Hydrogen-assisted stabilization of Ni nanowires in solution

Manabu Kiguchi1, Tatsuya Konishi1, and Kei Murakoshi1,2

1 Department of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, 060-0810, Japan
2 PRESTO, Japan Science and Technology Agency, Sapporo, 060-0810, Japan

(March 12, 2021)

We have studied conductance characteristics of mechanically fabricated Ni nanoconstrictions under controlling electrochemical potential and pH of the electrolyte. Conductance histogram showed clear feature peaked at 1-1.5 $G_0 (=2e^2/h)$ when the potential of the constriction was kept at more negative potential than -900 mV vs. Ag/AgCl in pH=3.7. Comparable feature also appeared at more positive potential when lower pH solution was used. We have revealed that Ni mono atomic contact or mono atomic wire can be stabilized in solution at room temperature under the hydrogen evolution.

Construction of metal nanowires is in the central issue of the current technology, because the techniques may be applied to fabricate ultimate electrical circuits in an atomic scale. Electrical conductance through a metal nanowire in an atomic scale is expressed by $G = 2e^2/h \sum T_i$; where $T_i$ is the transmission probability of the $i$-th conductance channel, $e$ is the electron charge, and $h$ is Plank’s constant. Conductance quantization depends not only on the atomic structure of the nanoconstriction but also on inherent properties of the metal [1]. Conductance at mono-atomic point contact of transition metals with partially occupied d orbitals is expected to be 1.5-3 $G_0$ based on the theoretical calculation [1]. Recently, quantized conductance of Ni nanoconstrictions has attracted much attention because of the expectation that ferromagnetic nanowire may shows the conductance quantization in units of 0.5 $G_0$, since there is no spin degeneracy. The up- and down-spin electrons contribute independently to the electric transport. As well as Ni, other ferromagnetic metals, Fe and Co, have been extensively studied to confirm spin-dependent conductance quantization. However, previously documented data at experiments was less consistent each other. Various conductance values, such as 1.6 $G_0$ [2], 1 $G_0$ [3], and 0.5 $G_0$, have been reported [4]. In addition, histogram of the conductance becomes featureless at room temperature [5]. The poor agreement between former reported results may originate from the chemical instability of the nanoconstrictions of ferromagnetic metals. Novel experimental approach under controlling the chemical reactivity of ferromagnetic metals is required to study the characteristics of the conductance quantization of ferromagnetic metals.

Electrochemical method has been recognized to be also another powerful approach to study the conductance quantization [6,7]. Electrochemical potential determines the potential energy of electrons of the nanoconstriction, resulting in the control of the bonding strength between the metal atoms, and the interaction of the metals with molecules in surrounding medium. The characteristics of the system lead to successful fabrication of very stable metal nanostructures showing the conductance quantization which cannot be observed in UHV. For example, we reported that clear conductance quantization for Pd nanoconstrictions can be observed by the careful control of Pd deposition and dissolution [6]. It should be noteworthy that conductance quantization was not observed in UHV at room temperature [8]. The experiments were performed in an electrochemical cell mounted in a chamber that was filled with high purity N$_2$ gas (>99.999%) to avoid effect of oxygen in air. The tip was made of a gold wire (diameter ∼0.25 mm, >99.9%) coated with wax to reduce Faradic current between the tip and a counter electrode. The substrate was Au(111) prepared by flame annealing and quenching method. The electrochemical potential ($\Phi_0$) of the Au substrate and tip was controlled using potentiostat (Pico-Stat, Molecular Imaging Co.) referring a Ag/AgCl reference electrode. The potential difference between the tip and substrate (bias voltage) was kept at 20 mV. A Pt wire was used as counter electrode. The electrolyte was 10 mM NiSO$_4$, 10 mM H$_3$BO$_3$ and H$_2$SO$_4$. Solution pH was adjusted by changing the concentration of H$_2$SO$_4$.

Nanoconstrictions of Ni were prepared as the following manner. First, Ni was electrochemically deposited both on the Au tip and the substrate by the polarization to negative potential than $\Phi_0 = -650$ mV where Ni bulk deposition proceeded [9]. After the confirmation of the bulk deposition of Ni on the tip and a substrate, the tip was pressed into the substrate and then pulling out of contact at a typical rate of 50 nm/s in the electrochemical cell. During the contact breaking, a Ni nanoconstriction was formed between the tip and the substrate as schematically shown in Fig. 1. Conductance was measured by applying the bias of 20 mV between a tip and a substrate.

Figure 2(a) shows the conductance histogram observed at $\Phi_0 = -800$ mV in the electrolyte solution with pH=3.7. There was no clear feature in the conductance histogram, suggesting that any certain atomic configurations were not preferentially formed between Ni-deposited tip and a substrate. When the electrochemical potential of the nanoconstriction was kept at more negative ($\Phi_0 =$ -
900 mV), clear feature appeared near 1-1.5 $G_0$ (see Fig. 2(b)). Further polarization to negative potential of the tip and the substrate did not change the conductance histograms. The clear feature in the conductance histogram showing 1-1.5 $G_0$ also appeared when the solution pH became lower than 2.7. Figure 2 (c) shows the conductance histogram at $\Phi_0 = -800$ mV in pH=2.3. Comparable feature as that of at $\Phi_0 = -800$ mV and pH=3.7 was clearly observed in the histogram. Further decrease in pH did not change the conductance histogram. The potential in which clear feature at 1-1.5 $G_0$ was observed corresponds to the hydrogen evolution region at Ni electrode [10]. Thus, the present result shows that the chemical reaction of hydrogen evolution affects significantly the conductance of Ni nanoconstriction in solution.

At the hydrogen evolution potential, the surface of Ni electrode is covered by the dissociated atomic hydrogen [10]. The coverage of adsorbed hydrogen was evaluated by in-situ infrared-reflection spectroscopy and the qualitative analysis of current-potential curves for hydrogen evolution [10,11]. The coverage of adsorbed hydrogen gradually increases as the electrochemical potential becomes negative. Based on the results at the Ni polycrystalline electrode, the coverage of adsorbed hydrogen was estimated to be 0.20 and 0.40 at $\Phi_0 = -800$ and -900 mV in pH=3.7, respectively. In more acidic solution with pH = 2.3, comparable coverage can be achieved at more positive potential by 100 mV. Comparable feature in the histograms in pH = 3.7 at -900 mV and that in pH = 2.3 at -800 mV proves that the dissociated atomic hydrogen play an important role to define the geometrical and/or the electronic structure of the ferromagnetic metal nanoconstriction in solution.

It should be noteworthy that the observed conductance histogram (Fig. 2 (b)) was similar to that observed in UHV at ultra low temperature. In UHV, clear 1-1.5 $G_0$ feature appears in the conductance histogram at ultra low temperature [12], while the histogram becomes entirely featureless at room temperature [5]. Thermal fluctuation of atoms at room temperature may prevent the long-term stability of the nanocontact, resulting in the broad feature in the histogram. At low temperature in UHV, thermal fluctuation is small. Thus the nanostructure can change into a thermally stable one showing specific values of the conductance. Although the fluctuation of atoms in solution at room temperature should be much larger than that in air and UHV, the specific feature of the Ni nanoconstriction was found to be kept during the hydrogen evolution reaction even at room temperature. The results prove that the control of electrochemical potential and solution pH leads to successful preparation of the Ni nanoconstrictions showing clear conductance quantization at room temperature.

At the present stage, it is not clear how the adsorbed atomic hydrogen stabilize the certain atomic arrangement of the Ni nanoconstriction. The result proves that the effects of hydrogen on the conductance values at the present system are different from those at UHV. In the previously documented result at UHV, introducing hydrogen suppressed the characteristic conductance of Ni at 1-1.5 $G_0$ by the replacement due to the evolution of a new value appears near 1 $G_0$ in the histogram [12]. The origin of the value is a single hydrogen molecule bridging between two electrodes [13]. In the case of Pd, introducing hydrogen also suppresses the characteristic conductance of 1.8 $G_0$, giving new values appear near 0.5 and 1 $G_0$ in the histogram [14]. These values of 0.5 and 1 $G_0$ are attributable to a bridging single hydrogen molecule, and a Pd$_2$H$_2$ complex, respectively. On the other hand, at the present system in solution, the conductance histogram under the hydrogen evolution reaction was similar to that of a bare Ni metal in UHV. The observation suggests that the hydrogen molecules did not bridge between the electrodes, despite of the existence of the adsorbed hydrogen at the Ni surface.

Electrochemical potential control of the Ni nanoconstriction in solution leads to the control of the electronic density of the Ni atoms at the constriction. Characteristics of the electronic structure of the Ni nanoconstriction under the electrochemical potential control should be maintained as the same as a bare Ni constriction in UHV, even at the situation in which hydrogen adsorbed on the surface. As well as the effect of potential control of the system, the adsorbed hydrogen is known to alter the surface stress, because of modulation of the bonding strength between Ni atoms at the surface [15]. In the present system, adsorbed hydrogen as well as evolved hydrogen molecules in the vicinity of the Ni nanoconstriction may contribute to stabilize the specific structure of the constriction mechanically via relatively weak physical and/or chemical interactions. These specific effects in the electrochemical system may lead to comparable feature of the conductance histogram observed at the nanoconstriction of a bare Ni in UHV at ultra-low temperature, even under the hydrogen evolution in solution at room temperature.

The conductance trace contains structural information on the Ni nanoconstriction in solution. Figure 3(a) shows the typical conductance trace at $\Phi_0 = -800$ mV in pH=3.7. As general tendency, the conductance change occurred continuously, rather than a stepwise fashion. Although conductance occasionally showed small steps and plateau-like structures, their appearance and conductance values were non-reproducible, resulting in the featureless conductance histograms (see Fig. 2 (a)). Figure 3 (b) and (c) show the typical conductance trace at $\Phi_0 = -800$ mV in pH=2.3. Although conductance change still occurred in a continuous fashion as at $\Phi_0 = -800$ mV in pH=3.7, the conductance of 1-1.5 $G_0$ was preferentially taken. It is the reason of an appearance of broad 1-1.5 $G_0$ feature in the histogram shown in Fig. 2 (c).

At $\Phi_0 = -800$ mV in pH=2.3, the plateau was stretched
as long as 0.8 nm (see Fig. 3 (b)), and reversible transition between 1 $G_0$ and 0.6-0.7 $G_0$ were occasionally observed in the long plateau (see Fig. 3(c)). The conductance of a mono atomic contact is evaluated to be around 1.5-2.5 $G_0$ for transition metals [1]. Therefore, the long plateau indicates high stabilization of the Ni mono atomic contact in solution. At the present stage, it is not clear whether the long plateau originated from the formation of the Ni mono atomic wire or it originated from deformation in a stem part of the nanoconstriction. This long plateau, however, implies the possibility of indicating the formation of a mono atomic Ni wire in solution. The formation of a mono atomic wire was supported by the reversible transition between 1 $G_0$ and 0.6-0.7 $G_0$ (Fig. 3(c)). A similar reversible transition of conductance between 1 $G_0$ and 0.6-0.7 $G_0$ were reported for Au mononanoatomic wires in the presence of physically adsorbed hydrogen in UHV at low temperature (10-30 K) [16]. The reversible transition are explained by the dynamical structure transition between a dimerized Au wire and an equal-spacing wire, and the dimerization is a characteristic of a mono atomic wire [17].

In conclusion, the dependence of the electrochemical potential and the solution pH on the conductance value was studied for the electrochemical deposited Ni nanoconstrictions. Under hydrogen evolution reaction, clear 1-1.5 $G_0$ feature appeared in the conductance histogram, suggesting that certain mono atomic arrangements were stabilized in solution. The analysis of the conductance trace showed the possibility of the formation of a one-dimensional Ni mono atomic wire in solution at room temperature. This hydrogen-assisted stabilization of metal nanostructure can be applied as an effective method to control the structure of the nanoconstriction in an atomic scale, and fabricate various interesting structures for the study of one-dimensional systems.

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

[1] N. Agrait, A.L. Yeyati, J.M. van Ruitenbeek, Physics Reports 377, 81 (2003).
[2] C. Sirvent, J. G. Rodrigo, S. Vieira, L. Jurczyszyn, N. Mingo, and F. Flores, Phys. Rev. B 53, 16086 (1996).
[3] Y. Ooka, T. Ono, H. Miyajima, J. Mag. Mag. Mat. 226-230, 1848 (2001).
[4] F. Elhoussine, S. Matefi-Tempfi, A Encinas, and L. Piriaux, Appl. Phys. Lett. 81, 1681 (2002).
[5] J. L. Costa-Kramer, Phys. Rev. B 55, R4875 (1997).
[6] C. Shu, C. Z. Li, H. X. He, A. Bogozi, J. S. Bunch, and N. J. Tao, Phys. Rev. Lett. 84, 5196 (2000).
[7] J. Li, T. Kanzaki, K. Murakoshi, Y. Nakato, Appl. Phys. Lett. 81, 123 (2002).
[8] A. Enomoto, S. Kurokawa, and A. Sakai, Phys. Rev. B 65, 125410 (2002).
[9] M. Zhou, N. Myung, X. Chen, K. Rajeshwar, J. Electroanal. Chem. 398, 5 (1995).
[10] G. Kreyss, B. Hakansson, P. Ekdunge, Electrochimica Acta 33, 1351 (1988).
[11] J.O. Bockris, J. L. Carabajal, B. R. Scharifker, K. Chandrasekaran, J. Electrochem. Soc. 134, 1957 (1987).
[12] C. Untiedt, D. M. T. Dekker, D. Djukic, and J. M. van Ruitenbeek, Phys. Rev. B 69, 81401 (2004).
[13] R. H. M. Smit, Y. Noat, C. Untiedt, N. D. Lang, M. C. van Hemert and J. M. van Ruitenbeek, Nature 419, 909 (2002).
[14] Sz. Csonka, A. Halbritter, and G. MihaLly, O. I. Shklyarevskii, S. Speller, and H. van Kempen, Phys. Rev. Lett. 93, (2004) 16802.
[15] S. Armyanov and G.S.Sotirova-Chakarova, Metal Finishing 91, 59 (2003).
[16] Sz. Csonka, A. Halbritter, G. Mihaly, E. Jurdik, O. I. Shklyarevskii, S. Speller, and H. van Kempen, Phys. Rev. Lett. 90, 116802 (2003).
[17] M. Okamoto and K. Takayanagi, Phys. Rev. B 60, 7808 (1999).
FIG. 2. Conductance histograms of Ni nanoconstrictions kept at (a, c) $\Phi_0 = -800$ mV, (b) $\Phi_0 = -900$ mV. Solution pH of the electrolytes was (a, b) 3.7 and (c) 2.3.

FIG. 3. Typical conductance traces of Ni nanoconstrictions observed at $\Phi_0 = -800$ mV in pH=3.7 (a), and pH=2.3 (b, c). Arrows in Figure 3 (c) indicate reversible transition between $1 G_0$ and 0.6-0.7 $G_0$ plateaus.