J|A|C|S
COMMUNICATIONS

Bond Fluctuation of S/Se Anchoring Observed in Single-Molecule Conductance Measurements using the Point Contact Method with Scanning Tunneling Microscopy

Satoshi Yasuda,[†] Shoji Yoshida,[†] Jiro Sasaki,[†] Yoshitaka Okutsu,[†] Tohru Nakamura,[‡]
Atsushi Taninaka,[†] Osamu Takeuchi,[†] and Hidemi Shigekawa*,[†]

Institute of Applied Physics, CREST-JST, 21st Century COE, University of Tsukuba, Tsukuba 305-8573, Japan, and
National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan

Received March 26, 2006; E-mail: hidemi@ims.tsukuba.ac.jp

Understanding and controlling the characteristics of the electric contact between a molecule and an electrode has become one of the major objectives in recent research.[1−3] For example, stochastic switching of wired molecules exhibits interesting but puzzling phenomena, which is a hotly debated issue.[4−6] Additionally, the effect of the different anchoring groups and their adsorption sites on the electric contact is another urgent issue to be clarified.[7] To achieve further advances, precise measurement of the electronic properties of a specific single molecule, which is wired to metal electrodes, is extremely important.

Here, we show the results obtained using the point contact method with scanning tunneling microscopy (STM) that enables us to selectively perform a repeated analysis of a chosen target molecule.

We used α,ω-bis(acetylthio)terthiophene ($3TS_2$) and α,ω-bis-(acetylseleno)terthiophene ($3TSe_2$) molecules as illustrated in Figure 1a as samples because of their high potential for application in molecular devices.[8,9] Isolated $3TS_2$ or $3TSe_2$ molecules embedded in a self-assembled monolayer (SAM) of octanethiol (C_8) molecules were prepared by immersing a Au(111) substrate into a solution containing a predefined amount of $3TS_2$ (or $3TSe_2$) and C_8 molecules. (Free thiol and selenol groups were prepared by adding pyrrolidine molecules.) All conductance measurements were performed in ultrahigh vacuum (UHV) at room temperature. In UHV, contamination of the sample surface is prevented, and the STM tip can be cleaned and fabricated by heat treatment.

Figure 1b shows an STM image of isolated $3TS_2$ molecules embedded in a C_8 SAM, where bright spots are $3TS_2$ molecules.

After we located target molecules, we placed a Au STM tip above a $3TS_2$ molecule and moved it toward the chosen molecule until an electric contact was achieved, where the sample bias voltage was kept at 0.5 V during the process. Since the thiol group at one end of the isolated $3TS_2$ molecule is exposed to the STM tip, a chemical bond is formed between the thiol group and the Au tip (Figure 1c).

Graphs a and b of Figure 2 show plots of the $I-Z$ curves obtained for a C_8 molecule and a $3TS_2$ molecule, respectively. The exponential change in the current exhibits two different slopes; see inset in Figure 2a. This is explained by the change in the local barrier height caused by the contact of the STM tip with the C_8 molecule. In contrast, an abrupt jump in the current was observed for the $3TS_2$ molecule (Figure 2b) because of the formation of a chemical bond between the Au tip and the $3TS_2$ molecule, as shown in Figure 1c. The current observed for the $3TS_2$ molecule was insensitive to further approach of the STM tip (∼0.2 nm) after the formation of the electric contact, indicating that a slight change in the molecular conformation has little influence on the subsequent conductance measurement.[1]

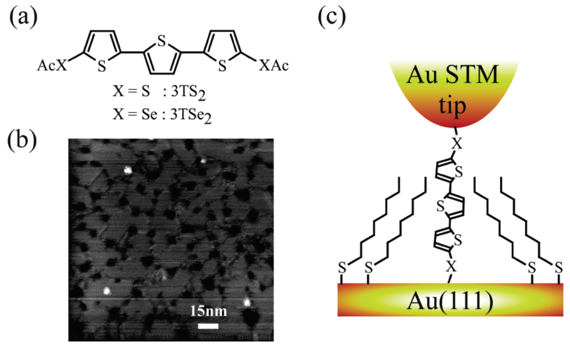

Figure 1. (a) Molecular structure. (b) An STM image of isolated single $3TS_2$ molecules embedded in a C_8 SAM (sample bias +1.0 V, tunneling current 10 pA). (c) Measurement conformation by the "point contact method" using STM.

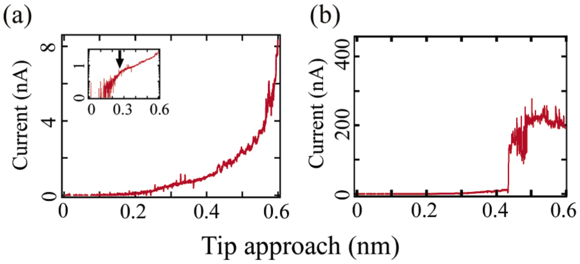

Figure 2. $I-Z$ curves obtained for (a) C_8 and (b) $3TS_2$ molecules. Inset in (a) is the logarithmic plot of the $I-Z$ curve. Tip approach position is related to the set point (sample bias +1.0 V, tunneling current 10 pA).

After a junction was formed, the bias voltage was swept repeatedly between −1 and +1 V, and the corresponding change in the current for each sweep was measured. The $I-V$ curves are almost linear between −0.1 and +0.1 V, as shown in Figures 3 and 4, and the conductance of each measurement was determined from the gradient of each $I-V$ curve in this voltage region.

In Figure 3a, all of the $I-V$ curves obtained from more than 400 individual measurements are presented as a contour plot, where several measurements were performed for each molecule. Contrast of the overlapped $I-V$ curves in the low bias voltage region clearly shows the existence of several groups of $I-V$ curves. Since the $I-V$ curves were observed over the different $3TS_2$ molecules, the obtained result represents the characteristic response of this molecule, including the electric contact with the electrodes.

Figure 3b is a histogram consisting of all the values of conductance determined from the $I-V$ curves in Figure 3a. In accordance with the groups in Figure 3a, the histogram consists of several subpeaks, as indicated by arrows. To examine the details,

---

[†] University of Tsukuba.
[‡] National Institute of Advanced Industrial Science and Technology.

10.1021/ja062066l CCC: $33.50 © 2006 American Chemical Society

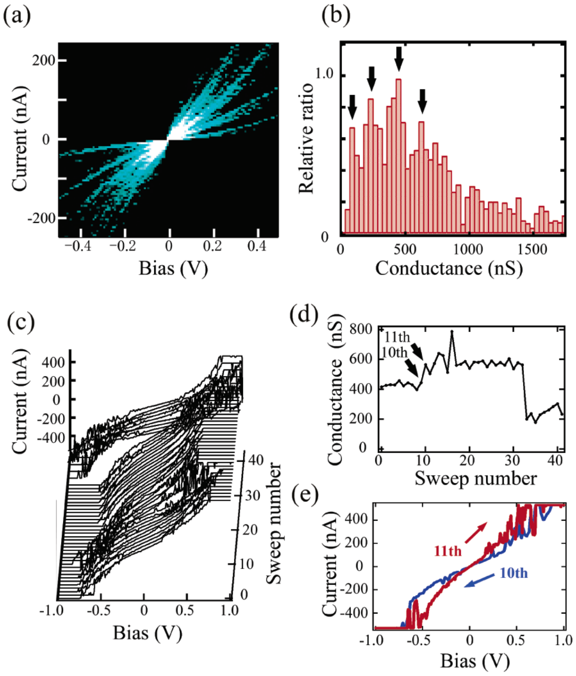

Figure 3. Results obtained for the $3TS_2$ molecule. (a) All $I-V$ curves obtained for the single $3TS_2$ molecules. (b) Histogram consisting of all values of conductance obtained form all $I-V$ curves in (a). Peaks indicated by the arrows are at 70, 220, 440, and 620 nS. (c) $I-V$ curves sequentially obtained for 20 cycles, and (d) conductance obtained from the $I-V$ curves. Flat area in (c) at high bias voltage region is due to saturation of the current. (e) Two sequential $I-V$ curves corresponding to the 10th and 11th measurements in (d).

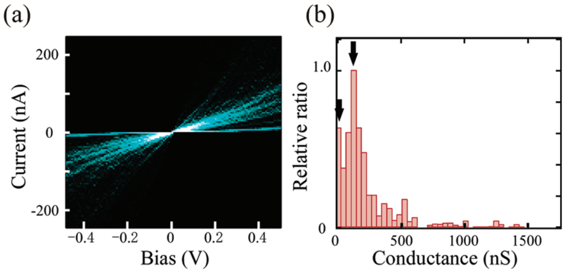

Figure 4. All $I-V$ curves (a) and the conductance histogram (b) obtained for $3TSe_2$ molecules, respectively. Peaks indicated by the arrows are at 10 and 120 nS.

$I-V$ curves were sequentially measured for 20 cycles on the same $3TS_2$ molecule (Figure 3c), and the obtained values of conductance are plotted as a function of the number of bias voltage sweeps (Figure 3d). Figure 3c shows smooth slopes in the low bias voltage region, where stable measurement can be obtained. As seen in panels c and d of Figure 3, there are three or four groups of different conductance, the values of which correspond to the peaks in the histogram of Figure 3b.

What causes the instability of the junction? Figure 3e shows two sequential $I-V$ curves corresponding to the 10th and 11th measurements in Figure 3d. In the high bias voltage region, there appear to be rapid changes in the current between the two envelopes of the $I-V$ curves extrapolated from those in the low bias region. This fluctuation between the two states resulted in the observed change in the conductance. In some cases, for a high voltage region, the current measured was found to be zero, which can correspond to the off-states in the stochastic switching process that have been observed for various molecules.[4,5] The fluctuation occurs in both the positive and negative bias voltage regions. Since conformational change, which, for example, is induced for the azo-molecule because of the interaction between the applied electric field and the molecular dipole moment,[10] does not exist for this molecule, the role of the current in the production of such phenomena as inelastic tunneling and electro-migration processes may be essential to the case.[6,11,12]

A possible mechanism to explain the observed change in the conductance is the thiol−gold bond fluctuation among the adsorption sites, which has been discussed in recent papers.[7,13] It is important to note that the relative relationship among the observed values of the conductance is comparable with that predicted by the theoretical analysis.[7]

A similar experiment was performed for a single $3TSe_2$ molecule. Figure 4a shows all the $I-V$ curves obtained for the single $3TSe_2$ molecules. Figure 4b is a histogram of all the values of conductance obtained from the $I-V$ curves in Figure 4a. In contrast to the case of the $3TS_2$ (Figure 3b), two dominant peaks are apparent in the low conductance region for the 3TSe molecule. This difference is considered to reflect the difference in the stability of the S/Se anchoring on the Au surface.

In summary, we have shown the results of single-molecule conductance measurements that enable us to selectively perform a repeated analysis of a chosen target molecule. Bond fluctuations of the S/Se anchoring, which may explain the stochastic switching observed in previous works,[4,5] were directly observed at the single-molecule level. As mentioned earlier, understanding and controlling the characteristics of the electric contact between a molecule and an electrode is the major challenge. The method outlined is expected to contribute to the understanding of single-molecule electronics and to the future development of molecular devices.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We thank Ms. Rie Yamashita for her help preparing this paper.

References

(1) Cui, X. D.; Primak, A.; Zarate, X.; Tomfohr, J.; Sankey, O. F.; Moore, A. L.; Moore, T. A.; Gust, D.; Harris, G.; Lindsay, S. M. *Science* **2001**, *294*, 571−574.
(2) Lindsay, S. M. *J. Chem. Educ.* **2005**, *82*, 727−733.
(3) Xu, B.; Tao, N. J. *Science* **2003**, *301*, 1221−1223.
(4) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W., Jr.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, *292*, 2303−2307.
(5) Ramachandran, G. K.; Hopson, T. J.; Rawlett, A. M.; Nagahara, L. A.; Primak, A.; Lindsay, S. M. *Science* **2003**, *300*, 1413−1416.
(6) Pitters, J. L.; Wolkow, R. A. *Nano Lett.* **2006**, *6*, 390−397.
(7) Ke, S.-H.; Baranger, H. U.; Yang, W. *J. Am. Chem. Soc.* **2004**, *126*, 15897−15904.
(8) Zhitenev, N. B.; Meng, H.; Bao, Z. *Phys. Rev. Lett.* **2002**, *88*, 226801-1−226801-4.
(9) Xu, B. Q.; Li, X. L.; Xiao, X. Y.; Sakaguchi, H.; Tao, N. J. *Nano Lett.* **2005**, *5*, 1491−1495.
(10) Yasuda, S.; Nakamura, T. Matsumoto, M.; Shigekawa, H. *J. Am. Chem. Soc.* **2003**, *125*, 16430−16433.
(11) Komeda, T.; Kim, Y.; Kawai, M.; Persson, B. N. J.; Ueba, H. *Science* **2002**, *295*, 2055−2058.
(12) Park, H.; Lim, A. K. L.; Alivisatos, A. P.; Park, J.; McEuen, P. L. *Appl. Phys. Lett.* **1999**, *75*, 301−303.
(13) Li, X.; He, J.; Hihath, J.; Xu, B.; Lindsay, S. M.; Tao, N. J. *J. Am. Chem. Soc.* **2006**, *128*, 2135−2141.

JA062066L