Three reversible states controlled on a gold monoatomic contact by the electrochemical potential

Manabu Kiguchi^{1,2}, Tatsuya Konishi¹, Kouta Hasegawa¹, Satoshi Shidara¹, and Kei Murakoshi^{11,2}

¹¹Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, 060-0810, Japan

²²Precursory Research for Embryonic Science and Technology (PRESTO),

Japan Science and Technology Agency, Sapporo, Hokkaido 060-0810, Japan

(Dated: October 24, 2018)

Conductance of an Au mono atomic contact was investigated under the electrochemical potential control. The Au contact showed three different behaviors depending on the potential: 1 G_0 ($G_0 = 2e^2/h$), 0.5 G_0 and not-well defined values below 1 G_0 were shown when the potential of the contact was kept at -0.6 V (double layer potential), -1.0 V (hydrogen evolution potential), and 0.8 V (oxide formation potential) versus Ag/AgCl in 0.1 M Na₂SO₄ solution, respectively. These three reversible states and their respective conductances could be fully controlled by the electrochemical potential. These changes in the conductance values are discussed based on the proposed structure models of hydrogen adsorbed and oxygen incorporated on an Au mono atomic contact.

PACS numbers: PACS numbers: 73.63.Rt, 73.40.Cg, 73.40.Jn

INTRODUCTION

Study of charge transport in atomic scale metal or molecular nano wires is of fundamental interest, with potential applications for ultra-small electronic devices [1, 2]. In order to use these nano wires for devices, their conductance should be tunable by some external field, such as light or magnetic field. There are some experimental challenges to controlling the conductance of nano wires by an external field [3, 4, 5, 6, 7]. The switching of a photochromic molecular wire from the conducting state to the insulating state was observed by radiation of visible light [3]. A change in the conductance behavior by molecular adsorption was observed for Au, Pt, Cu, Fe, Co, and Ni nano wires [4, 5, 6, 7]. Here, it should be noted that the conductance can be switched from the off state to the on state or vice versa (among two states) in most studies. If the conductance of the nano wires could be controlled among three different conductance states, it would have attracted wide attention for fundamental science and technological applications.

In the present study, we paid attention to the electrochemical potential as an external field [8, 9, 10, 11, 12]. The electrochemical potential can control the procession of two individual electrochemical reactions on a metal surface by changing the electrochemical potential of the metal electrode by only several volts. For example, hydrogen or oxygen evolution proceeds when the electrochemical potential of Pt electrodes is maintained at more negative than -0.2 V or more positive than +1.3 V versus Ag/AgCl in 0.1 M H₂SO₄ solution, respectively [13]. The clean hydrogen or oxygen adsorbed states can be selectively prepared by controlling the electrochemical potential. Several states of the surface condition, at least three, can be maintained under the electrochemical potential control. If the conductance of the metal nano wire can be defined by the surface condition of the wire, the

conductance of the metal nano wire may be controlled by the electrochemical potential. Au was investigated in the present study for the following reasons. First, the hydrogen and oxygen evolution can proceed without dissolving the Au ions from the Au electrode; this is a characteristic of the Au electrode in solution. In the case of Ni, Ni rapidly dissolves at the oxygen evolution potential [13]. It is thus difficult to prepare stable Ni nano wires under oxygen evolution. Second, the Au mono atomic contact shows a well defined fixed conductance value. It normally shows 1 G_0 ($2e^2/h$), and it shows 0.5 G_0 under hydrogen evolution [8, 12]. Showing well defined conductance values is useful for the understanding and utilization of the metal nano wire. Under ultra high vacuum (UHV) condition, the Au mono atomic contact does not show a well-defined fractional conductance value by the introduction of hydrogen molecule [4]. In solution, the Au mono atomic contact shows well defined fractional conductance. Hydrogen incorporated wire, dimerized wire, and other atomic and electronic structures of the wire, were proposed to be the origin of the fractional conductance value [8, 12]. However, the actual origin is not clear at present. In addition, the effect of oxygen on the Au mono atomic contact, such as the structure, stability, and conductance, in solution is not clear. In the present study, we have studied the Au mono atomic contact under the electrochemical potential control to reveal the effect of hydrogen and oxygen on the conductance behavior and to control the conductance of the Au mono atomic contact among three different states.

EXPERIMENTAL

The experiments were performed with the modified scanning tunneling microscope (STM: Pico-SPM, Molecular Imaging Co.) with a Nano ScopeIIIa controller (Dig-

ital Instruments Co.) in an electrochemical cell (see Ref [10, 11, 12] for a detailed description of the experimental setup and conditions). The STM tip was made of an Au wire (diameter 0.25 mm, > 99 %) coated with wax to eliminate ionic conduction. The Au(111) substrate was prepared by a flame annealing and quenching method. Figure 1(a) shows a schematic view of the experimental setup. The electrochemical potential (ϕ) of the Au tip and substrate was controlled using a potentiostat (Pico-Stat, Molecular Imaging Co.) with an Ag/AgCl reference electrode. A 0.50 mm diameter Pt wire was used as a counter electrode. The STM tip was repeatedly moved into and out of contact with the Au substrate at a rate of 50 nm/s in an electrolyte solution. The electrolyte solution was 0.1 M Na₂SO₄ or 50 mM H₂SO₄. Conductance was measured during the breaking process under an applied bias of 20 mV between the tip and substrate. All statistical data was obtained from a large number (over 1000) of individual conductance traces. Figure 1(b) shows the cyclic voltammogram (CV) of an Au electrode in the 0.1 M Na₂SO₄ solution. The double layer regime extended from $\phi = -0.7$ V to 0.8 V. When the electrochemical potential of the Au electrode was kept at a potential more positive than $\phi = 1.3$ V, the oxygen evolution proceeded via the formation of an oxide layer on the Au electrode. The hydrogen evolution proceeded at a potential more negative than $\phi = -0.7 \text{ V} [13, 14, 15].$ Conductance of the Au nano contacts was measured at $\phi = -0.6 \text{V}$ (double layer potential), $\phi = -1.0 \text{ V}$ (hydrogen evolution potential) and $\phi = 0.8 \text{ V}$ (oxide formation potential).

RESULTS AND DISCUSSION

Figure 2 shows the typical conductance traces and histograms of the Au nano contacts in 0.1 M Na₂SO₄ solution during breaking the contact at the double layer, hydrogen evolution and oxide formation potentials. At the double layer potential (Fig. 2(b), (e)), the conductance decreased in a stepwise fashion with each step occurring at integer multiples of G_0 . The corresponding conductance histograms showed a well-defined peak near 1 G_0 , which corresponded to a clean Au atomic contact or wire [2]. At the hydrogen evolution potential (Fig. 2(a), (d)), reversible transition of the conductance between 1 G_0 and 0.5 G_0 was observed. This conductance fluctuation resulted in the $0.5 G_0$ peak in the conductance histogram. At the oxide formation potential (Fig. 2(c), (f)), the conductance continuously decreased stepwise at various conductance values below 1 G_0 . The corresponding histogram showed a broad feature at 1 G_0 together with a large background. The conductance of the Au mono atomic contact could be controlled among three different conductance states (1 G_0 , 0.5 G_0 and conductance below 1 G_0) by the electrochemical potential of the contact. These electrochemical potential dependent changes were fully reversible. The potential in which the 0.5 G_0 peak (or large background) appeared in the conductance histogram agreed with the onset potential of the hydrogen evolution (or oxide formation) reaction on the Au electrode. In the conductance histogram, the intensity of the 0.5 G_0 peak normalized by the 1 G_0 peak increased, and then saturated, as the potential was scanned from the double layer potential to the hydrogen evolution potential. The intensity of the background continuously increased, as the potential was scanned from the double layer potential to the oxide formation potential. The 1 G_0 peak was not apparent in the conductance histogram at more positive than $\phi=1.0$ V.

The conductance behavior of the Au mono atomic contact was investigated in other electrolytes, 0.1 M NaCl, 0.1 M NaOH, 50 mM H₂SO₄, and 0.1 M HClO₄. In the conductance histogram, a large background below 1 G_0 was observed at the oxide formation potential, while the $0.5 G_0$ peak was observed at the hydrogen evolution potential. In acid solution (50 mM H₂SO₄, 0.1 M HClO₄), the 0.1 G_0 peak was observed in the conductance histogram, in addition to the $0.5 G_0$ peak at the hydrogen evolution potential. Figure 3 shows the typical conductance traces and histogram of the Au nano contacts in 50 mM H₂SO₄ solution during breaking the contact at the hydrogen evolution potential. Reversible transitions of the conductance between 1 G_0 and 0.5 G_0 , 0.5 G_0 and $0.1 G_0$ were observed in the conductance traces. This conductance fluctuation resulted in the $0.5~G_0$ and 0.1 G_0 peaks in the conductance histogram. The 0.1 G_0 peak in Fig. 3(b) seems very sharp compared to other 1 G_0 and 0.5 G_0 peaks. The half width at half maximum (W) of the histogram was 0.14, 0.15, 0.08 G_0 for the 1, $0.5, 0.1 G_0$ peaks, respectively. On the other hand, the relative peak width (W / conductance ratio) was 0.14, 0.28, 0.74 for the 1, 0.5, 0.1 G_0 peaks, showing that the $0.1 G_0$ peak became broader than the $0.5 G_0$ and $1 G_0$

The electrochemical potential dependence of the stability of the Au atomic contact was investigated in 0.1 M Na₂SO₄ solution. Figure 4(a) shows the distribution of lengths for the last conductance plateau (D_{last}) . The length of the last plateau was defined as the distance between the points at which the conductance dropped below 1.3 G_0 and 0.05 G_0 , respectively. At the double layer potential, the contact broke within 0.2 nm. The contact could be stretched a longer distance at the hydrogen evolution and oxide formation potential. The average length of the Au mono atomic contact was 0.08 nm, 0.15 nm, and 0.18nm at the double layer, hydrogen evolution, and oxide formation potentials, respectively. At the hydrogen and oxygen potential, the mono atomic contact could be stretched 0.4 nm in length. Considering the Au-Au distance of 0.25 nm in the Au mono atomic contact obtained at low temperature in UHV [16], the Au mono atomic

wire could be formed in solution at the hydrogen evolution and oxide formation potential. Of course, the long stretched length did not directly indicate the formation of a mono atomic wire; the stem part of the Au contact might be deformed during the stretching. Although the formation of the Au mono atomic wire was not clear, the Au mono atomic contact was found to be stabilized at the hydrogen evolution and oxide formation potential.

In order to investigate the transformation process of the Au mono atomic contact in more detail, the distribution of lengths was analyzed for the 1 G_0 plateau, which corresponded to a clean Au mono atomic contact [2] $(D_{1G}$: see Fig. 4(b)). The length of the 1 G_0 plateau was defined as the distance between the points at which the conductance dropped below 1.3 G_0 and 0.8 G_0 , respectively. At the double layer and hydrogen evolution potential, the D_{1G} was similar to the D_{last} . The 1 G_0 plateau could be stretched 0.4 nm in length at the hydrogen evolution potential. On the other hand, the 1 G_0 plateau was very short (< 0.2 nm) at the oxide formation potential, although the last conductance plateau could be stretched 0.4 nm in length. The D_{1G} at the oxide formation potential was close to the D_{1G} and D_{last} at the double layer potential. At the hydrogen evolution potential, the close agreement between the D_{1G} and D_{last} indicated that the formation of the structure showing $0.5 G_0$ would not relate with the stabilization of the Au mono atomic contact at the hydrogen evolution potential. At the oxide formation potential, the conductance of the Au contact continuously decreased stepwise at various conductance values after showing 1 G_0 . Combing with this continuous change in conductance value, the close agreement between the D_{1G} at the oxide formation potential and the D_{1G} at the double layer potential suggested the following transformation process of the Au atomic contact. Initially, the clean Au mono atomic contact was formed during the stretching the contact. Then, the structure showing conductance value below 1 G_0 would be formed at the oxide formation potential.

Here, the present experimental results are compared with our previously reported results measured in 0.1 M Na₂SO₄ and 50 mM H₂SO₄ solution [12]. In our previous study, it was revealed that the electrochemical potential significantly affected the stability and conductance of the Au mono atomic contact. At the hydrogen evolution potential, the conductance histogram showed the 0.5 G_0 peak, whose intensity could be tuned by the electrochemical potential. The stability of the Au mono atomic contact could be also tuned by the electrochemical potential. As the potential of the Au electrodes was scanned from $\phi = 0.5$ V to negative, the average length of the last conductance plateau decreased at $\phi = -0.2$ V, and then reached a minimum value at $\phi = -0.4 \text{ V}$ in 0.1 M Na_2SO_4 solution. Polarization more negative than $\phi =$ -0.6 V led to the recovery of the length. At the hydrogen evolution potential ($\phi < -0.6 \text{ V}$), the 1 nm long Au mono

atomic wire could be occasionally fabricated. The distribution of lengths for the last conductance plateau was investigated at the hydrogen evolution potential. The same behavior was observed again in the present system. In addition to previously reported characteristics, several interesting features appeared in the present system. First, the Au atomic contact showed the third conductance value (various conductance values below 1 G_0) at the oxide formation potential. Second, the Au mono atomic contact showed not only $0.5 G_0$ but also $0.1 G_0$ in acid solution at the hydrogen evolution potential. This $0.1 G_0$ peak was not apparent in the conductance histogram in Fig. 6 of Reference [12], because the intensity of the background around $0.1 G_0$ was beyond the vertical axis range of the conductance histogram in Fig. 6 of Reference [12]. Third, the Au atomic contact was stabilized at the oxide formation potential. Fourth, the distribution of lengths for the last conductance plateau was investigated at the double layer and oxide formation potential. The distribution of lengths was also shown for the 1 G_0 plateau, which provided information about the transformation process of the Au mono atomic contact during the stretching the contact. Fifth, the distribution of lengths for the conductance plateau was precisely determined by the statistical analysis with a large number of measurements for 10 different samples (20000 traces). In our previous report, the distribution of lengths for the last conductance plateau was obtained from limited number of conductance traces (~ 1000 traces) for one extraordinarily stable sample at the hydrogen evolution potential [12]. Although very stable Au mono atomic wire occasionally could be fabricated, most of the Au atomic contact broke within 0.4 nm in length. So, the obtained distribution of lengths for the last conductance plateau shifted to the shorter distance compared to the previous result. The effect of hydrogen and oxygen on the Au mono atomic contacts is discussed based on these new findings and improvements.

The conductance behavior of the Au mono atomic contact is compared with that in UHV. The effect of hydrogen and oxygen on the Au mono atomic contact was investigated at low temperature in UHV [4, 5]. The broad feature appeared below 1 G_0 in the conductance histogram of the Au contacts after the introduction of hydrogen gas. The feature below 1 G_0 was much smaller than the 1 G_0 peak [4]. The conductance histogram did not change with the introduction of oxygen gas [5]. On the other hand, in solution, clear $0.5 G_0$ and $0.1 G_0$ peaks appeared in the conductance histogram at the hydrogen evolution potential. A broad feature appeared below 1 G_0 at the oxide formation potential. These results suggest that a specific structure of the Au mono atomic contact with a well-defined fractional conductance value (0.5 G_0 or 0.1 G_0) was formed at the hydrogen evolution potential, and various structures in which oxygen strongly interacted with the atomic contact were formed at the

oxide formation potential. The electrochemical potential determines the potential energy of electrons of the metal nano contact, resulting in the control of the bonding strength between the metal atoms, and of the interaction of the metals with molecules in the surrounding medium. These facts make it possible to use the environment to set the metal contacts, which cannot be set in other environments such as in UHV and in air, leading to successful fabrication of very stable metal nano structures showing the conductance quantization which cannot be observed in UHV.

The structure of the Au mono atomic contact at the hydrogen evolution and oxide formation potential is discussed based on the previously reported experimental result of a flat Au surface and theoretical calculation result. The hydrogen and oxygen evolution reaction on the flat Au electrodes in solution has been investigated by the analysis of current-potential curves [13, 14, 15]. When the electrochemical potential of the Au electrode is kept positive ($\phi > 1.6 \text{ V}$) in acidic solution, oxygen evolution has been proposed to proceed through the following process. First, hydroxyl ions adsorb onto the Au surface forming surface hydroxides (1), second, surface hydroxides convert to oxides (2), and third, O₂ (gas) desorbs from the surface (3).

$$Au+H_2O \rightarrow Au-OH + H^+ + e^-$$
 (1)
 $2Au-OH \rightarrow Au-O + Au + H_2O$ (2)
 $2Au-O \rightarrow 2Au+O_2$ (3)

When the electrochemical potential of the Au electrode is kept negative ($\phi < -0.3$ V) in acid solution, hydrogen evolution proceeds through the following process. First, protons adsorb onto the Au surface (4), and H₂ (gas) desorbs via surface diffusion and recombination of two adsorbed H atoms (5) or a combination of adsorbed H atoms and proton (5').

$$\begin{array}{l} Au + H_3O^+ \, + \, e^- \to Au - H \, + H_2O \, \left(4 \right) \\ 2Au - H \to 2Au + H_2 \, \left(5 \right) \\ Au - H + \, H_3O^+ \, + \, e^- \to Au \, + \, H_2 \, + \, H_2O \, \left(5^{\circ} \right) \end{array}$$

In the CV of the Au electrode in 0.1 M Na₂SO₄ solution (Fig. 1(b)), the main anodic peak above $\phi = 0.8 \text{ V}$ and an increase in the oxidation current above $\phi = 1.3$ V correspond to the oxide formation process (2) and the O_2 (gas) desorption process (3). As for the surface oxide, higher oxide (Au₂O₃) or hydroxide (Au(OH)₃) was proposed [15]. The increase in redox current below $\phi = -0.7$ V corresponds to the H_2 (gas) desorption process (5). The surface coverage of hydrogen was estimated to be very small (< 0.3 %)[14]. Here, it should be noticed that the detail reaction mechanism of the oxygen and hydrogen evolution reaction on the Au electrode has not been fully understood up to now. In addition, the reaction on the Au mono atomic contact might not be the same as that on the flat Au electrode. However, the observed conductance behavior and the reaction on the flat metal surface strongly suggested that the oxygen or hydrogen is adsorbed on or incorporated into the Au mono atomic

contact at the oxide formation and hydrogen evolution potential.

The structure of the Au mono atomic contact is discussed with the previously reported theoretical calculation result. The interaction between the Au mono atomic wire and oxygen or hydrogen has been investigated with theoretical calculations [17, 18, 19]. Theoretical calculation results showed that the hydrogen 1s orbital or oxygen 2p orbital effectively hybridized with the Au 5d and Au 6s orbitals. Due to the strong interaction, oxygen and hydrogen molecules dissociated on the Au mono atomic wire, and then were stably incorporated into the Au mono atomic wire. In the hydrogen (oxygen) incorporated wire, we can expect electron transfer from hydrogen to Au (from Au to oxygen). The Au wire would be, thus, positively (negatively) charged for the hydrogen (oxygen) incorporated wire. Because of the formation of hydrogen or oxygen incorporation into the wire, the conductance of the Au mono atomic wire decreased to 0.6-0.01 G_0 , possibly due to scattering or interference of conducting electrons in the wire. No preferential atomic configurations were found for the hydrogen or oxygen incorporated Au mono atomic wire. Jelinek et al. calculated the conductance of the Au mono atomic wire in which a hydrogen atom or an undissociated molecule adsorbed on it [18]. The conductance value was calculated to be 0.7-0.5 G_0 and 1.05-0.95 G_0 for the Au atomic contact in which a hydrogen atom and molecule adsorbed on it, respectively. The adsorbed atomic hydrogen effectively affected the conductance of the Au mono atomic wire, as is the case for the incorporation of hydrogen into the Au wire. On the other hand, the conductance value of the Au atomic wire with an adsorbed undissociated hydrogen molecule did not change from that of the clean Au atomic wire $(1 G_0)$. The adsorbed undissociated hydrogen molecule would not affect the conductance of the Au mono atomic wire, in contrast with the adsorbed hydrogen atom and incorporated hydrogen.

Now, we try to propose the structure model of the Au mono atomic contact at the hydrogen evolution and oxide formation potential based on the above discussion. At the oxide formation potential, various conductance values were observed for the Au mono atomic contact (see Fig. 2(c,f)). This conductance behavior agreed with the calculated conductance behavior of the oxygen incorporated Au wire [17, 18, 19]. So, the conductance value below 1 G_0 would originate from the oxygen incorporated Au mono atomic contact. Combing with the result of the plateau length analysis showing the long last conductance plateau and short 1 G_0 plateau which was comparable to the 1 G_0 plateau at the double layer potential, the following transformation process of the Au atomic contact could be proposed. Initially, the clean Au mono atomic contact was formed during the stretching the contact. Then, the oxygen incorporated Au mono atomic contact would be formed. In contrast to the oxide formation potential, reversible transition between 1 G_0 and the well defined fractional conductance value $(0.5 G_0)$ were observed in the conductance trace at the hydrogen evolution potential (see Fig. 2(a)). The reversible transition suggests the successive adsorption and desorption of hydrogen on the Au mono atomic contact. In the case of the atom or molecular adsorption on flat metal surfaces, atoms or molecules often adsorb with a fixed atomic configuration [19]. Therefore, hydrogen could also adsorb on the Au mono atomic contact with a certain fixed atomic configuration showing a fixed conductance value. When the hydrogen incorporates into the Au contact, the Au mono atomic contact would not show a fixed conductance value, in contrast to the present experimental result. So, the hydrogen adsorbed Au mono atomic contact would be formed at the hydrogen evolution potential. As discussed in the previous section, the surface coverage of hydrogen is very low on the Au electrode [14], and thus, the number of hydrogen atoms or molecules adsorbed on the Au mono atomic contact would be very small. The conductance value was calculated to be about 1.0 G_0 and 0.6 G_0 for the Au atomic contact in which one hydrogen molecule and atom adsorbed on it, respectively [18]. Therefore, $0.5 G_0$ would originate from the Au mono atomic contact, in which one hydrogen atom adsorbed on it.

The above discussion about the Au mono atomic contact with an adsorbed hydrogen atom could be supported by the conductance behavior of the Au nano contacts in acid solution. In acid solution, the rate determining process of the hydrogen evolution reaction on Au electrodes is the surface diffusion and desorption process of H₂ gas (5). The surface coverage of hydrogen atoms on the Au surface in acid solution is expected to be higher than that in neutral solution (Na₂SO₄) [13]. Therefore, more than one hydrogen atom occasionally could adsorb on the Au mono atomic contact in acid solution under the hydrogen evolution reaction. The Au mono atomic contact with two adsorbed hydrogen atoms would show a smaller conductance value than that with one hydrogen atom. In 50mM $\rm H_2SO_4$ and 0.1 M $\rm HClO_4,$ the 0.1 G_0 peak appeared in the conductance histogram in addition to the $0.5 G_0$ peak at the hydrogen evolution potential (see Fig. 3(b)). The 0.1 G_0 peak would originate from the Au mono atomic contact in which two atomic hydrogen atoms adsorbed on it. This hypothesis about the origin of $0.1 G_0$ peak can be supported by the conductance behavior of the Au atomic contact in acid solution at the hydrogen evolution potential. In the conductance traces, the reversible transitions of the conductance between $0.5 G_0$ and $0.1 G_0$, $1 G_0$ and $0.5 G_0$ were observed (see Fig. 3(a)). The reversible transitions of the conductance between $0.5 G_0$ and $0.1 G_0$ suggested the successive adsorption and desorption of hydrogen atom on the Au mono atomic contact, as is the case for the reversible transitions of the conductance between 1 G_0 and 0.5 G_0 .

The appearance of the 0.1 G_0 peak in the conductance histogram also suggested that the origin of the fractional conductance value was not the dimerized wire proposed in previous study [12]. It is because the dimerized wire would show one fixed conductance value (\sim 0.5 G_0). But, the Au mono atomic contact showed both 0.1 G_0 and 0.5 G_0 in acid solution under the hydrogen evolution.

Improved stability of the Au mono atomic contact at the hydrogen evolution and oxide formation potential is discussed. In UHV at 4 K, stabilization of Au or Ag mono atomic wire was observed by oxygen incorporation into the wire. As for the Ag, a 2nm long mono atomic wire could be formed by oxygen incorporation into the wire, while a clean Ag forms only short atomic contact [5]. The theoretical calculation results showed that the incorporated oxygen strengthened Au-Au and Ag-Ag bonds in the wire, leading to stabilization of the Au and Ag mono atomic contact [20]. The stabilization of the metal nano wires by molecular adsorption was also observed for Au, Fe, Co, and Ni nano wires [21]. This stabilization was explained by the decrease in the surface energy caused by the molecular adsorption on the metal nano wires. Therefore, the stabilization of the Au mono atomic contact at the oxygen formation potential could be explained by the increase in the bond strength in the atomic contact caused by the oxygen incorporation into the contact. The stabilization of the contact at the hydrogen evolution potential could be explained by the decrease in the surface energy caused by the hydrogen adsorption on the Au mono atomic contact. The plateau length analysis revealed that the 1 G_0 plateau was much longer at the hydrogen evolution potential than the double layer potential. Since the conductance of the Au mono atomic contact with an adsorbed hydrogen molecule was calculate to be about 1 G_0 [18], the long 1 G_0 plateau at the hydrogen evolution potential suggested that the Au mono atomic contact would be stabilized by the adsorption of a hydrogen molecule on the Au mono atomic contact.

In the present study, the structure models of the Au mono atomic contact at the hydrogen evolution and oxide formation potential were proposed based on the experimental and theoretical calculation result. Although our model of the hydrogen adsorbed and oxygen incorporated Au mono atomic contact could explain the experimental results, we did not obtain direct evidence for the formation of the hydrogen adsorbed and oxygen incorporated Au mono atomic contact proposed in this study. In addition, it is not completely clear whether a hydrogen (or oxygen) molecule or atom adsorbed on (or incorporated into) the Au mono atomic contact. The model proposed in this study is one of the possible models. Further investigation is needed to fix the structure formed at the hydrogen evolution and oxide formation potential. Although the structure model is not defined yet, our experimental results clearly showed the existence of hydrogen or oxygen at the Au mono atomic contact as a change of conductance. Up to now, there is little experimental results which directly show the existence of hydrogen on the Au surface under the hydrogen evolution reaction. Based on the qualitative analysis of current-potential curves, the surface coverage of hydrogen has been estimated. Thus, our present study might shed light on the understanding the mechanism of the hydrogen evolution reaction on the Au surface, as well as the conductance modulation of metal nanowire.

CONCLUSIONS

The conductance behavior of the Au mono atomic contact was studied under the electrochemical potential control. The stability and conductance of the Au contact could be fully controlled by the electrochemical potential. The conductance could be defined among three different conductance states at respective potentials: 1 G_0 at the double layer potential, $0.5~G_0$ at hydrogen evolution and conductance below 1 G_0 at the oxide formation potential. Based on the comparison between the conductance behavior and previously documented surface processes, we proposed the structural model. An oxygen would incorporate into the contact at the oxide formation potential. Atomic hydrogen would adsorb on the Au mono atomic contact at the hydrogen evolution potential. At the hydrogen evolution and oxide formation potential, the Au mono atomic contact was stabilized. The stabilization could be explained by the oxygen incorporation into the contact or hydrogen adsorption on the contact. Control of the three conductance states, stabilization of a fixed conductance state with hydrogen, and the appearance of the structure showing strong interaction between Au or oxygen were observed only for the metal contact under the electrochemical potential control, which could not be observed in other environments. The present results showed that electrochemical potential is one of the promising external fields for controlling the properties of nano scale materials.

This work was partially supported by a Grant-in-Aid for Scientific Research A (No. 16205026) and Grant-in-Aid for Scientific Research on Priority Areas (No. 17069001) and Global COE Program (Project No. B01: Catalysis as the Basis for Innovation in Materials Sci-

ence) from MEXT, and Asahi Glass Foundation.

- [1] N.J. Tao, Nature Nanotechnology 1, 173 (2006).
- [2] N. Agrait, A.L. Yeyati, and J.M. van Ruitenbeek, Phys. Rep. 377, 81(2003).
- [3] D. Dulic, S.J. van der Molen, T. Kudernac, H.T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, and B. J. van Wees, Phys. Rev. Lett. 91, 207402 (2003).
- [4] S. Csonka, A. Halbritter, G.Mihaly, Phys. Rev. B. 73, 75405 (2006).
- [5] W H A Thijssen, D. Marjenburgh, R H Bremmer, J. M. van Ruitenbeek, Phys. Rev. Lett. 96, 026806 (2006).
- [6] R. H. M. Smit, Y. Noat, C. Untiedt, N. D. Lang, M. C. van Hemert and J. M. van Ruitenbeek, Nature 419, 906 (2002).
- [7] M. Kiguchi, R. Stadler, I. S. Kristensen, D. Djukic, and J. M. van Ruitenbeek, Phys. Rev. Lett. 98, 146802 (2007).
- [8] C. Shu, C. Z. Li, H. X. He, A. Bogozi, J. S. Bunch, and N. J. Tao, Phys. Rev. Lett. 84, 5196 (2000).
- [9] J.L. Li, T. Kanzaki, K. Murakoshi, and Y. Nakato, Appl. Phys. Lett. 81, 123 (2002).
- [10] M. Kiguchi, T. Konishi, and K. Murakoshi, Appl. Phys. Lett. 87, 043104 (2005).
- [11] M. Kiguchi and K. Murakoshi, Appl. Phys. Lett. 88, 253112 (2006).
- [12] M. Kiguchi, T. Konishi, and K. Murakoshi, Phys. Rev. B 73, 125406 (2006).
- [13] J. Bockris and S. Khan, Surface Electrochemistry, Plenum (1993)
- [14] B.E. Conway and L. Bai, Electrochimica Acta 31, 1013 (1986)
- [15] L.D. Burke and M. Mcrann, J. Electroanal. Chem. 125, 387 (1981).
- [16] A.I. Yanson, G.R. Bollinger, H.E. van den Brom, N. Agrait, and J.M. van Ruitenbeek, Nature 395, 783 (1998).
- [17] R. N Barnett, H. Hakkinen, A. G. Scherbakov, U. Landman, Nano Lett. 4, 1845 (2004).
- [18] P. Jelinek, R. Perez, J. Ortega, and F. Flores, Phys. Rev. Lett. 96, 46803 (2006).
- [19] A. Zangwill, Physics at Surfaces, Cambridge University Press, (1998).
- [20] F. D. Novaes, A.J.R. da Silva, E. Z. da Silva, and A. Fazzio, Phys. Rev. Lett. 96, 16104 (2006).
- [21] H.X. He, C. Shu, C.Z. Li, and N.J. Tao, J. Electroanal. Chem. 522, 26 (2002).

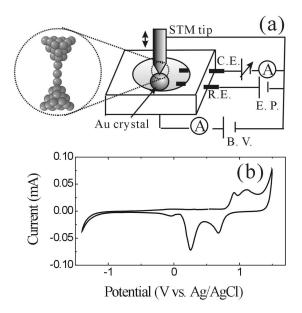


FIG. 1: (a) Schematic view of the electrochemical STM, C.E.: counter electrode, R.E.: reference electrode, E.P.: electrochemical potential, B.V. Bias voltage, (b) Cyclic voltammogram of the Au electrode in $0.1 \mathrm{M}~\mathrm{Na_2SO_4}$.

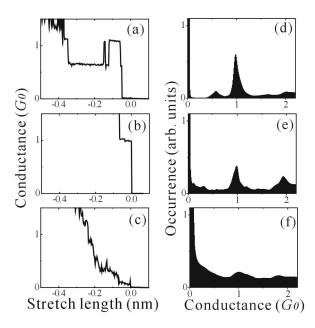


FIG. 2: Conductance traces and histograms of the Au nano contacts in 0.1M Na₂SO₄ solution. The electrochemical potential was (a, d) ϕ = -1.0 V (hydrogen evolution potential) (b, e) ϕ = -0.6 V (double layer potential), and (c, f) ϕ = 0.8 V (oxide formation potential). The conductance histograms were obtained from 5000 conductance traces of breaking the Au contacts. The intensity of the conductance histograms was normalized with the number of the conductance traces.

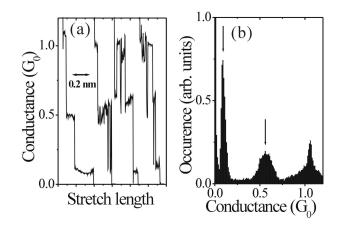


FIG. 3: (a) Conductance trace and (b) histogram of the Au nano contacts in 50 mM $\rm H_2SO_4$ solution. The electrochemical potential was $\phi{=}$ -0.3 V (hydrogen evolution potential). The conductance histogram was obtained from 3000 conductance traces of breaking the Au contacts.

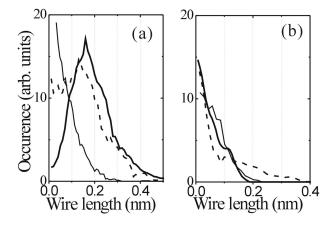


FIG. 4: Length histogram of the Au mono atomic contact in 0.1M Na₂SO₄ solution. The thin, thick, and dotted lines show the result at ϕ = -0.6 V(double layer potential), ϕ = +0.8 V (oxide formation potential), and ϕ = -1.0 V (hydrogen evolution potential), respectively. The length was defined as the distance between the points at which the conductance dropped below (a) 1.3 G_0 and 0.05 G_0 , (b) 1.3 G_0 and 0.8 G_0 , respectively.