In-situ preparation of a single molecular junction with mechanically controllable break junctions in vacuum

M Kiguchi\textsuperscript{1,2,3}, N Sekiguchi\textsuperscript{1} and K. Murakoshi\textsuperscript{1}
\textsuperscript{1}Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, 060-0810, Japan
\textsuperscript{2}PRESTO, Japan Science and Technology Agency, Sapporo, 060-0810, Japan
E-mail: kiguti@sci.hokudai.ac.jp

Abstract. We have developed the mechanically controllable break junction system (in-situ MCBJ) to investigate the conductance of a single molecular junction in ultra high vacuum (UHV). Gas or liquid sample of bridging molecules was introduced to metal electrodes with a gas doser. For the introduction of solid sample, a Knudsen cell was used. In the present system, molecular junctions can be prepared without breaking vacuum. Thus, the atomic structure and chemical property of single molecular junction could be well defined. The electrical conductance of a single ethanedithiol molecule bridging between two Au electrodes was investigated with this in-situ MCBJ system. The conductance was determined to be 0.2 \( G_0 \) (\( G_0 = 2e^2/h \)).

1. Introduction
Recently, the search for molecular devices becomes a worldwide effort since these devices represent the ultimate size limit of functional devices \([1]\). In search for the molecular devices, it is important to understand the electron transport properties through a single molecule connecting two metal electrodes. Various single molecular junctions have been fabricated and their electron transport properties have been studied with mechanically controllable break junctions (MCBJ) and scanning tunnelling microscopy (STM) \([2-6]\). While various studies have been investigated for single molecular junctions, the conductance of a single molecular junction has not been determined precisely even for a simple molecule. For example, the conductance of a single 1,4-benzenedithiol bridging between two Au electrodes, which has been most extensively studied, can differ by two orders of magnitude among reports \( \{ 1.1 \times 10^{-2} \, G_0 \ (G_0 = 2e^2/h) \} [7] \sim 4.1 \times 10^{-4} \, G_0 \ [2] \} \). One of the reasons for large discrepancy of the conductance value is the chemical instability of the single molecular junction. In most of studies, single molecular junctions are exposed to air or solution during the sample preparation. The atomic structure and chemical property might not be well defined under these conditions. It is important to fabricate and investigate the single molecular junctions whose atomic structure and chemical property are well defined.

In order to prepare well defined single molecular junctions, we pay attention to MCBJ. By breaking the metal wire in ultra high vacuum (UHV) with MCBJ, well defined metal nano wire and nano gap can be fabricated. Atomic scale metal nano contacts can be successfully fabricated in UHV with MCBJ, and the conductance of metal nano contacts has been investigated for various metals \([8]\).
Although detailed studies has been done for metal nano contacts in UHV with MCBJ, the single molecular junctions was investigated only for small molecules, such as H₂, CO, O₂ [5,9]. It is because molecule was introduced with a capirally, and it is hard to introduce a molecule with low vapour pressure. For further investigation of the single molecular junction, method for the introduction of a molecule with low vapour pressure should be developed.

In the present study, we have constructed the novel MCBJ system (in-situ MCBJ) to investigate the conductance of a single molecule with low vapour pressure in UHV. The metal nano gap electrodes were fabricated in UHV with the in-situ MCBJ system. Gas or liquid sample of bridging molecules was introduced to metal electrodes with a gas doser. For the introduction of solid sample, a Knudsen cell was used. By preparing the molecular junction in UHV, the atomic structure and chemical property of the single molecular junction were well defined. In the present study, the conductance of a single ethanedithiol bridging between Au electrodes was investigated in UHV with the in-situ MCBJ system.

2. Experimental system

Figure 1(a) and (b) show the schematic side view and picture of MCBJ. The bending substrate was a plate of phosphor bronze about 1 mm thick, 20 mm long and 8 mm wide. The surface of the plate was insulated with a thin polymer foil (Kapton). The center of the 0.1 mm diameter metal wire was notched by a surgical knife to create a weak spot. Then, the wire was glued onto the bending beam by two drops of epoxy adhesive (Stycast 2850FT). The distance between the drops was manually reduced under the microscope. The whole assembly was mounted on a three-point bending mechanism, consisting of a stacked piezo-element (PI: P-249K007) and two fixed counter supports. By bending the substrate, the top surface of the substrate was expanded, and the wire was elongated. At some critical strain, the wire finally broke, forming two separated electrodes. By relaxing the bending of the substrate, the contact could be re-established.

MCBJ is set on the Cu stage of the insert. Figure 1(c) and (d) show the bottom and side view of the insert. To cool the sample effectively, the sample stage was thermally well connected to the liquid nitrogen reservoir (see Fig. 2). The sample temperature was monitored with a chromel-alumel thermocouple, which is attached to the stage.

Figure 2 shows the schematic view of the in-situ MCBJ system. The vacuum chamber is evacuated by turbo molecular pump (TMP) or sputter-ion pump (IP). The base pressure was $2 \times 10^{-7}$ Pa. Since the mechanical vibration from TMP affects the conductance measurements of the single molecular junctions, the chamber was evacuated by only IP during the conductance measurements. To introduce a sample with low vapour pressure, a gas doser and a Knudsen cell (up-to 700 K) are mounted on the vacuum chamber.
The gas or liquid sample is introduced to the clean metal electrodes with a gas doser. Solid sample is introduced to the metal electrodes with a Knudsen cell. The amount of gas introduced to the metal electrodes is monitored with the pressure gauge. The introduced solid sample was monitored with a quartz crystal oscillator.

3. Results and Discussion

Before investigating single molecular junctions, the conductance of Au nano contact was investigated with the in-situ MCBJ system. Figure 3(a) shows the typical conductance trace of the Au nano contacts in UHV at 100 K. The conductance decreased in a stepwise fashion with each step occurring at integer multiples of $G_0$. The corresponding conductance histogram (Fig. 3(b)) shows well-defined peaks near 1, 2, 3 $G_0$. The observed conductance quantization behaviour agrees with the previous results studied in UHV, air [8] and solution [10], indicating that the conductance quantization behaviour of metal nano contacts can be successfully observed with the in-situ MCBJ system.

The conductance of the single molecular junction was investigated with the in-situ MCBJ system. In the present study, we have measured alkane dithiol bridging between Au electrodes. This system has been investigated by many groups, and the reported conductance values were not affected by the surrounding, such as in air, solution [1,11]. Therefore, this system is an ideal system to evaluate the measurement system. Figure 4 shows the typical conductance trace and conductance histogram of Au point contact broken in ethanedithiol gas atmosphere ($1 \times 10^{-5}$ Pa) at 300 K. In addition to a plateau near 1 $G_0$, which originate from Au mono atomic contact, the plateau near 0.2 $G_0$ appeared in the conductance trace. The corresponding histogram shows a feature near 0.2 $G_0$. In the absence of molecules, neither steps nor peaks were observed below 1 $G_0$ (see Fig. 3 (a,b)). The plateau in the conductance trace and feature in the conductance histogram likely originate from the formation of a stable, Au/ethanedithiol/Au junction, possibly binding an alkane molecule to Au atoms via the S atom.

The conductance of alkanedithiol (HS-(CH$_2$)$_n$-SH: n=6,8,10) has been investigated as a function of molecular length [11]. The conductance exponentially decreased with the molecular length and it could be described by $G = A \exp(-\beta N)$, where $G$ is the conductance, $N$ is the number of methylene units, $A$ and $\beta$ are constants. Assuming that this molecular length dependence of the conductance can be extrapolated to short length, the conductance of ethane dithiol (n=2) is expected to be 0.2 $G_0$, which agrees with the results measured with the in-situ MCBJ system. The close agreement between the expected conductance value and our results, indicates that 0.2 $G_0$ observed in the present study originates from a single ethanedithiol molecule bridging between Au electrodes. The conductance of a single molecular junction could be successfully investigated with the in-situ MCBJ system.
system. The close agreement also indicates that the Au/ethanethiol/Au system was not affected by the contamination from the surroundings. It is because Au is chemically inert compared to other metals, and a clean surface could be obtained even in air. In addition, thiol end group bind to Au via a strong covalent bond. Because of this strong Au-S bond, an air stable single molecular junction could be formed between Au electrodes.

4. Conclusion

We have developed the in-situ MCBJ system to prepare single molecular junctions in UHV. Gas doser and Knudsen cell were mounted on the vacuum chamber to introduce the molecule with low vapour pressure. With this system, the electrical conductance of a single ethanethiol molecule bridging two Au electrodes was investigated. Not only gas or liquid but also solid sample can be investigated with the present in-situ MCBJ system. A investigation on molecular junctions of C_{60} or benzene is in progress in our laboratory.

Acknowledgments

We would like to express our sincere gratitude to Prof. J.M. van Ruitenbeek in Leiden University for many stimulating discussions and Mr. T. Kato in Hokkaido University for his technical support in preparing the in-situ MCBJ system. This work was supported by a Grant-in-Aid for Scientific Research A (No. 16205026) and Grant-in-Aid for Scientific Research on Priority Areas "Electron transport through a linked molecule in nano-scale" (No. 17069001) from MEXT.

References

[1] Tao N J 2006 Nature Nanotechnology 1 173
[2] Reed M A, Zhou C, Muller C J, Burgin T P and Tour J M 1997 Science 278 252
[3] Xu B and Tao N J 2003 Science 301 1221
[4] Kiguchi M, Miura S, Hara K, Sawamura M and Murakoshi K 2006 Appl. Phys. Lett. 89 213104
[5] Kiguchi M, Stadler R, Kristensen I S, Djukic D, and van Ruitenbeek J M 2007 Phys. Rev. Lett. 98 146802
[6] Park J, Pasupathy A N, Goldsmith J I, Chang C, Yaish Y, Petta J R, Rinkoski M, Sethna J P, Abruna H D, McEuen P L and Ralph D C 2002 Nature 417 722
[7] He J, Sankey O, Lee M, Tao N J, Li X and Lindsay S 2006 Faraday Discussion 131 145
[8] Agrait N, Yeyati A L, and van Ruitenbeek J M 2003 Phys. Rep. 377 81
[9] Thijsse W H A, Marjenburgh D, Bremmer R H, van Ruitenbeek J M 2006 Phys. Rev. Lett. 96 026806
[10] Kiguchi M, Konishi T and Murakoshi K 2006 Phys. Rev. B 73 125406
[11] Chen F, Li X, Hihath J, Huang Z and Tao N J 2006 J. Am. Chem. Soc. 128 15874