

Facile Preparation of Sustainable Metal Thin Wire Showing Quantized Conductance in Solution

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Sustainable Cu thin-wires showing quantized conductance were prepared by means of electrochemical dissolution in solution. The conductivity of a wire decreased as its etching proceeded. Just before the wire was broken, the conductance quantization was observed. The quantization was also observed upon recovery of electrical contact by electrochemical metal deposition. Anions in the electrolyte affected the stability of the wires showing the conductance quantization during the deposition process. The magnitude of the quantized conductance could be controlled by regulating the electrochemical potential of the Cu wires.

1. Introduction

Construction of metal nano-wire and nano-junction is in the central issue of the recent nano-technology. If one can control metal nano-structure precisely, the resulting structure could be used for various novel devices based on their characteristics, such as quantized conductance properties,^{1, 2} single-electron charging,^{3, 4} electronic transport properties of single molecules.^{5, 6} Thus, the way to prepare the metal nano-structure should be developed.

We have shown the possibilities of chemical techniques to apply to the fabrication of nano-structures on solid surfaces as novel, effective, and low-energy processes.⁷⁻¹¹ Among them, an electrochemical method should be one of the most promising techniques to fabricate nano-structures. The controlled absolute potential of the electrode in solution results in precise control of atomic processes on solid surfaces.^{12, 13}

Recently, it was proved that electrochemical metal deposition / dissolution can be used for the fabrication of ultra-thin nano-junctions either a gap between tip and substrate surface of a scanning tunneling microscope (STM),¹⁴⁻¹⁶ or a gap between micro-electrodes prepared by photolithography.¹⁷⁻¹⁹ Tao et al. showed the formation of nano-junctions showing quantized conductance during Cu deposition and dissolution at a gap between a tip and a substrate of an electrochemical STM. The phenomenon is quite similar to that observed in the systems of mechanical break junctions and STM in which metal nano-wire consisting of several atoms forms at the gap.²⁰ Such conductance quantization was also observed when metal deposition and/or dissolution carried out at a gap between micro-electrodes.^{21, 22} Marcus et al. reported that conductance quantization was observed during Au deposition / dissolution at a sub-micron meter (50 ~ 400 nm) gap between micro-electrodes prepared by photolithography.²² Tao et al. Also proved that the technique using micro-electrodes seems to be more useful to fabricate stable metal nano-wires in solution, than that using STM, because the precise control of the

electrochemical potential allowed us to maintain the structure of nano-wires showing unit value of quantized conductance for several hours.²¹ In spite of the advantage of the latter method, the preparation of micro-electrode always needs precise control of the thickness of insulating layers on the micro-electrode surfaces, typically less than a few hundred nm, to reduce additional electrochemical reactions at exposed area of the electrodes to the electrolyte. Background currents due to the additional reactions were believed to affect the stability of the nano-wires in solution. Furthermore, adsorption of molecules in solution also contributes to the change in the stability of the nano-wires. To establish the method to fabricate metal nano-junctions in solution, it could be desirable to investigate a contribution of exposed areas of the electrodes, as well as the effect of adsorbates in the electrolyte solution.

In this report, Cu wires with the diameter of 30 μm were used to prepare the nano-junctions showing the quantized conductance. The wire was covered by an insulating tape except for a region of a few tens μm in length. The non-covered area of the wire exposed to the solution was just determined by the position of the attached insulating tape regulated by hand. Electrochemical dissolution of the area resulted in the

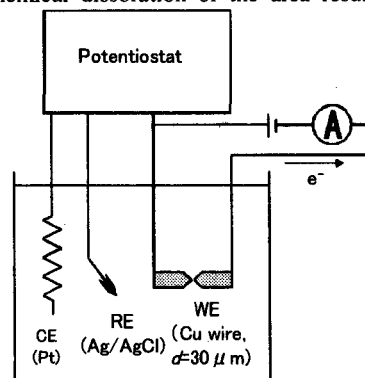


Figure. 1 Schematic presentation of electrochemical cell.

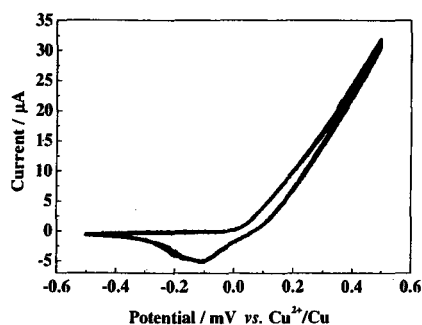


Figure 2. Cyclic voltammogram of a Cu electrode in 0.1 M H_2SO_4 containing 1 mM CuSO_4 . Sweep rate 100 mV s^{-1} .

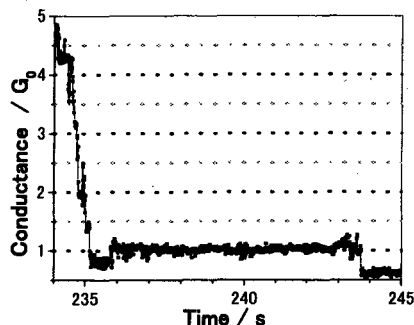


Figure 3. Time courses of the conductance change of a Cu wire during the electrochemical dissolution at 0.03 V in (a) 1 mM CuSO_4 + 0.1 M H_2SO_4 .

formation of sustainable metal a thin-wire with the diameter of a few μm . The conductance quantization was observed when the electrochemical potential was kept at an appropriate potential. The occurrence of the quantization depended on the kind of anions (SO_4^{2-} , ClO_4^- , Cl^-) in the electrolyte.

2. Experimental Procedures

The electrochemical dissolution and deposition were carried out in an electrolyte solution using a three electrodes system (Figure 1). Three kinds of electrolyte solutions (0.1 M H_2SO_4 , 0.2 M HClO_4 , and 0.2 M HCl) containing 1 mM CuSO_4 were used in the experiments. The electrochemical potential of the electrode (Cu wire) was regulated against a Cu^{2+}/Cu reference electrode. During the electrochemical Cu dissolution and deposition, a current flowing through the Cu wire was simultaneously monitored with an electrometer (Keithley 6517A) under a constant bias (18.8 mV). The experiment was repeated at least 10 times to confirm the reproducibility and the tendency described below.

3. Results and Discussion

Figure 2 shows a cyclic voltammogram of a Cu wire in 0.1 M H_2SO_4 containing 1 mM CuSO_4 . Typical behavior of Cu dissolution and deposition was observed at positive and negative polarization, respectively. To prepare a thin wire, the electrode potential was kept at 0.2 V. The exposed part of the wire was dissolved by this positive polarization, which led to the formation of a thin metal wire. A sustainable thin wire with the diameter of a few μm was prepared in solution. The length of the thin wire depended on the exposed area determined by the position of the attached insulating tape. In the present

experiments, approximately 100 – 300 μm length of the wire was successfully prepared by dissolution. The sustainable wire was relatively stable in solution as far as the electrochemical potential was kept at around 0 V.

After the preparation of a thin Cu wire, the potential was then kept at 0.03 V. At the slightly positive polarization, the Cu dissolution proceeded slowly. The monitored current flowing through the wire indicated that the wire was broken by the dissolution in a certain period of time. The dissolution of the wire was also confirmed by the microscopic image observation (data is not shown here).²³ Formation of the sustainable metal nano-wire was formed at the not-tape covered part of the wire. Figure 3 shows time courses of the conductance of the wire calculated from the current and bias voltage, using a unit of the quantized conductance ($2e^2/h$), observed just before the wire was broken. In this experiment, 1.46 μA corresponded to a current flowing at the junction showing a unit conductance. All in three solutions (0.1 M H_2SO_4 , 0.2 M HClO_4 , and 0.2 M HCl), each containing 1 mM CuSO_4 , step-wise conductance changes were observed. Some conductance plateaus correspond to the values of the quantized conductance. Also, the unit conductances were clearly observed all in three solutions just before the conductance became zero. The observed behavior is essentially the same as the previously reported conductance quantization in nano-wires prepared by electrochemical fabrication.^{20, 24} Such quantization indicates the formation of nano-wires or nano-point contacts consisting of a few metal atoms, bridging the metal nano-gaps.^{15, 16, 22} The present results imply that Cu metal wires with relatively large exposed areas (a few

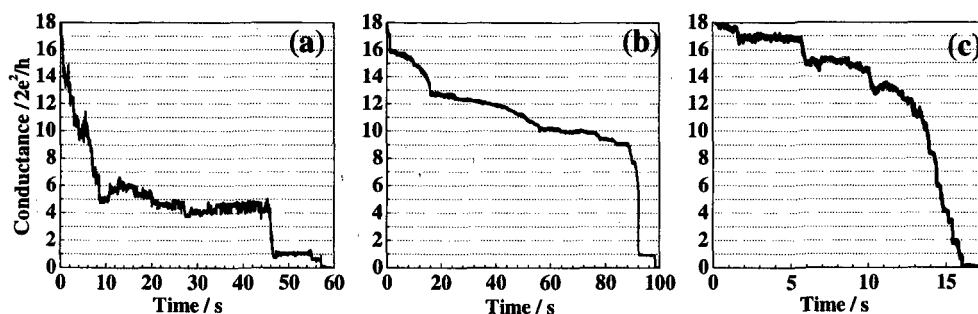


Figure 4. Time courses of the conductance change of a Cu wire during the electrochemical dissolution at 0.03 V in (a) 1 mM CuSO_4 + 0.1 M H_2SO_4 , (b) 1 mM CuSO_4 + 0.2 M HClO_4 , (c) 1 mM CuSO_4 + 0.2 M HCl

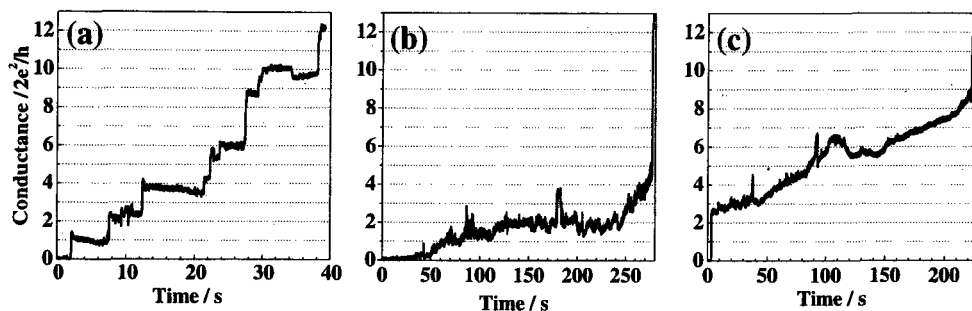


Figure 5. Time courses of the conductance of a Cu wire during the electrochemical deposition at -0.08 V in (a) $1\text{ mM CuSO}_4 + 0.1\text{ M H}_2\text{SO}_4$, (b) $1\text{ mM CuSO}_4 + 0.2\text{ M HClO}_4$, (c) $1\text{ mM CuSO}_4 + 0.2\text{ M HCl}$.

hundred μm length) can be used to prepare sustainable metal thin-wires showing the conductance quantization.

The stability of the quantization depended on the kind of anions in solution. Sulfate anions (SO_4^{2-}) (Figure 4(a)) showed longer plateaus of the unit conductance than the other anions (ClO_4^- and Cl^-) (Figure 4(b) and (c)) for the dissolution. In the systems of ClO_4^- and Cl^- , step-wise decreases of the conductance and the unit conductance were observed as in the case of SO_4^{2-} , but the maintained times of the unit conductance was less than one second (Figure 4(b) and (c)). The results imply that the stability of the nano-junction prepared in SO_4^{2-} is better than that in ClO_4^- and Cl^- when the junction is prepared by dissolution.

The difference in the quantization behavior among the anions was observed much more clearly for the Cu deposition at the gap. Figure 5 shows time courses of the conductance changes during the Cu deposition onto the nano-gap of the wire. The Cu deposition was carried out at -0.08 V. Clear step-wise changes in the conductance were observed for the deposition in a solution of SO_4^{2-} (Figure 5(a)). Other two electrolytes containing ClO_4^- or Cl^- did not show clear plateaus of the conductance during the deposition (Figure 5(b) and (c)). Especially in the case of Cl^- , the conductance jump from zero to approximately $n = 3$ occurred, and then increased monotonously to higher values. For the Cu deposition to recover the nano-junction, the choice of SO_4^{2-} anions in electrolytes seems to be more critical than the case for the dissolution.

These results suggest that the stability of the nano-junction in solution strongly depends on the electrolyte anions. The difference in the stability may be due to a difference in the adsorption strength of anions onto the Cu surface. The adsorption strength becomes larger in the order of ClO_4^- , SO_4^{2-} , Cl^- .²⁵ The high stability of the wire in SO_4^{2-} solutions seems to imply the importance of the moderate adsorption strength to form the stable nano-junction. The appropriate adsorption strength is likely to contribute to stabilize the structure of the nano-junction. Improvement in the mechanical stability of the nano-junction was reported previously both in the systems of electrochemical and mechanical fabrication of nano-wires.^{21, 26} It is reported that repeated dissolution-deposition cycles or pulling down-up cycles often leads to improvement in the control of the conductance quantization. These repeated cycles could improve the crystallinity of the nano-wire. In the present system, dissolution-deposition cycles were not adopted,

thus the effect of the anions could be explained in terms of stabilization of the nano-junction by the anion adsorption. Weak adsorption of ClO_4^- seems to contribute no structural stabilization. Strongly adsorbed Cl^- may lead to higher activation energy for the Cu deposition or dissolution. The sudden change of the conductance at the initial stage (Figure 4 (c)) seems to reflect this characteristic.

In the present system of sustainable thin wires with relatively large exposed areas to the electrolyte, the control of the quantized conductance in the magnitude was also possible. Figure 6 shows an example of the conductance-value control. After the Cu wire dissolution at 0.03 V to reach a relatively higher quantized conductance of $n = 11$, the conductance of $n = 11$ was maintained for a long time of the order of a thousand seconds if the potential was kept slightly negative. The slight dissolution of the Cu wire at 0.01 V for a few minutes led to a decrease of the conductance by a unit conductance was observed after the potential was switched back to -0.05 V. The value was maintained for a long time again at -0.05 V. The result indicates that the magnitude of the quantized conductance can be controlled for the present sustainable thin wires with relatively large exposed areas.

Unfortunately, maintaining the unit conductance for a long time by controlling the electrochemical potential has not been achieved yet in the present system. The precise control of the unit conductance has been possible already for the nano-junctions prepared using micro-electrodes prepared by photolithography or the wires with small exposed areas.²¹ As pointed out by Tao et al., larger exposed areas to the electrolyte lead to

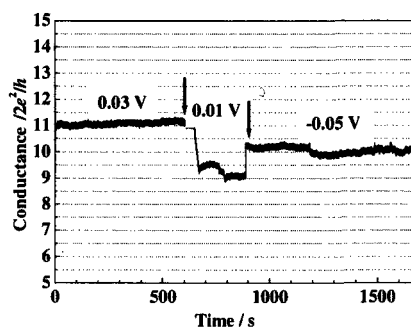


Figure 6. Time course of the conductance of a Cu wire. The electrochemical potential of the wire was changed at the arrows.

instability of the wire. The background current flowing through the wire and the counter electrode often cause additional reactions at the surface of the exposed area. Such reactions are expected to cause structural changes of the wire and the nano-junction. Modulation of the localized electrochemical potential of the wire might also contribute to change the observed conductance. In the present system, fractional quantized conductance was often observed as shown in Figures 3, 4, and 5. Such behavior is the characteristic of the electrochemically prepared-nano junctions, and is speculated to be peculiar to the structure formed in solution. More precise control of the electrochemical potential may lead to the improvement in the stability of the conductance. To clarify the characteristics of the geometrical and the electronic structure of the wires in solution, further studies are needed.

4. Conclusions

Sustainable thin metal wires showing the quantized conductance were successfully prepared by means of electrochemical dissolution and deposition. The behavior of the conductance quantization depended on the kind of anions in electrolyte solutions. The values of the quantized conductance could be controlled by regulating the electrochemical potential using the wire with relatively large exposed area. Present facile method to prepare the sustainable thin wire having the nano-junctions could be applied to evaluate various characteristics of nano-materials in solution.

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