most probable case was the conductance decrease with the stretch length, which agreed with the present results.

The electronic structure of the BDT single molecular junction can be also evaluated by the transition voltage spectroscopy (TVS) [21, 23]. TVS refers to the ln(I/V^2) vs 1/V plot, or the so-called Fowler-Nordheim plot. It is used to study the tunneling to field emission transition in solid-state junctions. The transition is indicated by a minimum in the F-N plot, and the position of the minimum is called the transition voltage, V_{tran}. The previously study showed that V_{tran} was proportional to the energy difference between the conduction orbital and Fermi level of metal electrode, that is, ε_0 obtained by fitting I-V with Eq. (1) assuming the single channel model [22]. Figure 5(a) shows the example of the F-N plot for the BDT single molecular junction. The minimum was clearly visible (V_{tran} = 0.59 V). Figure 5(b) shows the average V_{tran} as a function of Δd. The V_{tran} increased with Δd. Although V_{tran} does not directly provide energy difference between conduction orbital and Fermi level, the TVS results showed that energy difference increased with Δd, which was consistent with the results obtained by the analysis based on the single channel model. The small but slight positive energy shift was confirmed by the two methods based on the I-V curves.

Finally, we comment on the energy shift of the molecular orbital by stretching the single molecular junction. In the case of BDT, the conduction orbital is the HOMO, which is revealed by the thermopower measurement and theoretical calculation [19]. The present results showed that the energy of HOMO approached to the Fermi level with decreasing the molecule-metal distance. Similar experimental results were reported for the thiol-terminated zinc-porphyrin and C_{60} single molecular junction [31, 32]. Perrin et al. studied the alignment of the molecular energy level for the zinc-porphyrin single molecular junction as a function of electrode separation [32]. They reported the decrease in the HOMO-LUMO gap by the decrease in the electrode separation. The decrease in the HOMO-LUMO gap and level shift was explained by the image charge effects in the single molecular junction. The combination of the negatively charged thiols and the positive core of the molecule led to a contribution of the image charge effect [32]. Garcia et al. experimentally and theoretically studied the effect of pressure on thermopower of C_{60} single molecular junction [31]. They showed that the thermopower could be reversely controlled by the mechanical force. The origin of the change in thermopower was explained by the approach of the LUMO to the Fermi level at the compressed state. These experimental results agree with the present experimental results that the conduction orbital approached to the Fermi level with decreasing the molecule-metal distance. The previously reported theoretical studies showed the gap renormalization and closing were caused by the many body effect, and image charge effects [32–34]. Further theoretical analysis on the BDT single molecular junction is required to fix the origin of the energy shift of the HOMO.

IV. CONCLUSION

The electronic structure of the BDT single molecular junction as its dependence on the junction-stretch distance was investigated by lithographically fabricated mechanically controllable break junction technique. The lithographic nanofabrication allowed us to control and stretch the junction with 10 pm resolution, while I-V curves of the junction was repeatedly recorded. The analysis of the I-V curves based on the single channel tunneling analysis revealed the stretch-induced reduction of the conductance was mainly due to the reduction of the degree of the metal-molecule electronic coupling from 80 meV to 20 meV. In addition, the single channel tunneling analysis as well as the TVS analysis indicated that small upshift of the HOMO to the Fermi level of the electrode contributed to the stretch-induced reduction of the molecular conductance.
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