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Fabrication of Stable Metal Nanowire showing Conductance Quantization in Solution

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Abstract

We have mechanically fabricated Cu nanowires in solutions with and without thiourea. In both solutions, the conductance was quantized in units of G_0 ($2e^2/h$). A well-defined $1 G_0$ peak was observed in the conductance histogram. While the conductance value was not changed, the stability of the mono atomic contact was improved by adding thiourea. The effect of thiourea on the stability of the atomic contact was investigated by measuring the stretched length of the atomic contact. The average length of the last plateau was 0.044 nm in the solution without thiourea. The length increased to 0.076 nm in the solution with thiourea. The stabilization could be explained by the decrease in the surface energy caused by adsorption of thiourea molecules on the Cu nanowires.

Keywords: Electrical transport measurements, Electrochemical potential control, Scanning tunneling microscopy, Conductance quantization, Nanowire, Organic molecules, Copper

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1. Introduction

Preparation of metal nano structures, such as nanowires and nano-gaps, is an important subject in nano technology. Recently, metal nanowires on an atomic scale have been fabricated with a scanning tunneling microscope (STM) and mechanically controllable break junctions (MCBJ) [1]. Electrical conductance through the metal nanowire 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 [1]. The value of $G_0 = 2e^2/h$ is a unit of the quantized conductance. Conductance quantization depends not only on the atomic structure of nanowires but also on inherent properties of metals. In the case of noble metals, the conduction channel is a single s channel with transmission probability of 1, and thus, the conductance is quantized in units of G_0 . The quantized conductance behavior has been studied for nanowires of noble metals. Well-defined peaks are generally observed near 1, 2, and 3 G_0 in the conductance histogram for Au. In the case of Cu and Ag, the conductance histograms have a dominant peak at 1 G_0 [1]. While the quantized conductance behavior is similar among noble metals, the structure of the nanowire depends on the metals. Only Au can form a mono atomic wire. Mono atomic wires of Cu and Ag have not been fabricated even in ultra high vacuum (UHV) at low temperatures [2]. Cu is much more abundant than Au or Ag, and thus, stabilization of Cu nanowires should be a challenging issue in fabrication of metal nano structures.

Recently, the electrochemical method has been recognized to be a powerful approach to fabricate stable metal nanowires [3-7]. Electrochemical potential determines the potential energy of the electrons of the nanowires, 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 make possible to fabricate very stable metal nanowires, which has not been prepared in UHV. Fabrication of stable Au, Ag, Cu, Pb, Fe, Co, Ni, and Pd nanowires and interesting phenomena characteristic of the electrochemical system have been reported in solution at room temperature[3-7]. Although a Cu nanowire in a solution was more stable than that in UHV at room temperature, the stretched length

of the nanowire was still rather short, typically less than 0.1 nm.

For further stabilization of Cu nanowires in a solution, organic additives are attractive [8,9]. It has been known that the organic additives are very important for obtaining brighten electrodeposited ferromagnetic films by reducing pits, removing strains in the film, improving corrosion resistance, and so on [8-13]. Since organic additives adsorb strongly onto the film surface, the adsorption often affects the process of the metal deposition, leading to the change in the electrodeposited structure at macroscopic and atomic scales. Various organic additives such as, polyethylene glycol, 3-mercapto-1-propanesulfonate, benzotriazole, thiourea, sodium dodecyl sulfate have been used for the Cu deposition [10-13]. It is noticed that most of the molecules have S, N, or triple bond, which strongly react with Cu. In the present study, thiourea was investigated as a model system, since thiourea is the simplest molecule with both S and N atoms. We have mechanically fabricated Cu nanowires and studied the conductance of the Cu nanowires in solutions with and without thiourea. The stretched length of the Cu nanowire was investigated to discuss the stability of the Cu nanowire.

2. Experimental

The experiments have been performed with the modified STM system in an electrochemical cell mounted in a chamber that was filled with high purity N₂ gas to reduce contamination. The STM tip was made of a Au wire (diameter ~0.25 mm) coated with wax to eliminate ionic conduction. The substrate of Au(111) was prepared by a flame annealing and quenching method. Figure 1 shows the schematic view of the experimental setup. The electrochemical potential (Φ_0) of the Au tip and substrate was controlled using a potentiostat (Pico-Stat, Molecular Imaging Co.) with a Ag/AgCl reference electrode. A 0.50 mm diameter Pt wire was used as a counter electrode. The electrolytes consisted of 10 mM CuSO₄ and 50mM H₂SO₄. In the following discussion, the electrolyte is referred to as the Cu solution. Molecules of thiourea was added to the solution at a 1 mM concentration. The Cu nanowires were prepared in the following manner. First, the

electrochemical potential of both the STM tip and substrate were maintained at lower than the potential where bulk Cu deposition proceeds ($\Phi_0 = -100\text{mV}$) [13]. After sufficient deposition of the metals onto the surfaces of the STM tip and the substrate, it was confirmed that **the STM tip and substrate exposed to the solution were completely covered with a thick Cu film by the electrochemical stripping analysis**. The tip was pressed into the substrate and then pulled out from the substrate. Separation of these contacts resulted in the formation of a Cu nanowire between the tip and substrate. **Since the STM tip and substrate were completely covered with a thick Cu film, it is expected that the nanowire was a pure Cu wire**. Conductance was measured during the breaking process under an applied bias of 20 mV between the tip and substrate.

3. Results and Discussion

Before discussing about the Cu nanowires, it is useful to discuss the effect of thiourea on the structure of the electrodeposited Cu at a macroscopic scale. Figure 2 shows the STM image of the Cu electrodeposited film on the Au electrode in the Cu solutions with and without thiourea. The Cu film was rough and granular consisting of large islands in the Cu solution without thiourea. By adding thiourea, the number of islands increased and the size of islands decreased. The change in the structure of the Cu film agreed with the previous results [10]. Thiourea inhibited the crystal growth process, and thus, a relative enhancement of the nucleation process was induced in the presence of thiourea. This resulted in more regular and refined islands of the Cu film. In addition, the inhibition of the crystal growth process by thiourea affected the electrochemical reaction. The Cu deposition peak was retarded by 300 mV in the cyclic voltammogram of the Au electrode in the Cu solution with thiourea [13]. Therefore, the electric conductance of the Cu nanowire was studied at $\Phi_0 = -450\text{ mV}$ and $\Phi_0 = -100\text{ mV}$ in the solutions with and without thiourea, respectively.

Now, it is clear that adsorbed thiourea affected the structure of electrodeposited Cu at a macroscopic scale. The effect of thiourea on the structure at an atomic scale, Cu nanowire, is discussed in the following. Figure 3 shows the typical conductance traces of the Cu nanowires in

the Cu solutions with and without thiourea during the retraction process. The electrochemical potential of the nanowire was kept at $\Phi_0 = -450$ mV in the solution with thiourea, while the potential was kept at $\Phi_0 = -100$ mV in the solution without thiourea. As a general tendency, the conductance changed in a stepwise, rather than a continuous, fashion. Immediately prior to breaking the contacts, plateaus showing the conductance of $1 G_0$ were frequently observed in the traces. Figure 4 shows the conductance histogram of the Cu nanowires in the Cu solutions with and without thiourea. The histograms were obtained from 1000 individual conductance traces. A well-defined $1 G_0$ peak appears in the histogram. The observed conductance histograms were similar to those observed in UHV, which also agreed with our previous results in the solution at room temperature [14].

While the conductance of the last plateau and peak value of the conductance histogram did not depend on the presence of thiourea, the last plateau was elongated in the presence of thiourea. In the case of conductance traces in Fig. 3, the last plateau was elongated to 0.20 nm. In accordance with the elongation of the last plateau, the area below the histogram curve around $1 G_0$ increased by addition of thiourea (see Fig. 4). Since the conductance of a mono atomic contact of noble metals was estimated to $1 G_0$ by theoretical calculations [1], the observed $1 G_0$ feature could be attributable to the mono atomic contacts of Cu. The present results showed that the stable Cu mono atomic contact was fabricated in the solution with thiourea. To evaluate the stability of the Cu mono atomic contact quantitatively, the distribution of lengths was examined for the last conductance plateau [7]. Figure 5 shows the distribution of lengths for the last conductance plateau in the solutions with and without thiourea. The distribution was obtained from 2000 individual conductance traces. The length of the last plateau was defined as the distance between the points at which the conductance dropped below $1.3 G_0$ (start point) and $0.7 G_0$ (stop point), respectively. It is clear that the length of the last plateau was elongated by the addition of thiourea. **The average length of the last plateau was obtained by averaging lengths of the last conductance plateau of 2000 individual conductance traces.** The average length was 0.044 nm in the solution without thiourea and 0.076 nm in the solution with thiourea. **These lengths were much smaller than an atomic diameter of**

Cu (~0.25nm). The atomic contact would break before forming two atom chains, and thus the last plateau length was smaller than an atomic diameter. The small length indicated that the Cu atomic contact was relatively unstable. Although the absolute value of the increment in the stretched length is small, the elongation of the plateau length from 0.044 nm to 0.076 nm proves that its stability of the Cu atomic contact was improved by the introduction of thiourea.

Improved the stability of the Cu nanowire by thiourea could be explained by adsorption of the thiourea molecule on the Cu surface [8,9]. Thiourea adsorbs on the Cu surface via a strong S-Cu covalent bond. The strong bonding would increase the strength of the Cu-Cu bond in the nanowire and/or at the junction between the nanowire and electrode, although it is not clear whether the molecule adsorbs on the nanowire or the stem part of the electrode. In terms of surface energy, the strong bonding would decrease the surface energy of the Cu nanowire [9]. The increase in the strength of the Cu-Cu bond and decrease in the surface energy lead to the stabilization of the Cu nanowire by thiourea. Improved stability of the metal nanowires by organic molecules was observed for other metals, such as Au, Fe, Co, Ni [8,9]. The Au nanowire was stabilized by bipyridine, adenine, and mercaptopropionic acid. The Fe, Co and Ni nanowires were stabilized by 2-butyne-1,4-diol. On the other hand, the stability of the Cu nanowire was not improved by propargyl alcohol (not shown). At this moment, the improved stability of the metal nanowire by organic molecules has not been completely understood. Systematic investigation would clarify the stabilization mechanism of the metal nanowire.

4. Conclusion

We have observed conductance quantization behavior of mechanically fabricated Cu nanowires in the solutions with and without thiourea. The addition of thiourea increased the stability of the Cu nanowires, while the conductance value of the mono atomic contact did not change. The stabilization of the nanowire could be explained by the strong adsorption of thiourea molecules to

the surface of the nanowire.

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Figures captions

Fig. 1: Schematics view of the experimental setup. Cu was deposited on the Au single crystal substrate and tip. An atomically thin Cu wire was suspended between two electrodes in the presence of thiourea. RE: reference electrode, WE: working electrode, CE: counter electrode.

Fig. 2: STM height image of Cu deposits on Au(111) in the absence (a) and in the presence of 1 mM thiourea (b).

Fig. 3: Typical conductance traces of Cu nanowires in the absence (dot-dashed line) and in the presence of 1 mM thiourea (line). The electrochemical potential of the nanowire was kept at $\Phi_0 = -450$ mV and $\Phi_0 = -100$ mV in the solution with and without thiourea, respectively.

Fig. 4: Conductance histograms Cu nanowires in the absence (dot-dashed line) and in the presence of 1 mM thiourea (line). The histograms were obtained from 1000 individual conductance traces.

Fig. 5: Distribution of stretched lengths for the last conductance plateau for Cu nanowires in the absence (line with circle) and in the presence of 1 mM thiourea (line with filled-box). The distribution was obtained from 2000 individual conductance traces.

Figure 1

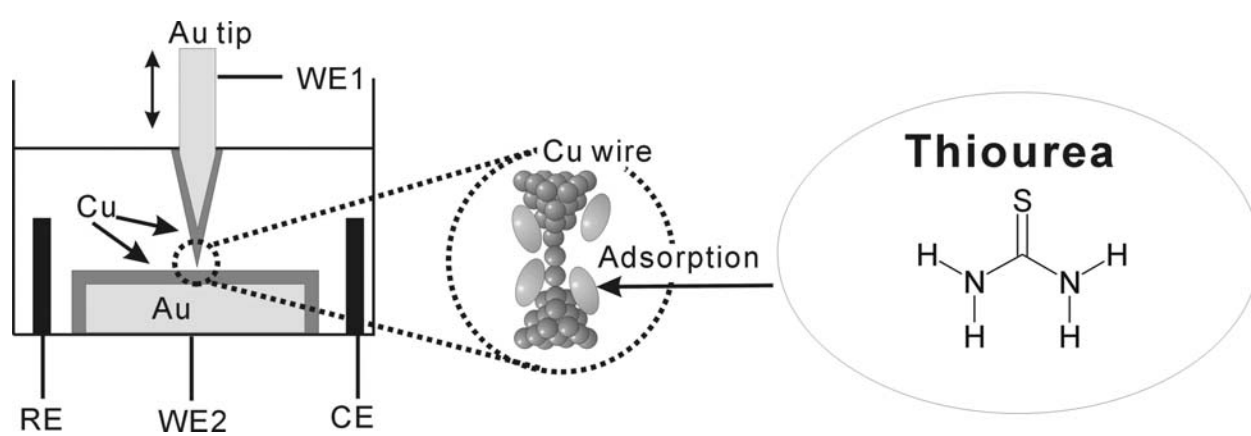


Figure 2

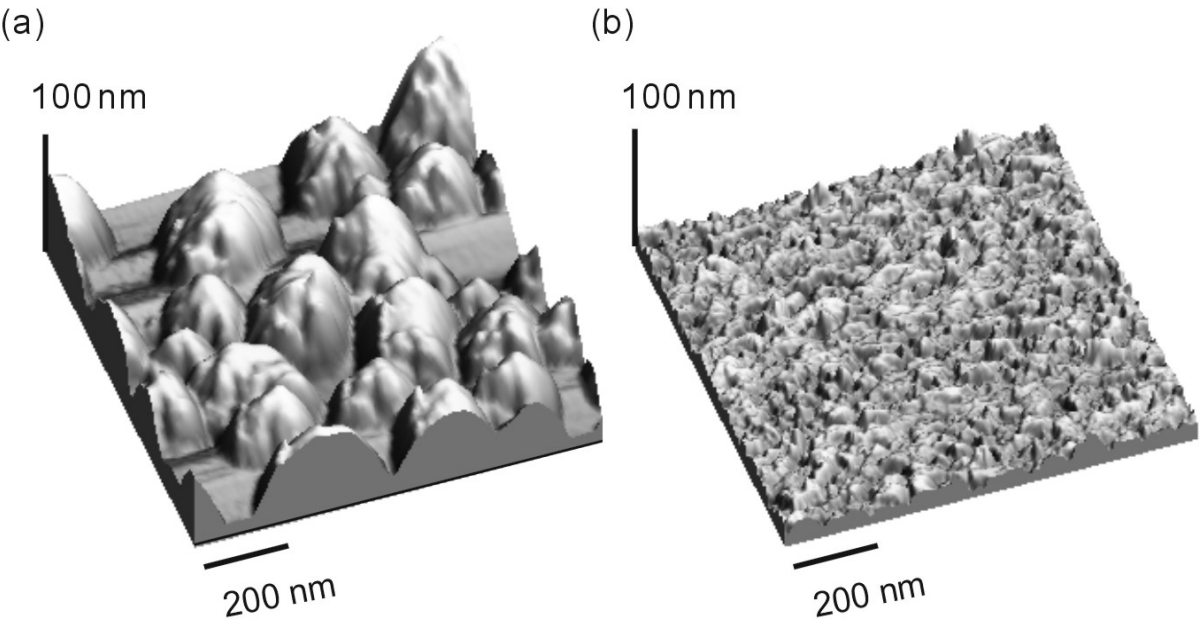


Figure 3

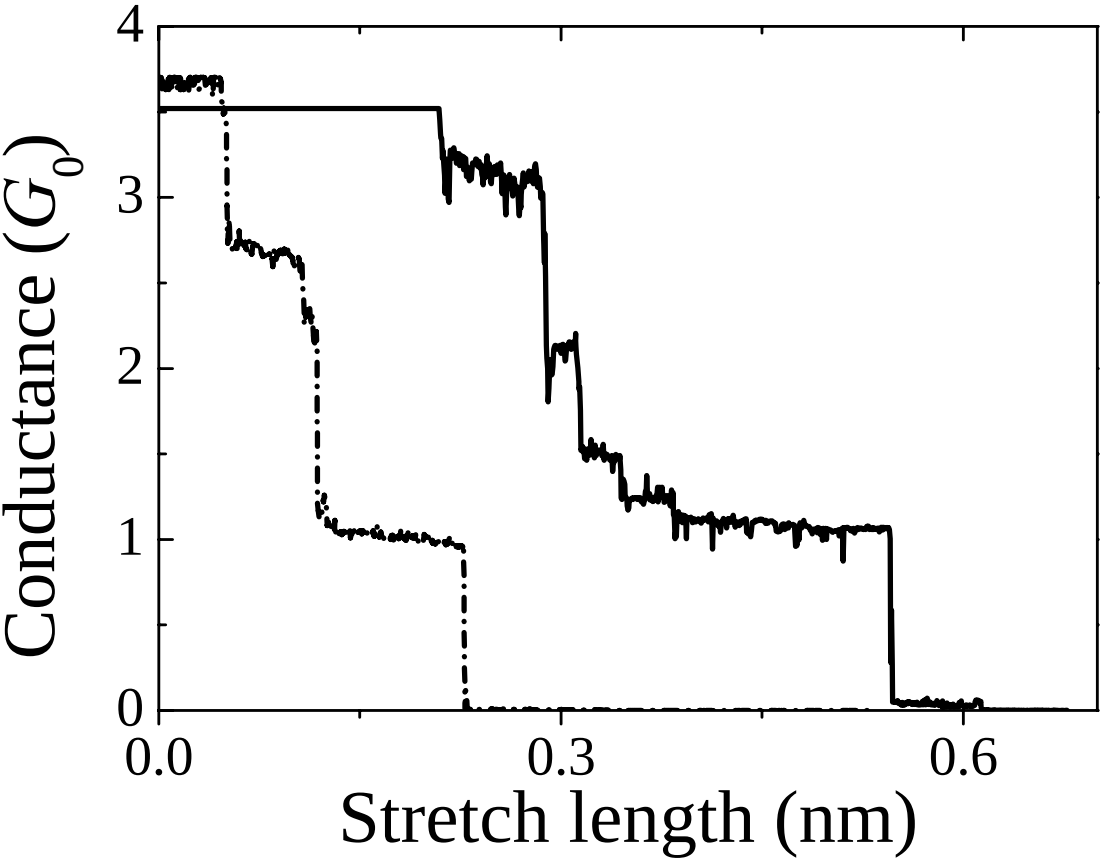


Figure 4

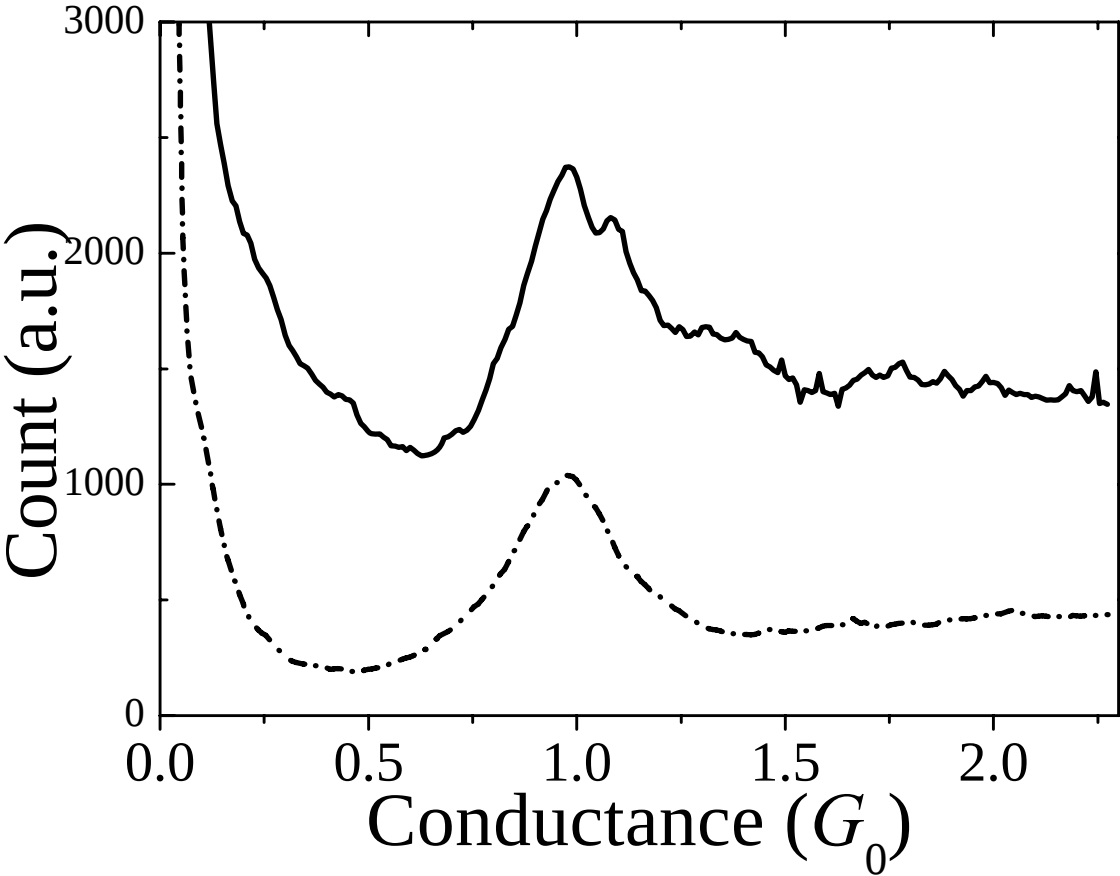


Figure 5

