

Conductance of a Single Molecule Junction Formed with Ni, Au, and Ag Electrodes

Taekyeong Kim*

Department of Physics, Hankuk University of Foreign Studies, Yongin, Korea.

**E-mail: tkim5562@gmail.com*

(Received September 13, 2014; Accepted October 10, 2014)

ABSTRACT: We measure the conductance of a 4,4'-diaminobiphenyl formed with Ni electrodes using a scanning tunneling microscope-based break-junction technique. For comparison, we use Au or Ag electrodes to form a metal-molecular junction. For molecules that conduct through the highest occupied molecular orbital, junctions formed with Ni show similar conductance as Au and are more conductive than those formed with Ag, consistent with the higher work function for Ni or Au. Furthermore, we observe that the measured molecular junction length that is formed with the Ni or Au electrodes was shorter than that formed with the Ag electrodes. These observations are attributed to a larger gap distance of the Ni or Au electrodes compared to that of the Ag electrodes after the metal contact ruptures. Since our work allows us to measure the conductance of a molecule formed with various electrodes, it should be relevant to molecular electronics with versatile materials.

Key words: Scanning tunneling microscope based break-junction, Single molecule, Ni electrodes, Statistical analysis

INTRODUCTION

Understanding molecule-metal junctions is of critical importance for the design of molecular electronic circuits since the electrical properties of the junctions extremely depend on the type of metal and on its contact with molecules.¹⁻⁶ The scanning tunneling microscope based break-junction (STM-BJ) technique is one of the most versatile techniques that can generate single metal-molecule junctions.^{7,8} However, these measurements have been mostly carried out using gold (Au) and silver (Ag) metal electrodes since Au is chemically inert and is a strong optical enhancer while Ag has a high catalytic activity.⁹⁻¹² However, little has been done to experimentally characterize the electrical properties of molecular junction formed with nickel (Ni).

In this study, we measured the characteristics of a 4,4'-diaminobiphenyl molecule when using Ni electrodes under an STM-BJ technique in ambient conditions. For comparison, we also use Au or Ag metal to measure the conductance of the molecule formed with the other metal electrodes. A higher junction conductance with Ni or Au electrodes is obtained than with Ag electrodes, which follows the trend of the work function for the metals for the amine terminated molecules in which the conducting path is the highest occupied molecular orbital (HOMO). Furthermore, we observe a shorter molecular junction length for Ni or Au electrodes, as compared to Ag electrodes. These observations are attributed to a larger gap distance

for the Ni or Au electrodes than that for the Ag electrodes after the metal contact ruptures.

EXPERIMENTAL

We measure the conductance of a junction by repeatedly forming and breaking Ni, Au, and Au point contacts in the presence of target molecules by using a modified STM-BJ setup that was previously described in detail.^{2,7,13} Mechanically polished Ni and Ag slugs (Alfa-Aesar 99.99% purity) with freshly cut Ni and Ag wire tips (Alfa-Aesar, 99.9985% purity) were used for the Ni and Ag measurements. We also deposited a 100-nm Au film on the mica substrate and used the Au/mica substrate with an Au wire (Alfa-Aesar, 99.998% purity) to make the Au measurements. The STM operates in ambient conditions at room temperature, and the junctions are broken in a 1 mM solution of the molecules in 1,2,4-trichlorobenzene (Sigma-Aldrich 99% purity). Each conductance measurement starts by moving the tip of the STM into the substrate to create a metal point-contact with a conductance of at least 50 G_0 which ensures that a new electrode structure is created for each measurement. The tip is then withdrawn from the substrate at a speed of about 250 nm/s while the current is recorded at a fixed applied bias voltage of 25 mV at a 40 kHz data acquisition rate. This yields a conductance (current/voltage) versus displacement trace. Thousands of curves were collected for all measurements reported here to allow for detailed statistical analysis.

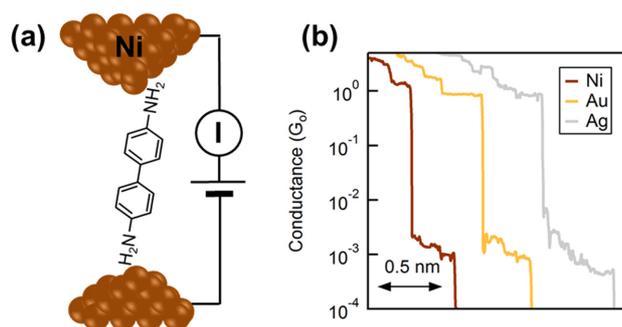


Figure 1. (a) Schematic of the molecular junctions with Ni electrodes. (b) Sample conductance versus displacement traces of a 4,4'-diaminobiphenyl molecule measured with Ni (brown), Au (yellow) and Ag (gray) electrodes.

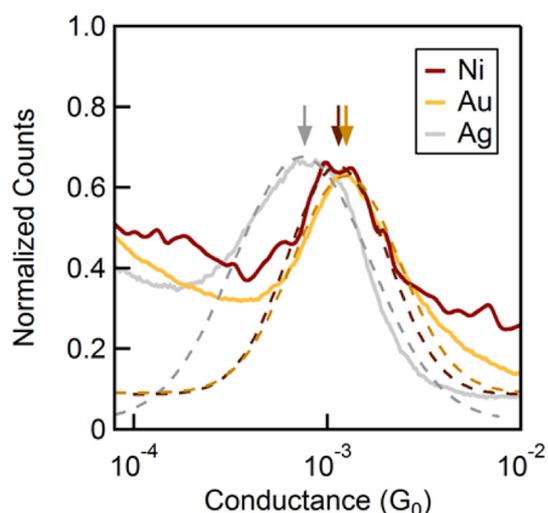


Figure 2. Logarithmically binned conductance histograms generated from over 5,000 traces for each of the metal junctions. The dashed curves are Gaussian fits and the arrows represent the average conductance.

RESULTS AND DISCUSSION

Fig. 1a shows the schematics of a 4,4'-diaminobiphenyl-metal junction after the metal-metal contact ruptured while using Ni electrodes. *Fig. 1b* shows the individual conductance traces from the measurement of a 4,4'-diaminobiphenyl by using Ni (brown), Au (yellow), and Ag (gray) metal electrodes. Initially all of the electrodes have conductance plateaus at and above a $1 G_0$ ($G_0 = 2e^2/h$, the quantum conductance) metal-metal contact. In addition, clear plateaus are seen at around $10^{-3}G_0$ in these metal electrodes due to the formation of stable metal-molecule-metal junctions.

Fig. 2 shows log-binned conductance histograms measured with a 4,4'-diaminobiphenyl molecule using Ni (brown,

Table 1. Each metal work function and the average conductance determined from the conductance histogram for Ni, Au and Ag electrodes

	Ni	Au	Ag
Average Conductance ($10^{-3}G_0$)	1.13	1.16	0.85
Work Function (eV)	5.04–5.35	5.1–5.47	4.26–4.74

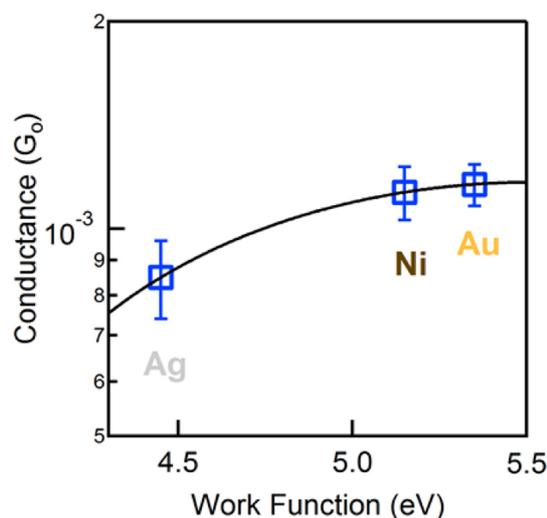


Figure 3. Conductance as a function of the metal work functions for the molecular junctions. The solid curve is a guide for the eye.

1000 traces), Au (yellow, 1500 traces), and Ag (gray, 1200 traces) electrodes without any data selection. The dashed curves are the Gaussian fits for the molecular peaks and we obtain the average conductance values from the center of these Gaussian fits as indicated by the arrows. The most probable junction conductance is $1.13 \times 10^{-3} G_0$ for the Ni junctions, $1.16 \times 10^{-3} G_0$ for the Au junctions, and $0.85 \times 10^{-3} G_0$ for the Ag junctions. These results are consistent with the trends for the metal work function summarized in *Table 1*. The work function of metals are 5.04–5.35 eV for Ni, 5.1–5.47 eV for Au, and 4.26–4.74 eV for Ag.^{5,14,15}

Fig. 3 shows a plot of the conductance versus metal work function resulting from these measurements. Each data point and error bar represent the average conductance and the standard deviation determined from full width at half maximum (FWHM) of the width of the conductance histograms in *Fig. 2*. The solid curve is the best-fit of these data points. *Fig. 3* shows a clear trend where the conductance increases as the metal work function increases.^{5,6}

To understand these results, we show a schematic energy-level diagram for these junctions that have formed with each metal electrode (*Fig. 4*). The highest occupied molecular

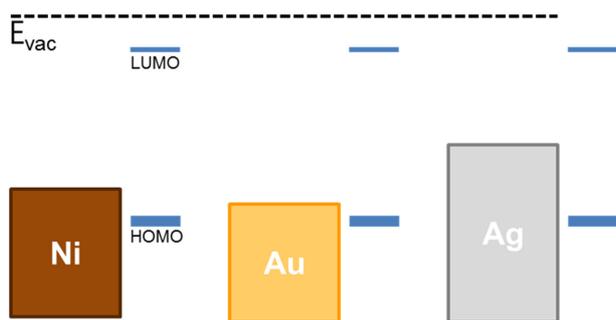


Figure 4. A schematic diagram indicating the molecular orbital levels relative to the Ni, Au and Ag chemical potentials.

orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of a 4,4'-diaminobiphenyl molecule, with respect to each metal Fermi energy (E_F), are shown. The estimated energy level alignment in *Fig. 4* indicates that the HOMO levels lie much closer to E_F , which means that the HOMO plays an important role in the conducting path of our metal-molecular junctions. Therefore, the conductance is higher when the metal chemical potential is closer to the HOMO, i.e., when Ni or Au electrodes are used to measure the conductance.

To understand the difference of the molecular junction length of the Ni, Au, and Ag electrodes, we measure the gap distance created after the Ag and Au metal contacts rupture, as shown in previous studies.^{13,16} Briefly, we elongate a metal contact until it ruptures, and then we push the electrodes back together to determine the net distance that the electrodes need to move before a contact with a conductance of $1 G_0$ is formed. The gap distance is the net distance measured for each metal contact without additional molecules. *Fig. 5a* shows a normalized histogram of the gap distance for Ni (brown), Au (yellow) and Ag (gray) electrodes with over 2,000 traces, and the Gaussian fits are shown with solid lines. We obtain an average gap distance of ~ 0.9 nm for Ni or Au electrodes and of ~ 0.6 nm for Ag electrodes, which shows that the gap distance for Ni or Au electrodes is larger than that for Ag electrodes.

Fig. 5b shows the molecular length profiles of the molecular-metal junctions formed with Ni (brown), Au (yellow), and Ag (gray) electrodes determined from the two dimensional conductance-displacement histograms of over 1,000 traces for each profile, as shown in previous papers.^{2,17} The brown and yellow profiles formed from measurements with Ni and Au electrodes show that the molecular conductance peak extends to approximately 0.5 nm along the x-axis, and the gray profiles formed with Ag electrodes show that the molecular conductance peak extends to

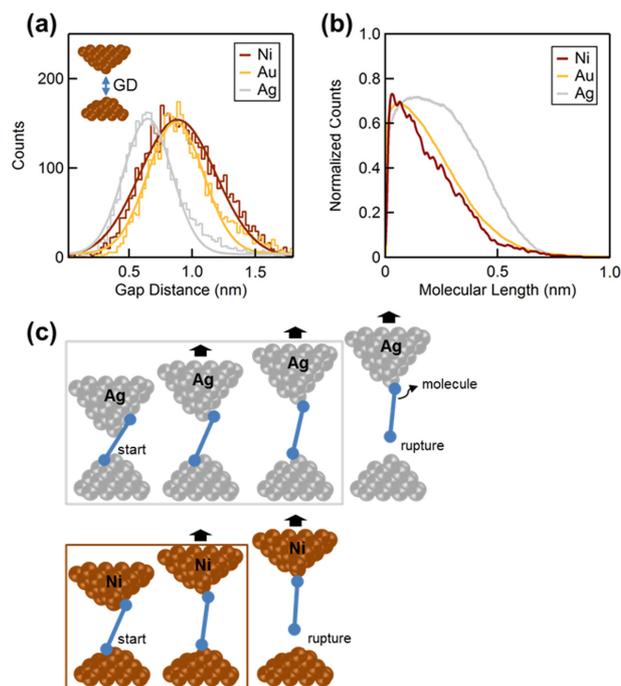


Figure 5. (a) Histogram of the gap distance measured for Ni (brown), Au (yellow), and Ag (gray) electrodes. The inset shows the illustration of the gap distance (GD) between the tip and the substrate electrodes. Gaussian fits are also shown. (b) Molecular length profiles for each metal junctions. (c) Schematic diagram of the molecular junction geometries for Ag and Ni electrodes.

approximately 0.7 nm along the x-axis. By comparing all of the profiles, we find that the molecular junction length formed with Ni or Au electrodes is shorter than that formed with Ag electrodes.

The essential point for the present discussion is that the initial gap distance between the electrodes is smaller by about 2–3 Å for Ag as compared to that for Ni or Au electrodes. This qualitatively affects the molecular junction lengths observed in the length profiles shown in *Fig. 5b*. At the start of a molecular junction, the gap distance between the tip and substrate is smaller by about 2–3 Å with Ag electrodes when compared against those with Ni or Au electrodes. This allows molecular junctions to be extended an additional 2–3 Å with Ag electrodes before the metal-molecule ruptures as shown in the schematic diagram in *Fig. 5c*. The boxes indicate the molecular length for each of Ag and Ni electrodes during the piezo movement (black arrow). Actually, the conductance measurement starts by approaching the tip to the substrate to make the metal point-contact. The metal channel undergoes an initial relaxation opening up the gap distance of the top and bottom electrodes as soon as the metal contact is ruptured owing to the diffusion of the metal atoms with the elastic and plastic

deformations.^{18,19}

Then 4,4'-diaminobiphenyl can be inserted in the gap, and the metal-molecule-metal junction is formed, where the amine (NH₂) linker groups bind to the apex atom of the tip and substrate.

CONCLUSION

In conclusion, we measure the conductance of a 4,4'-diaminobiphenyl formed with Ni electrodes by using an STM-BJ technique under ambient conditions. We also compare the conductance of the molecule-Ni junction with those of other metal junctions, including Au or Ag electrodes. We obtain a higher conductance for the molecule formed with Ni or Au electrodes than for that formed with Ag electrodes, a finding that is consistent with the trends of the metal work function. Furthermore, we confirm that the molecular junction lengths for Ni or Au electrodes are shorter than those for Ag electrodes due to the smaller gap distance of Ag after the metal contact ruptures. Our work thus opens a new possibility for fabrication of single-molecule electronic circuits using Ni electrodes.

Acknowledgments. This work was supported by Hankuk University of Foreign Studies Research Fund.

REFERENCES

1. 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.
2. Kim, T.; Vazquez, H.; Hybertsen, M. S.; Venkataraman, L. *Nano Lett.* **2013**, *13*, 3358.
3. Frei, M.; Aradhya, S. V.; Hybertsen, M. S.; Venkataraman, L. *J. Am. Chem. Soc.* **2012**, *134*, 4003.
4. Frei, M.; Aradhya, S. V.; Koentopp, M.; Hybertsen, M. S.; Venkataraman, L. *Nano Lett.* **2011**, *11*, 1518.
5. Kim, B.; Choi, S. H.; Zhu, X. Y.; Frisbie, C. D. *J. Am. Chem. Soc.* **2011**, *133*, 19864.
6. Beebe, J. M.; Engelkes, V. B.; Miller, L. L.; Frisbie, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 11268.
7. Venkataraman, L.; Klare, J. E.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nature* **2006**, *442*, 904.
8. Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nano Lett.* **2006**, *6*, 458.
9. Jiang, N.; Foley, E. T.; Klingsporn, J. M.; Sonntag, M. D.; Valley, N. A.; Dieringer, J. A.; Seideman, T.; Schatz, G. C.; Hersam, M. C.; Van Duyne, R. P. *Nano Lett.* **2011**, *12*, 5061.
10. Lee, S. J.; Baik, J. M.; Moskovits, M. *Nano Lett.* **2008**, *8*, 3244.
11. van Schrojenstein Lantman, E. M.; Deckert-Gaudig, T.; Mank, A. J. G.; Deckert, V.; Weckhuysen, B. M. *Nat Nano* **2012**, *7*, 583.
12. Liu, X.; Wang, F.; Niazov-Elkan, A.; Guo, W.; Willner, I. *Nano Lett.* **2012**, *13*, 309.
13. Quek, S. Y.; Kamenetska, M.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Hybertsen, M. S.; Neaton, J. B.; Venkataraman, L. *Nat Nano* **2009**, *4*, 230.
14. Ishii, H.; Sugiyama, K.; Ito, E.; Seki, K. *Adv. Mater.* **1999**, *11*, 605.
15. Yee, S. K.; Malen, J. A.; Majumdar, A.; Segalman, R. A. *Nano Lett.* **2011**, *11*, 4089.
16. 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.
17. 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.
18. Aradhya, S. V.; Frei, M.; Halbritter, A.; Venkataraman, L. *ACS nano* **2013**, *7*, 3706.
19. Rubio-Bollinger, G.; Bahn, S. R.; Agraït, N.; Jacobsen, K. W.; Vieira, S. *Phys. Rev. Lett.* **2001**, *87*, 026101.