Oxygen−Silver Junction Formation for Single Molecule Conductance

Han Yeol Jo, Pil Sun Yoo, and Taekyeong Kim*

Department of Physics, Hankuk University of Foreign Studies, Yongin, Korea
*E-mail: tkim5562@gmail.com

ABSTRACT. We use a scanning tunneling microscope based break-junction technique to measure the conductance of a 4,4'-dimethoxybiphenyl molecular junction formed with Ag and Au electrodes. We observe the formation of a clear molecular junction with Ag electrodes that result from stable Ag−oxygen bonding structures. However we have no molecular bonding formation when using Au electrodes, resulting in a tunneling current between the top and bottom metal electrodes. We also see a clear peak in the conductance histogram of the Ag−oxygen molecular junctions, but no significant molecular features are seen with Au electrodes. Our work should open a new path to the conductance measurements of single-molecule junctions with oxygen linkers.

Key words: STM break-junction, Single molecule electronics, Oxygen, Ag electrodes

INTRODUCTION

Understanding the transport characteristics of single molecules bonded between metal electrodes is crucial for molecular electronics.[1,2]

Transport through a single molecule junction depends on the nature of the chemical linker group used to bind molecules to the metal electrodes.[3]

Researchers have used chemical groups, such as thiols (SH), amines (NH$_2$), dimethyl phosphines (PMe$_2$), pyridine or methyl sulfides (SMe), etc., to achieve stable molecular junction formation with metal electrodes.[4,5]

However, for thiols on Au, which is the most common metal−molecule binding motif, the force required to break the Au−S bond is larger than that required for the Au−Au bond, leading to grain migration, pitting of the electrodes, and metal island formation, all which complicate the interpretation of the conductance measurements for a single molecule.[6−9]

On the other hand, molecular junctions formed using amine end groups with Au point contacts allow us to have reliable and reproducible conductance measurements due to the delocalization of the lone-pair of electrons from the amine nitrogen to the coordinatively unsaturated surface Au atoms.[2,10]

However, oxygen has not been used as a linker group for molecular electronics, and it is still challenging to carry out experimental and theoretical conductance measurements for a single molecule, even though doing so would be very useful for chemical and biological applications.

In the present paper, we use a scanning tunneling microscope based break-junction (STM-BJ) technique to measure the molecular conductance of 4,4'-dimethoxybiphenyl formed with Ag and Au electrodes under ambient conditions. We find that oxygen atoms, as a linker group, bind stably to Ag metal electrodes, resulting in the formation of Ag−oxygen molecular junctions and in a clear peak in the conductance histogram. However, we see no molecular junction formation for Au metal electrodes with oxygen linkers since oxygen atoms hardly bind to the Au metal. Therefore, Ag metal electrodes with oxygen atoms as a linker group allow for better measurements in order to study in situ reactions that can lead to the formation of novel single-molecule.[11−14]

EXPERIMENTAL

Molecular conductance measurements were performed by repeatedly forming and breaking Ag and Au point contacts in the presence of 4,4'-dimethoxybiphenyl using a STM-BJ technique under ambient conditions. A mechanically polished Ag slug (Alfa-Aesar 99.99% purity, diameter 5 mm) with a freshly cut Ag wire tip (Alfa-Aesar, 99.9985% purity, diameter 0.25 m) is used for the Ag measurements, and an Au/mica substrate and an Au wire tip (Alfa-Aesar, 99.998% purity, diameter 0.25 m) are used for the Au measurements. 4,4'-dimethoxybiphenyl was obtained from Sigma-Aldrich and was used without further purification. We drop the 1 mM solution of the 4,4'-dimethoxybiphenyl molecules in 1,2,4-trichlorobenzene (99% Aldrich) on the Au coated Si substrate for the Au-measurement and the Ag slug for the Ag-measurement.[2,4,11]

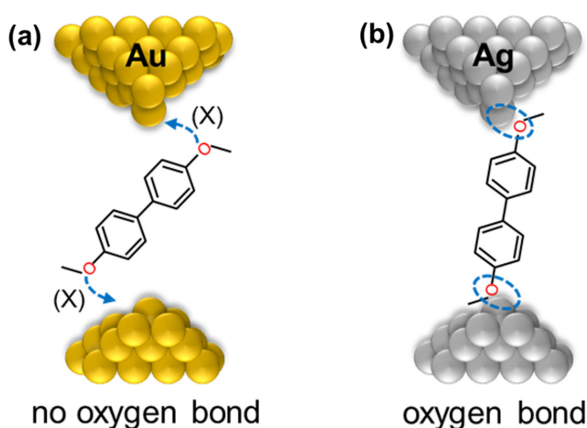Each conductance measurement starts by approaching the tip to the substrate to make a metal point-contact with a

Figure 1. Schematic diagram of a molecular junction formed using an oxygen linker end group with Au (a) and Ag (b) metal electrodes. The oxygen atoms bond to the Ag atoms but not to the Au atoms.
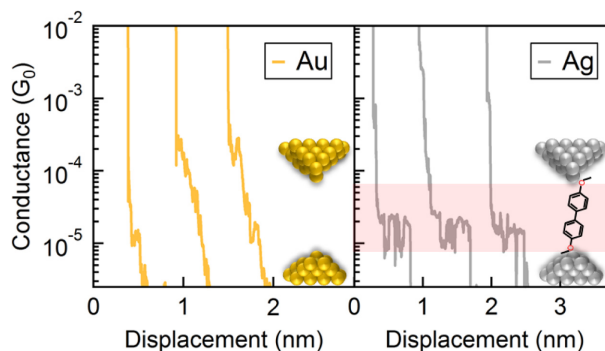

Figure 2. Sample conductance traces with and without molecules for Au (left panel) and Ag (right panel) electrodes. The light red box in the right panel indicates a clear molecular plateau of the individual conductance traces, as shown by the figure in the inset. A tunneling current below $10^{-3}G_0$ in the gap of the two metal electrodes is observed in the conductance traces of Au electrodes without molecular junctions.
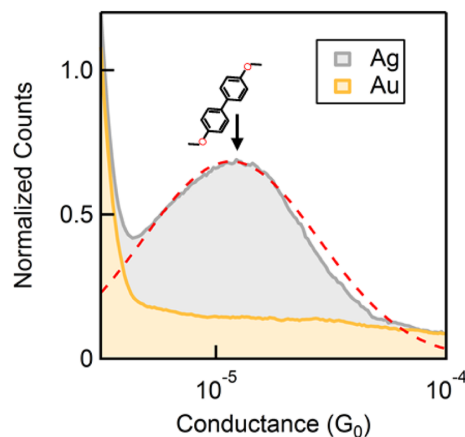
conductance of at least 20 G_0 ($G_0 = 2e^2/h$, the quantum of conductance). This ensures that a new electrode structure is created for each conductance measurement. The tip is then withdrawn from the substrate at a speed of about 25 nm/s while the current is recorded at a fixed applied bias voltage of 50 mV with a 40 kHz data acquisition rate. This gives us a conductance (current/voltage) versus displacement trace. Thousands of curves were collected for all the reported measurements to allow for detailed statistical analysis (see the Supporting Information for more information about the principle and the experimental procedure of the STM-BJ).

Figures 1a and b show schematic diagrams of the formation of molecular junctions with 4,4'-dimethoxybiphenyl in the gap between the top and bottom Au or Ag electrodes. The electrodes have a small gap distance of ~0.5 nm for Ag and ~0.7 nm for Au due to the initial relaxation as soon as the metal atomic contact is ruptured. In case of the Au electrodes (*Figure* 1a), the oxygen atoms that are the end group of the molecule do not bond to the Au atoms, resulting in no molecular junction structures between the two electrodes. However, Ag−molecule−Ag junction structures can be formed by using an oxygen linker group to bond between the molecule and the Ag atoms because the bonding events for oxygen are more pronounced in Ag atoms relative to Au, due to its higher reactivity.[14,15]

Furthermore, oxygen can make the chemical bonding with Ag atom via the physisorbed or chemisorbed states.[16-18]

RESULTS AND DISCUSSION

Figure 2 shows the individual sample conductance traces

Figure 3. Normalized conductance histogram for the 4,4'-dimethoxybiphenyl measurements with Ag (gray) and Au (yellow) electrodes using over 10,000 traces. The red dashed curve in the Ag measurement is the Gaussian fit to a molecular conductance peak of about $5.2 \times 10^{-5}G_0$.

from the measurements in a solution of 4,4'-dimethoxybiphenyl using Au (yellow, left panel) and Ag (gray, right panel) electrodes. When the Au atom chain is broken with no molecules remaining, the conductance decreases exponentially with electrode displacement due to tunneling between the top and bottom electrodes, as shown in the inset of the left panel. However, the conductance traces when using Ag electrodes show clear molecular steps near $10^{-4}G_0$ to $10^{-5}G_0$, as shown by the light red color box in right panel. This is attributed to the formation of a molecular junction structure of the oxygen linker group bonded to the Ag metal atom, indicated in the inset of the right panel.

Repeated measurements of the conductance traces allow us to perform a statistical analysis of the properties of the

molecular junction. We measure thousands of molecular junctions formed with Au and Ag electrodes in the same manner, and *Figure* 3 shows the logarithmically binned conductance histogram generated without data selection for 4,4'-dimethoxybiphenyl for Au (10,000 traces) and Ag (10,000 traces) using a linear bin size of $0.0001G_0$. The red dashed curve is the Gaussian fit for the molecular peak with the Ag electrodes. The most probable junction conductance is of $5.2 \times 10^{-5}G_0$ for the Ag–molecule–Ag junctions, as indicated by the arrow obtained from Gaussian fitting. This indicates that the oxygen end group of the molecule is well bonded to the Ag metal atoms, resulting in a stable formation of a molecular junction. However, there are no significant molecular features in the conductance histogram with Au electrodes, indicating that oxygen linkers do not bond to the Au metal atoms.

A two-dimensional (2D) conductance histogram containing displacement information is required in order to investigate the length of the molecular plateau.[11,19]

We create a 2D histogram by overlaying all measured conductance traces after aligning them along the positive displacement (x) axis at a conductance of $1G_0$ because the conductance plateau occurs in random locations along the displacement axis. Logarithmic bins are used for the conductance axis, and linear bins for the displacement axis. The normalized 2D conductance-displacement histogram and the conductance fitting profile (black dashed line) in *Figure* 4a shows that the molecular conductance peak extends to approximately 0.6 nm along the x-axis for the Ag metal electrodes. The arrow points to a fully extended molecular junction before breaking the bond between the molecule and the Ag electrodes. Once a molecular junction is formed, the binding sites of the oxygen atom to the

Ag atoms can move from one atom to the next during elongation by the piezo, as shown in the figure in the inset, in which the molecular plateau length is observed in the 2D histogram.

Figure 4b shows a normalized 2D conductance-displacement histogram with Au metal electrodes with no significant molecular features. This means that no molecular junctions exist between the top and bottom Au electrodes due to non-bonding of oxygen linker group to Au metal atoms. The black dashed line in *Figure* 4b represents the fitted conductance profile from the 2D conductance-displacement histogram, and it shows a tunneling current in the gap between the two Au electrodes without molecular junctions.

CONCLUSION

In conclusion, we used an STM-BJ technique to measure the conductance of 4,4'-dimethoxybiphenyl molecule with Ag metal electrodes under ambient conditions. We find that the oxygen end group of the molecule is bonded to the Ag metal atoms rather than the Au metal atoms, resulting in a stable Ag-molecule junction. A statistically analysis from more than 10,000 conductance traces indicates that the most probable conductance of a 4,4'-dimethoxybiphenyl molecule formed with Ag electrodes is of about $5.2 \times 10^{-5}G_0$ and that the plateau length of the molecule is of about 0.6 nm. Our work should help us to study the fundamentals and the applications of the oxygen atoms as a linker group for molecular electronics and future organic devices.

Figure 4. Two dimensional conductance-displacement histogram for the molecule with Ag (a) and Au (b) electrodes. The inset in (a) shows the schematic diagram of the evolution of the molecular junction during the elongation of the piezo. The black dashed lines indicate a molecular plateau (a) and a tunneling current (b) between top and bottom metal electrodes as shown in inset. The arrow in (a) indicates a molecular breaking point for the Ag electrodes.

REFERENCES

1. Venkataraman, L.; Klare, J. E.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nature* **2006**, *442*, 904.
2. Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nano Lett.* **2006**, *6*, 458.
3. Mishchenko, A.; Vonlanthen, D.; Meded, V.; Bürkle, M.; Li, C.; Pobelov, I. V.; Bagrets, A.; Viljas, J. K.; Pauly, F.; Evers, F.; Mayor, M.; Wandlowski, T. *Nano Lett.* **2009**, *10*, 156.
4. Park, Y. S.; Whalley, A. C.; Kamenetska, M.; Steigerwald, M. L.; Hybertsen, M. S.; Nuckolls, C.; Venkataraman, L. *J. Am. Chem. Soc.* **2007**, *129*, 15768.
5. Kamenetska, M.; Quek, S. Y.; Whalley, A. C.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Nuckolls, C.; Hybertsen,
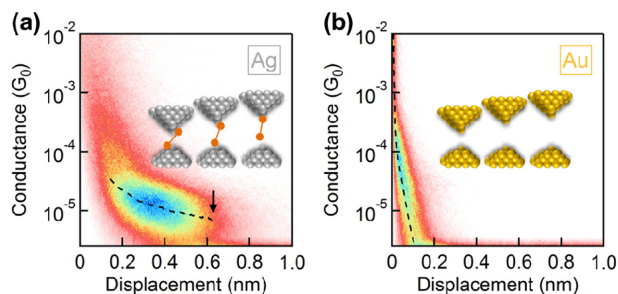
M. S.; Neaton, J. B.; Venkataraman, L. *J. Am. Chem. Soc.* **2010**, *132*, 6817.

6. Xu, B.; Tao, N. J. *Science* **2003**, *301*, 1221.

7. Kruger, D.; Fuchs, H.; Rousseau, R.; Marx, D.; Parrinello, M. *Phys. Rev. Lett.* **2002**, *89*, 186402.

8. Houck, A. A.; Labaziewicz, J.; Chan, E. K.; Folk, J. A.; Chuang, I. L. *Nano Lett.* **2005**, *5*, 1685.

9. Rubio, G.; Agrait, N.; Vieira, S. *Phys. Rev. Lett.* **1996**, *76*, 2302.

10. Quek, S. Y.; Venkataraman, L.; Choi, H. J.; Louie, S. G.; Hybertsen, M. S.; Neaton, J. B. *Nano Lett.* **2007**, *7*, 3477.

11. Kim, T.; Vazquez, H.; Hybertsen, M. S.; Venkataraman, L. *Nano Lett.* **2013**, *13*, 3358.

12. Kaneko, S.; Nakazumi, T.; Kiguchi, M. *J. Phys. Chem. Lett.* **2010**, *1*, 3520.

13. Qi, Y.; Guan, D.; Jiang, Y.; Zheng, Y.; Liu, C. *Phys. Rev. Lett.* **2006**, *97*, 256101.

14. Thijssen, W. H. A.; Marjenburgh, D.; Bremmer, R. H.; van Ruitenbeek, J. M. *Phys. Rev. Lett.* **2006**, *96*, 026806.

15. Jelínek, P.; Pérez, R.; Ortega, J.; Flores, F. *Phys. Rev. B* **2008**, *77*, 115447.

16. Bao, X.; Muhler, M.; Schedel-Niedrig, T.; Schlögl, R. *Phys. Rev. B* **1996**, *54*, 2249.

17. Boronin, A. I.; Koscheev, S. V.; Zhidomirov, G. M. *J. Electron. Spectrosc. Relat. Phenom.* **1998**, *96*, 43.

18. Prince, K. C.; Paolucci, G.; Bradshaw, A. M. *Surf. Sci.* **1986**, *175*, 101.

19. Kamenetska, M.; Koentopp, M.; Whalley, A. C.; Park, Y. S.; Steigerwald, M. L.; Nuckolls, C.; Hybertsen, M. S.; Venkataraman, L. *Phys. Rev. Lett.* **2009**, *102*, 126803.