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Author(s)	Kiguchi, Manabu; Konishi, Tatsuya; Miura, Shin-ichi et al.
Citation	Transactions of the Materials Research Society of Japan, 30(4), 1215-1218
Issue Date	2005
Doc URL	https://hdl.handle.net/2115/14479
Type	journal article
File Information	TransMRS-J_v30p1215.pdf



Fabrication of Sustainable Au Mono-atomic Wire showing Conductance Quantization in Solution

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Electric conductance of the Au nano constrictions was investigated in 0.1 M Na₂SO₄ solution under electrochemical potential control. Point contact of Au showing the unit of the quantum conductance, G_0 ($2e^2/h$), can be stretched as long as 1 nm when the electrochemical potential of the contact was kept at 0.5 V vs. Ag/AgCl. The result proves superior stability of Au mono atomic wire fabricated in solution. As the electrochemical potential changed to negative, the stretch length of the mono atomic wire decreased. The change of the stability was recovered as the potential became positive, indicating that the stability of the wire can be fully controlled by the electrochemical potential. In the time course of the conductance trace, fluctuation was observed. The change in the value in the conductance was less than -15 %. This fluctuation was attributed to the change in the number of atoms in the mono atomic wire. Observed changes in the conductance reflect the characteristics of the dynamical formation/deformation processes of the mono atomic wire showing conductance quantization in solution at room temperature.

Key words: mono atomic wire, conductance quantization, electrochemical potential, ion adsorption, anion

1. INTRODUCTION

When a metal nano contact is pulled with a scanning tunneling microscope (STM) or mechanically controllable break junctions (MCBJ), the width of the nano constriction is reduced, and an atomic scale nano constriction is formed just before breaking. At the atomic scale nano constriction, electrical conductance is expressed with an equation (1).

$$G = 2e^2/h \sum T_i \quad (1)$$

where T_i is the transmission probability of the i -th conductance channel and $G_0 = 2e^2/h$ is the unit of quantum conductance [1]. Conductance quantization depends not only on the atomic structure of the nano constriction but also on inherent properties of the metal [2-4]. In the case of Au, the conduction channel is single Au 6s channel with transmission of 1, and thus, the conductance is quantized in units of G_0 . In addition, a mono atomic wire can be easily fabricated for Au at the last stage of breaking, because of the characteristics of mechanical properties. As a model system, various studies have been done for the conductance quantization in the Au nano constrictions [5-7]. Ohnishi *et al.* reported atomic images of the Au mono atomic wire in ultra high vacuum (UHV) by the high resolution transmission electron microscopy together with the conductance of the wire [5]. Yanson *et al.* showed the formation of a 2 nm

long mono atomic wire by the conductance measurement in UHV at ultra low temperature (4.2 K) [6]. Smit *et al.* observed a parity oscillation in conductance of the mono atomic wire caused by the change in the numbers of atoms forming the wire [7].

While most of studies have been done in UHV at low temperature, in which fluctuation of environment is relatively small, preparation of stable metal ultra-small structures showing quantum conductance behavior at room temperature should be a challenging issue in this field. It has been demonstrated that electrochemical method can be used to solve the problem [8-11]. It is because potential energy of Fermi level, (i.e. electronic structure) and adsorption or desorption of molecules or ions can be controlled by electrochemical potential in solution to stabilize the nano-structure. The fact makes possible to fabricate novel metal nano structures which cannot be prepared in UHV, and to control electronic and geometrical structure in an atomic scale. Recently, we proved that clear conductance quantization for Pd nano constrictions can be observed by the careful control of Pd deposition and dissolution. It should be noteworthy that conductance quantization was not observed in UHV at room temperature at Pd nano constrictions [10,12]. The conductance behavior of the Au nano constrictions in solution via electrochemical deposition were also studied by Shu *et al.* and

they succeeded to observe conductance quantization in 0.1 M NaClO₄ [11]. However, there are little studies in structures on Au nano wire fabricated mechanically in solution.

In the present study, we have studied the quantum conductance behavior of the Au nano constrictions in 0.1 M Na₂SO₄ under electrochemical potential control. Since the conductance of the nano constriction provides the information on the structure of the constriction, we have analyzed the each conductance trace in detail. We then have discussed the formation process of the Au mono atomic wire and its stability, showing small variation in the conductance.

2. EXPERIMENTAL

The experiments have been performed with modified STM systems in an electrochemical cell mounted in a chamber that was filled with high purity N₂ gas to reduce contamination. The Au nano constrictions were created by driving a STM tip into and out of contact with an Au substrate. The STM tip was made of an Au wire (diameter ~0.25 μm) coated with wax to eliminate ionic conduction. The substrate of Au(111) was prepared by flame annealing and quenching method. Figure 1 shows the STM height image of Au(111) single crystal electrode surface in 0.1 M Na₂SO₄ solution. Figure 2 shows the schematic view of the experimental setup. The electrochemical potential of the Au tip (WE1) and substrate (WE2) was controlled with respect to the Ag/AgCl reference electrode (RE) using a potentiostat (Pico-Stat, Molecular Imaging Co.). A 0.50 mm diameter Pt wire was used as counter electrode (CE). The electrolyte solution was 0.1 M Na₂SO₄. The potential difference between Au tip and substrate (bias voltage) was 20 mV. Contribution of the Faradic current was carefully excluded for the determination of the conductance

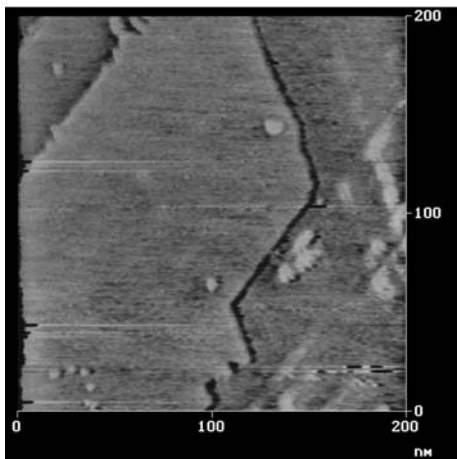


Fig. 1: STM height image of Au(111) prepared by flame annealing and quenching method. The electrochemical potential is +0.5 V vs. Ag/AgCl.

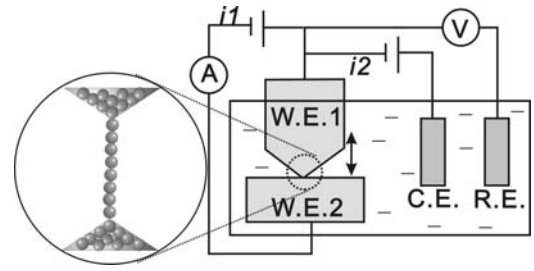


Fig. 2. Schematic view of the experimental setup. An atomically thin Au wire is suspended between two Au electrodes (W.E.1: STM tip, W.E.2: substrate). The electrochemical potential (V) of the electrodes are controlled with respect to a reference electrode (R.E.). C.E. is the counter electrode. i_1 : current through the metal wire, i_2 : faradic current.

of the nano constriction. In our experimental setup, the current through the metal nano wire (i_1 , see Fig. 2) is affected by the faradic current (i_2). The ratio between apparent conductance and real conductance depends significantly on i_1 . To obtain numerical relation for conductance correction, we have to know a circuit property of the conductance measurements in solution with three variable resistances (W.E.1-W.E.2, C.E.-W.E.1, and C.E.-W.E.2). The observed conductance / correct conductance ratio does not depend on the conductance, but depends on the faradic current. The correction function determined by the use of equivalent circuit with known conductance was used to determine the conductance of the metal nano constrictions in solution.

3. RESULTS AND DISCUSSION

Figure 3 shows the typical conductance trace of and schematic view of the atomic structure of the Au nano constriction in 0.1 M Na₂SO₄ solution. The STM tip was driven into contact with the substrate to reach the conductance set point ($3.7 G_0$ in the present study). Once the contact was fully established (Fig. 3 (a)), the STM tip was pulled at a typical rate of 50 nm/s. During pulling, the width of the nano constriction was reduced (Fig. 3 (b)), and the conductance decreased in a stepwise fashion. These steps were the result of atomic structural rearrangement. In case of monovalent metal, the conductance at the last plateau is usually close to $1 G_0$, and $1 G_0$ plateau corresponds to a contact with a single atom at the narrowest cross section. Before breaking, a Au mono atomic wire was fabricated (Fig. 3 (c)), and the nano contact broke at last (Fig. 3 (d)).

Figure 4 (a) and (b) show the conductance histogram of the Au nano constrictions in 0.1 M Na₂SO₄ solution at electrochemical potential of +0.5V and -0.2 V vs. Ag/AgCl. Each conductance histogram was obtained for a large number (over 3000) of individual conductance traces. In the

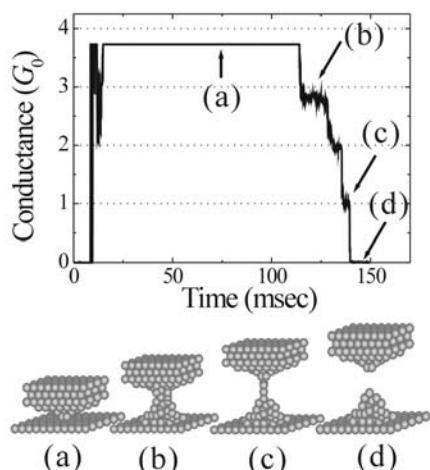


Fig. 3. (upper part) The time dependence of the conductance of the Au nano constrictions. (lower part) The schematic view of the atomic structure of the Au nano constriction. (a, b) thick nano constrictions, (c) mono atomic wire, and (d) breaking.

conductance histogram, well-defined peaks appeared near integer multiple of G_0 , in agreement with the previous studies in UHV and solution [6,11]. While the conductance of the first peak was just $1 G_0$, the conductance of the higher conductance peaks shifted to the lower conductance side. This small shift was based on the back scattering of the electrons on defects in the Au nano constrictions [13].

Figure 5 shows the typical conductance trace of the Au nano constriction. The plateau with a conductance of $1 G_0$ stretched as long as 0.6 nm (Fig. 5). Since the $1 G_0$ plateau corresponds to a contact with a single atom at the narrowest cross section, the length of the plateau with a conductance of $1 G_0$ corresponds to the length of the Au mono atomic wire. Relatively long length of the plateau indicates that an about 1 nm long mono atomic Au wire can be fabricated in solution at room temperature. In UHV, the 2 nm and 1 nm long mono atomic Au wires are fabricated at 4.2 K [6] and 300 K [5]. Although fluctuation of the environment in solution is much larger than that in UHV, such a high stable Au mono atomic wire can be fabricated in solution at room temperature. The fact implies that the electrochemical system can control electronic and mechanical properties of the metal nano constriction.

Stability of the Au nano-constriction depended on the electrochemical potential significantly. As the electrochemical potential decreased from +0.5 V to -0.2 V, the intensity of the integer peaks decreased (Fig. 4 (b)). The intensity of the $1 G_0$ peak reflects the length of the mono atomic wire. The decrease in $1 G_0$ peak height at negative potential indicates that the length of the Au mono atomic wire decreases as the electrochemical potential becomes negative. This electrochemical

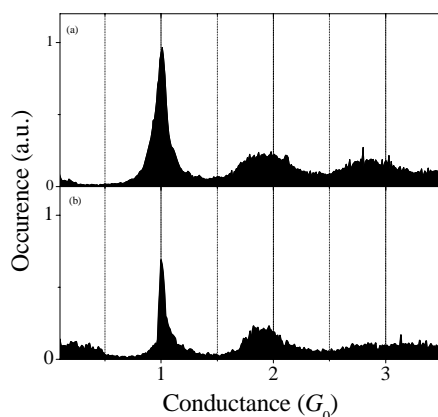


Fig. 4. (a) Conductance histograms of Au nano constructions in Na_2SO_4 at (a) +0.5 V, and (b) -0.2 V vs. Ag/AgCl.

potential dependence can be explained by the molecule adsorption on Au surface. Sulfate anions adsorb on Au surface at more positive potential than 0.0 V [14]. The coverage of the anions increases gradually as the potential becomes positive. Thus, sulfate anion may adsorb on the Au mono atomic wire at +0.5 V. Relatively strong adsorption of the sulfate anion may improve stability of the Au mono atomic wire in solution. Contribution of adsorbed anions can be considered for the origin of the successful preparation of very stable Au mono atomic in solution at room temperature. The stability of the wire may decrease as the coverage of anion decreases. The change in the stability of the Au mono atomic wire depending on the electrochemical potential can be explained by the changing the adsorption and desorption of adsorbates under the electrochemical potential

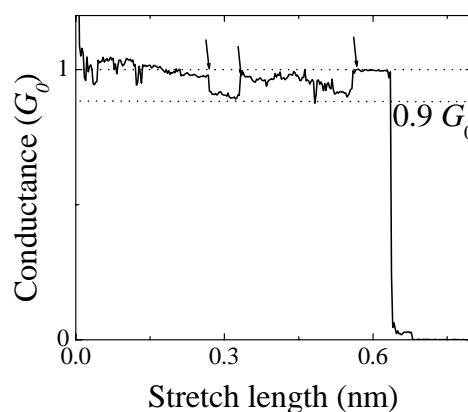


Fig. 5. Typical conductance trace of Au mono atomic chain at electrochemical potential of +0.5 V vs. Ag/AgCl. The arrow indicates the change in the structure of the chain when a new atom is pulled into the atomic chain.

control. Although solvent and solvated cation should be also considered as adsorbates in solution, the contribution is not clear at the present stage.

As shown in the conductance trace of Fig. 5, sudden decrease and recovery were observed at the plateau of the unit conductance. These changes in conductance (arrow in the figure) resulted from the change in the structure of the chain, and were attributed to the odd-even oscillation in the mono-atomic wire [7]. When the structure of the mono-atomic chain is changed by adding or subtracting one atom, the number of atoms composed of the chain changes between even and odd numbers. This number change is essentially to cause an interference effect on the conduction electron in a channel. The phenomenon can be understood in the frame of a simplified one-dimensional free electron model. In this model, the transmission of an electron at the Fermi energy can be written with an equation (2).

$$T = \frac{16r^2}{(1+r)^4 + (1-r)^4 - 2(1+r)^4(1+r)^4 \cos(\pi(n+1))} \quad (2)$$

where n and r are the number of the atoms in the chain, and constant (<1). The transmission $T=1$ for the case of an odd number of atom n , and $T=4r^2/(1+r^2)^2$ for n even. Therefore, the conductance for an odd number of atoms in a chain of a mono valent metal is G_0 , while the conductance for the even numbered chain is smaller than $1 G_0$ (since $r < 1$). Such oscillatory behavior of the conductance can be observed only for chains of a mono valent metal such as Au. In other words, the observed conductance oscillation proves the formation of mono atomic wire of Au. From changes in conductance, we can directly observe formation and deformation process of the Au mono atomic wire in solution at room temperature.

Conductance fluctuation was reported only for Au nano constrictions in UHV at 4.2 K, in which fluctuation of environment is small. The present result here suggests that mono-atomic chain of Au can be fabricated in solution at room temperature, in which fluctuation of environment is relatively large. Environmental control in an atomic and molecular scale by the electrochemical potential control plays a decisive role to maintain the structure showing conductance quantization. The mono atomic wire may be stabilized by anion in solution, and thus, we can observe conductance oscillation in solution at room temperature.

4. SUMMARY

Nano constrictions of Au were mechanically fabricated in 0.1 M Na_2SO_4 solution under electrochemical potential control. The stable 1 nm long Au mono atomic wire can be fabricated in solution at room temperature, in which the

environmental fluctuation is relatively large. The stability of the mono atomic wire can be controlled by changing the electrochemical potential. Contribution of adsorbed sulfate anion to the wire was discussed based on the potential dependent change of the adsorption. We also succeeded observation of dynamic formation and deformation processes of the Au mono atomic wire as a change in conductance.

Acknowledgement

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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