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

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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. The scanning tunneling microscope based break-junction (STM-BJ) technique is one of the most versatile techniques that can generate single metal-molecule junctions. 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. 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. 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 STM operates at a frequency of 40 kHz. When the junction is formed, the conductance is measured at a fixed applied bias voltage of 25 mV. 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.
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 molecule 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 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.

![Figure 1](image1.png)  
**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](image2.png)  
**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.

![Table 1](image3.png)  
<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Au</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Conductance ($10^{-3} G_0$)</td>
<td>1.13</td>
<td>1.16</td>
<td>0.85</td>
</tr>
<tr>
<td>Work Function (eV)</td>
<td>5.04–5.35</td>
<td>5.1–5.47</td>
<td>4.26–4.74</td>
</tr>
</tbody>
</table>

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

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 3](image4.png)  
**Figure 3.** Conductance as a function of the metal work functions for the molecular junctions. The solid curve is a guide for the eye.
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 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
Then 4,4'-diaminobiphenyl can be inserted in the gap, and the metal-molecule-metal junction is formed, where the amine (NH$_2$) 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.

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**REFERENCES**