Electrical conductance of Rh atomic contacts under electrochemical potential control

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The electric conductance of Rh atomic contacts was investigated under the electrochemical potential control. The conductance histogram of Rh atomic contacts varied with the electrochemical potential. When the electrochemical potential of the contact was kept at Φ_0=0.1 V vs Ag/AgCl (Rh potential), the conductance histogram did not show any features. At Φ_0=−0.1 V (under potential deposited hydrogen potential), the conductance histogram showed a feature around $2.3G_0$ ($G_0=2e^2/h$), which agreed with the conductance value of a clean Rh atomic contact, which was observed in ultrahigh vacuum at low temperature. At Φ_0=−0.25 V (over potential deposited hydrogen potential), the conductance histogram showed features around $0.3G_0$ and $1.0G_0$. The conductance behavior of the Rh atomic contact was discussed by comparing previously reported results of other metals, Au, Ag, Cu, Pt, Pd, Ni, Co, and Fe. The conductance behavior of the metal atomic contacts related with the strength of the interaction between hydrogen and metal surface.

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I. INTRODUCTION

A metal nanocontact on an atomic scale is of great interest in both fundamental science and nanotechnology.[1] The electrical conductance through a metal nanocontact is expressed by $G=2e^2/h\Sigma T_i$, where T_i is the transmission probability of the ith conductance channel, e is the electron charge, and h is Plank's constant. Conductance of the metal nanocontacts depends not only on the atomic structure of the nano contacts but also on inherent properties of the metal. The conductance of atomic contacts is G_0 ($2e^2/h$) for noble metals, Au, Ag, Cu; and $1.5G_0-3G_0$ for transition metals, Fe, Co, Ni, Pt, Pd.[1] Various metal nanocontacts have been fabricated using a scanning tunneling microscope (STM) and mechanically controllable break junction technique, and their electrical conductance was investigated in air, ultrahigh vacuum (UHV), and solution.[2–12] In the case of Au, the atomic contact can be easily prepared, and conductance quantization behavior has been observed even in air and solution at room temperature.[4,6,7] On the other hand, it is difficult to prepare atomic contacts showing fixed conductance values for transition metals. Featureless conductance histograms were observed at room temperature.[1] The difficulty may originate from the chemical and/or mechanical instability of the transition-metal nanocontacts. Previous report revealed that the conductance quantization behavior of the transition-metal nanocontact was sensitive to the molecular adsorption on the surface of the metal nanocontacts.[2]

To overcome the difficulty in preparing the stable transition-metal nanocontacts, the electrochemical method has been recognized as a powerful approach.[4–12] The electrochemical potential determines the potential energy of electrons of the nanocontact, resulting in the control of the bonding strength between the metal atoms, and the interaction of the metals with molecules of surrounding medium. These facts could make possible to fabricate stable metal nanocontacts, which cannot be stabilized in other environment. Using electrochemical method, stable Fe, Co, Ni, Pt, and Pd atomic contacts have been prepared at room temperature under the hydrogen evolution reaction.[8–12] Here, it should be noticed that the conductance of the metal atomic contact depended on the species of metals. For example, the conductance histogram of Ni contacts showed a feature around $G_0-1.5G_0$, which agreed with that obtained for clean Ni contacts prepared in UHV at 4 K.[2,10] On the other hand, the conductance histogram of Pd contacts showed a feature around G_0, which agreed with that obtained for the Pd contacts in hydrogen environment at 4 K.[3,11] The conductance behavior of metal atomic contacts prepared in solution may reflect the strength of the interaction between hydrogen and metals. It is important to clarify the relationship between the conductance of the metal atomic contacts and the interaction between hydrogen and metal atomic contacts. In the present study, we have investigated the conductance of the Rh atomic contacts under the electrochemical potential control. The conductance of Rh atomic contacts was discussed by comparing that of other metal atomic contacts in order to clarify the relationship between conductance of the metal atomic contacts and the interaction between hydrogen and metal atomic contacts.

II. EXPERIMENTAL

The experiments have been performed with the modified STM (Pico-SPM, Molecular Imaging) with the Nano ScopeIIIa controller (Digital Instruments). The detail of the experimental setup and condition was described in our previous reports.[6–12] The STM tip was made up of a Au wire (diameter of ~0.25 mm, >99%) coated with wax to eliminate ionic conduction. A 0.50-mm-diameter Pt wire was used as a counterelectrode. The substrate of Au(111) was prepared by a flame annealing and quenching method.[13] The electrochemical potential (Φ_0) of the STM tip and substrate was controlled using a potentiostat (Pico-Stat, Molecular Imaging) with a Ag/AgCl reference electrode. The electrolyte solution was 1 mM $RhCl_3$, 2 mM HCl, and 50 mM H_2SO_4 (Rh solution). The Rh atomic contacts were prepared in the following manner. First, the electrochemical potentials of both the STM Au tip and Au substrate were maintained at values

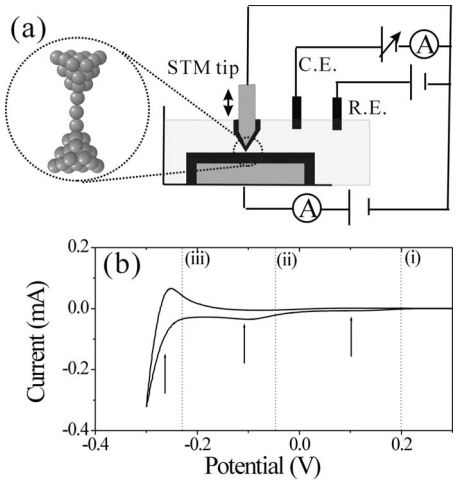

FIG. 1. (a) Schematic view of the electrochemical STM; C.E.: counterelectrode and R.E.: reference electrode. (b) Cyclic voltammogram of the Au electrode in the Rh solution. (i)–(iii) are the boundary between the Rh deposition, UPD of hydrogen (UPD-H), and hydrogen evolution reaction (OPD-H) potential. The arrows indicate the potential measured in the present study.

lower than the potential where bulk metal deposition proceeded (Φ_0=−0.1 V).[14] After sufficient deposition of Rh with estimated thickness of more than a few μm both onto the Au surfaces of the STM tip and the substrate, the tip was pressed into the substrate and then pulled out from the substrate. Separation of these contacts resulted in the formation of Rh atomic contacts between the tip and substrate. Conductance was measured during the breaking process under an applied bias of 20 mV between the tip and substrate. Statistical data were obtained from a large number (over 3000 times) of individual conductance traces.

III. RESULTS

Figure 1 shows the cyclic voltammogram of the Au electrode in the Rh solution. Bulk Rh deposition proceeded at Φ_0=0.2 V. A reduction current due to the under potential deposited hydrogen (UPD-H) was observed at a potential regime from Φ_0=0.2 to −0.05 V. The hydrogen evolution reaction occurred at a potential more negative than Φ_0=−0.2 V.[14] Conductance measurements were performed at Φ_0=0.3 V (Au potential), Φ_0=0.1 V (Rh potential), Φ_0=−0.1 V (UPD-H potential), and Φ_0=−0.25 V [over potential deposited hydrogen (OPD-H) potential].

Figures 2 and 3 show conductance traces and conductance histograms of metal contacts in the Rh solution obtained at four different electrochemical potentials. At the Au potential, conductance decreased in a stepwise fashion, with each step occurring at integer multiples of G_0. The corresponding conductance histogram [Fig. 3(a)] showed a peak at $1.0G_0$, which corresponded to a clean Au atomic contact.[1] At the Rh potential, the conductance trace decreased showing steps. The conductance values of the steps varied with the conductance traces, which led to the featureless conductance histogram [Fig. 3(b)]. At the UPD-H potential, the conductance

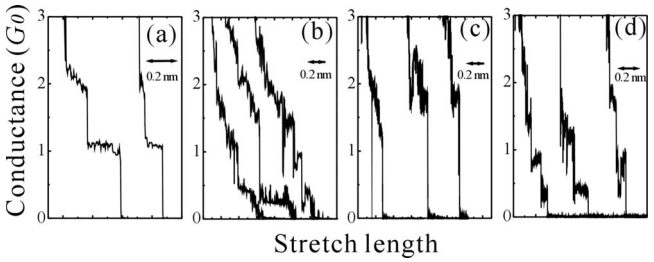

FIG. 2. Conductance traces in the Rh solution at (a) Φ_0=+0.3 V (Au potential), (b) +0.1 V (Rh potential), (c) −0.1 V (UPD-H potential), and (d) −0.25 V (OPD-H potential).

trace frequently showed steps around $2G_0$. The corresponding conductance histogram [Fig. 3(c)] showed a broad feature around $2.3G_0$. At the OPD-H potential, the conductance trace showed steps around $0.3G_0$ and $1.0G_0$. The corresponding conductance histogram [Fig. 3(d)] showed features around $0.3G_0$ and $1.0G_0$. The metal contacts in the Rh solution showed four different conductance behaviors depending on the electrochemical potential: $1.0G_0$ (Au potential), featureless (Rh potential), $2.3G_0$ (UPD-H potential), and $0.3G_0$ and $1.0G_0$ (OPD-H potential).

IV. DISCUSSION

The structure of the Rh atomic contact is discussed based on the present and previous experimental results, and theoretical calculation result.[8,15–18] The hydrogen adsorption and hydrogen evolution reaction on a flat Rh electrode has been investigated.[15] At the UPD-H potential, under potential deposited (UPD) hydrogen atoms adsorb in the hollow site of the Rh surface. The UPD hydrogen is observed only for Pt, Rh, Pd, Ir, and Ru. UPD hydrogen atoms are not observed for Au, Ag, Cu, and iron group metals. At the OPD-H potential, over potential deposited (OPD) hydrogen atoms adsorb in the atop site of the Rh surface. Both OPD and UPD hydrogen atoms adsorb on the Rh surface at the OPD-H potential. Only the OPD hydrogen atoms contribute to the hydrogen evolution reaction. The hydrogen evolution proceeds through the following process. First, protons adsorb onto the

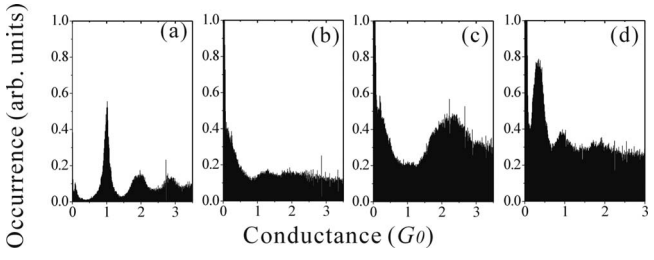

FIG. 3. Conductance histograms in the Rh solution at (a) Φ_0=+0.3 V (Au potential), (b) +0.1 V (Rh potential), (c) −0.1 V (UPD-H potential), and (d) −0.25 V (OPD-H potential). The conductance histograms were obtained from 1000 conductance traces of breaking the contacts. The intensity of the conductance histograms was normalized with the number of the conductance traces.

Rh surface [Eq. (1)], and H_2 (gas) desorbs via surface diffusion and recombination of two adsorbed H atoms [Eq. (2)],

$$\mathrm{Rh} + \mathrm{H_3O^+} + e \rightarrow \mathrm{Rh-H} + \mathrm{H_2O}, \quad (1)$$

$$2\mathrm{Rh-H} \rightarrow 2\mathrm{Rh} + \mathrm{H_2}. \quad (2)$$

Here, it should be noticed that the strength of the metal-hydrogen bond is larger for the UPD hydrogen than that for the OPD hydrogen.

The structure of the Rh atomic contact is discussed based on the above discussion. At the Rh potential, we did not observe any features in the conductance histogram, indicating that any preferential atomic configurations were not stabilized in solution. In solution, the fluctuation of atoms is large at room temperature. The stable atomic contact could not be formed because of the contribution from thermally excited motion of solvent and electrolyte molecules surrounding the atomic contacts. Therefore, any preferential atomic configurations would not be stabilized at the Rh potential. At the UPD-H potential regime, we observed a $2.3G_0$ feature in the conductance histogram, which agreed with the theoretical calculation results of the clean Rh atomic contact.[1] The close agreement between the measured and calculated conductance values indicated that the clean Rh atomic contact would be stabilized in solution at the UPD-H potential. At the UPD-H potential, the UPD hydrogen atoms adsorb on the Rh surface. The adsorbed atomic hydrogen could stabilize the Rh atomic contacts. Similar stabilization of metal atomic contacts was observed for the iron group metals under the hydrogen evolution reaction.[8,10] At the OPD-H potential, we observed features around $0.3G_0$ and $1.0G_0$ in the conductance histogram. Since the conductance values of $0.3G_0$ and $1.0G_0$ were different from the conductance value of clean Rh atomic contacts, the $0.3G_0$ and $1.0G_0$ features would not originate from the Rh atomic contact. The origin of the $0.3G_0$ and $1.0G_0$ features is discussed based on the previously reported results of Pt atomic contacts in hydrogen environment at 4 K, in which similar conductance histogram was observed.[16–18] The shot noise measurements, vibration spectra of single molecular junctions, and theoretical calculation revealed that a single hydrogen molecule bridged between Pt electrodes, showing the conductance value of $1.0G_0$. When additional hydrogen molecules adsorbed on the stem part of the single hydrogen molecule junction, the conductance decreased to $0.6G_0$ and $0.2G_0$, depending on the atomic configuration of the molecule junction. The $0.5G_0$ and $1.0G_0$ features were also observed for the Pt contacts at the OPD-H potential.[8] The $0.5G_0$ and $1.0G_0$ features were attributed to the hydrogen molecule bridge. Since the hydrogen evolution process and electronic structure of Rh are similar to those of Pt, the $0.3G_0$ and G_0 features observed in the present study would originate from the hydrogen single molecule junctions. In the present system, the atomic configuration and the conductance were well defined by the controlling the electrochemical potential of electrons in the contact at room temperature. Additional characteristic of the present electrochemical system is the precise control of the adsorbed species, which are not able to achieve in other systems, such as UHV and air. The origin of the $2.3G_0$, $0.3G_0$, and $1.0G_0$ features observed in the conductance histogram of the Rh contacts could be precisely clarified by the theoretical calculations of the electronic structure of the contact and the experimental verification of shot noise and vibration spectroscopy measurements of the single molecular junctions having the comparable structure.

Next, the conductance behavior of Rh contacts is compared with that of other metal contacts. Figure 4 shows our previous experimental results of the conductance histograms of Fe, Co, Ni, Cu, Pd, Ag, Pt, and Au atomic contacts under the hydrogen evolution reaction,[6–12] together with the present Rh results. For Rh contacts, the conductance histogram at the UPD-H potential is also shown. The conductance histogram roughly depended on the group of metal (gold-silver-copper group, iron group, and platinum group). In the case of Au and Cu contacts, a $0.5G_0-0.6G_0$ peak appeared in the conductance histogram together with the $1.0G_0$ peak, which corresponded to clean Au and Cu atomic contacts.[6,7,12] The additional $0.5G_0-0.6G_0$ peak was not observed for the Ag contacts. For iron group metal contacts, the conductance histogram showed features around $1.5G_0-2.0G_0$, which agreed with those obtained in UHV at 4 K.[9] For the platinum group metal contacts, the conductance histogram showed features around $0.5G_0$ and $1.0G_0$.[8] In the case of Pt and Pd contacts, the conductance histogram did not show any features at the UPD-H potential, while conductance histogram of Rh contacts showed a $2.3G_0$ feature at the UPD-H potential. Previous experimental and theoretical studies proposed the following structure model of the metal atomic contacts under the hydrogen evolution reaction. For Au and Cu contacts, hydrogen atoms would adsorb on the metal atomic contacts, leading to the appearance of $0.5G_0-0.6G_0$ peaks in the conductance histogram. For iron group metals, clean metal atomic contacts would be formed under the hydrogen evolution reaction. For platinum group metals (Pt and Pd), a single hydrogen molecule junction would be formed under the hydrogen evolution reaction. Our experimental results suggested the formation of the Rh atomic contact and the single hydrogen molecule junction at the UPD-H and OPD-H potentials, respectively. The Rh atomic contact showed the conductance behavior of both iron group and platinum group metals, depending on the electrochemical potential.

The conductance behavior of the metal atomic contacts under the hydrogen evolution reaction is discussed by considering the interaction between hydrogen and metals. The free energy of hydrogen adsorption on a metal surface (ΔG) was investigated by density-functional theory calculation.[19] ΔG was a reasonable descriptor of hydrogen evolution activity for a wide variety of metals.[19] The interaction between hydrogen and metal surface decreased with ΔG. The values of ΔG were 0.66, 0.28, 0.62, −0.16, −0.13, −0.08, and −0.12 eV for Au, Cu, Ag, Co, Ni, Pt, and Rh, respectively. The interaction between hydrogen and metal surface decreased in the order of iron group, platinum group, and gold-silver-copper group metals. Figure 4 suggests that the clean metal atomic contacts would be formed for the iron group metals, while the hydrogen incorporated or adsorbed metal contacts would be formed for the Pt group metals, Au and Cu. It seems that a clean metal atomic contact would be

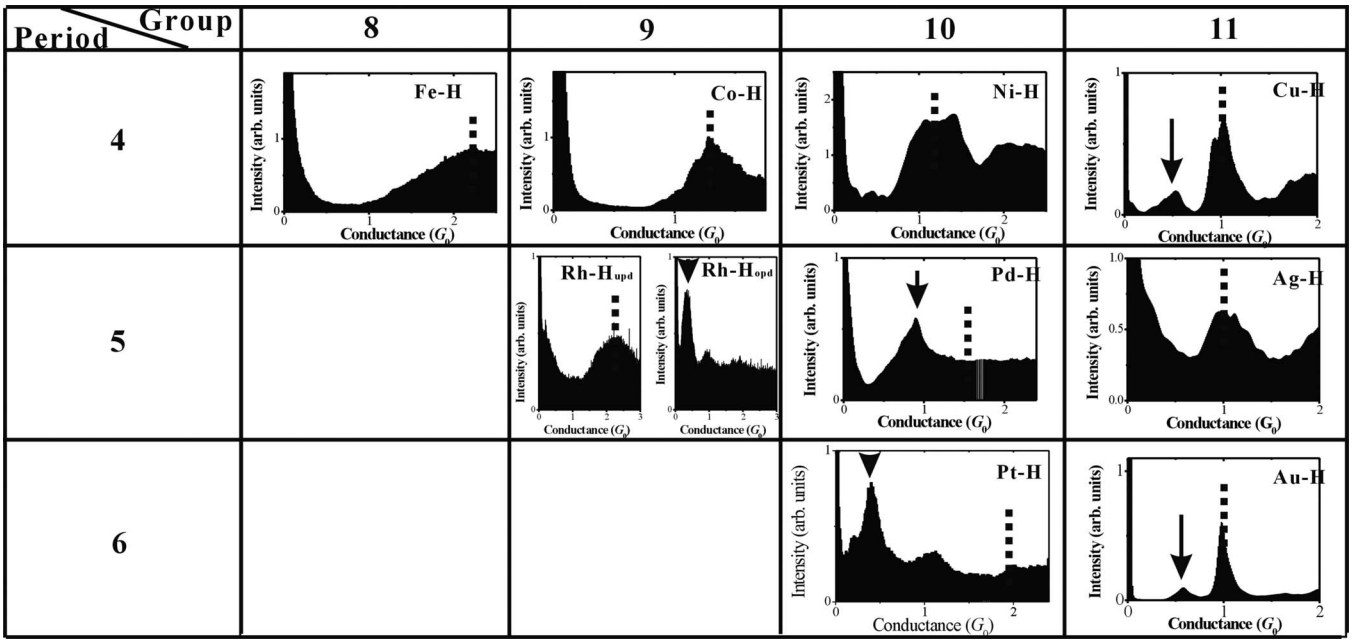

FIG. 4. Summary of the conductance histograms of Fe, Co, Ni, Rh, Pd, Cu, Ag, Au, and Pt atomic contacts under the hydrogen evolution reaction. The dotted line is the conductance value of clean metal atomic contact. The arrow shows a feature that is not observed for the clean metal atomic contacts in UHV.

formed, when the interaction between hydrogen and metal is large. Hydrogen incorporated (hydrogen molecule junction) or adsorbed metal contacts would be formed, when the interaction between hydrogen and metal is small. This peculiar conclusion was supported by the conductance behavior of Rh atomic contacts observed in the present study. The Rh atomic contact and hydrogen molecule junction were formed at the UPD-H and OPD-H potentials, respectively. The interaction between hydrogen and Rh surface is larger for the UPD hydrogen than the OPD hydrogen. The strongly interacting UPD hydrogen would stabilize the clean Rh atomic contact, while the weakly interacting OPD hydrogen would lead to the formation of the hydrogen incorporated atomic contact. Here, it should be noticed that the above discussion is based on the investigation of hydrogen on flat metal electrodes. The interaction between hydrogen and metal atomic contacts would be different from that on the metal flat surface. For example, there is little experimental results which directly show the existence of hydrogen on the Au surface under the hydrogen evolution reaction. On the other hand, the experimental results clearly showed the interaction between hydrogen and Au atomic contact as a change in conductance.[6,7] These results indicate the difference between the flat surface and the atomic contact. Further investigation is needed to discuss the interaction between hydrogen and the metal atomic contact under the hydrogen evolution reaction.

V. CONCLUSIONS

We have investigated the electric conductance of Rh atomic contacts under the electrochemical potential control. The conductance histograms showed no feature, $2.3G_0$ feature, and $0.3G_0$ and $1.0G_0$ features at the Rh, UPD-H, and OPD-H potentials. Clean Rh atomic contact would be formed at the UPD-H potential, while a single hydrogen molecule junction would be formed at the OPD-H potential. The conductance behavior of the Rh atomic contacts and other metal contacts could be explained by the strength of the interaction between hydrogen and a metal surface.

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