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Electrochemical Fabrication of Gold Quantum Wire with Atomic-Scale

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Stable gold quantum wire with atomic-scale was successfully fabricated with two kinds of electrochemical method in solution by a home-made electrochemically controlled system. The quantum wire could be obtained by careful controlling the process of electrochemical deposition on a preformed gold electrode pair as well as its reverse process-etching with addition of chloroauric acid in solution. The stepwise conductance behaviour could be observed clearly with the process. Another method was a self-terminated electrochemical mechanism. Compared with the first method, it was simpler, less interferential and more suitable for *in situ* study of quantum wire. The I-V curve of the formed gold quantum wire showed the ohmic behaviour with low bias voltage and electromigration phenomenon with high bias voltage.

Key Words: Gold, Quantum wire, Electrochemistry, Quantum conductance.

INTRODUCTION

Nanoscience and technology have attracted a tremendous amount of interest not only because materials and devices exhibit many novel quantum phenomena but also because they lead to many new applications in the fields of surface science[1], nano and molecular electronics[2] and chemical and biological sensors[3]. During the past decade, quantum conductance phenomena of atomic-scale metal quantum wires have been proved both theoretical and experimental studies[4,5]. When the length of a metal wire is shorter than the electron mean free path and the diameter of the metal wire is comparable to the electron wavelength, the current passing the quantum wire is ballistic and the electrical conductance can be expressed by $G = G_0 \sum_{i=1}^{N} T_i$, where $G_0 = 2e^2/h \approx 1/(12.9\ K\Omega)$. T_i is the transmission coefficient and for many metals at small contacts, the value is close to 1, thus the conductance changes in steps of the order of G_0, the quantum conductance. Conductance quantization in the metal junction has attracted much attention and been investigated in various systems.

In this paper, gold quantum wire was prepared with two kinds of electrochemical method and the preparation process was analyzed in detail. The gold quantum wire was electrically characterized with a two-electrode electrochemical system.

EXPERIMENTAL

The experimental setup was the same with our previous work[6,7], in which the main part was a home-made electrochemical system which had different function with different programmed control. A function generation was used as bias voltage supply. The electrochemical cell was made of an Ag/AgCl reference electrode, a platinum slice counter electrode and a gold wire that served as a working electrode onto which the metal was etched or deposited. All chemicals used were of analytical reagent grade. All solutions were prepared with deionized water (18.2 MΩ.cm).

Preparation of gold quantum wire: Fabrication consisted of two methods. First, a thin gold wire (25 μm in diameter, 99.999 % purity) was supported on the glass slide and coated with insulating glue which served as an insulation layer to reduce electrochemical leakage current except for a small region (< 1 μm) exposed to the etching solution of 0.5 mol/L KCl. An alternate current (AC) voltage (15 mV, 10 Hz) for monitoring and a direct current (DC) voltage (0.95 V) for etching were applied simultaneously. When the AC monitor current decreased abruptly, the program will automatically cut off the DC etching voltage and a small gap was formed. Then the solution was added a few drops of 0.02 mol/L of $HAuCl_4$ solution. By controlling the deposition potential, the gold ions were deposited back to the wire. When the AC monitor current reached the preset current value, the programmed switch turned the dissolution/deposition off by cutting off the electrochemical dissolution/deposition current that flow between one of electrodes and the counter electrode and an gold quantum wire could be obtained. Then the formed gold quantum wire would be transferred into pure water.

The second general strategy for forming an atomic-scale gold junction pursued here followed the method for Cu quantum wire preparation[8]. Briefly, a pair of insulated gold electrodes separated by a μm-scale gap on a glass substrate was immersed into a glass cell with 0.1 mol/L HCl in it. The formed two electrodes and the solution between them were placed in series with an external resistor (R_{ext}) to form a voltage divider circuit. The potentiostat was changed into two-electrode system by shorting the counter and reference electrode (Fig. 1). The whole circuit was applied a bias voltage with a magnitude of *ca.* 1 V. By changing the value of R_{ext}, the gold quantum wire with different conductance could be achieved.

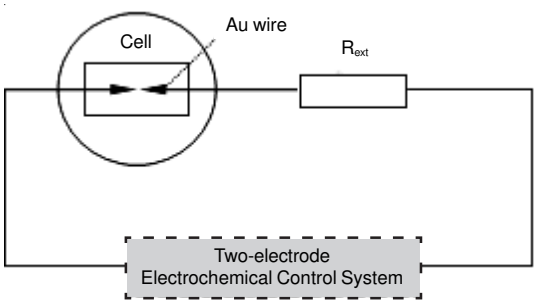

Fig. 1. Schematic diagram of the gold quantum wire fabricating system with a self-terminated electrochemical mechanism

Characterization of gold quantum wire: With our setup, gold growth was dendritic and many gold wires of different diameters were generated but only one of them was responsible for the contact between the two electrodes. TEM and scanning probe techniques were difficult to locate this particular wire and difficult to provide good evidence for atomic contact formation. As a result, we would have to rely on electrical transport measurements, like most groups working on such systems[9,10].

RESULTS AND DISCUSSION

Fig. 2 showed the cyclic voltammogram behaviour of the exposed thin gold wire in 0.5 mol/L KCl solution and the etching rate could be flexibly controlled by adjusting the electrochemical potential of the wire. However, the quantum plateau couldn't be observed with the process due to the mechanical stress coming from the metal itself and the insulating materials, which had been reported in previous work[7]. When the thin gold wire was completely breakdown, a few drops of 0.02 mol/L $HAuCl_4$ solution were added into the cell to ensure having enough gold ions to be deposited. By controlling the deposition potential, the gold ions were deposited back to the wire. The initial electrodes width was large and the AC monitor current was very low due to ion conductivity, then with the ongoing deposition process, the AC monitor current increased sharply due to tunnel conductivity. Fig. 3 showed a time evolution of the conductance across the electrodes during electrochemical deposition and subsequent etching process. The quantum conductance increase and decrease were clearly observed under a time resolution of 200 ms, as shown in the Fig. 3. These conductance plateaus indicated that the contact between the two electrodes consisted of a few gold atoms and are formed layer by layer in an atomic scale. These procedures

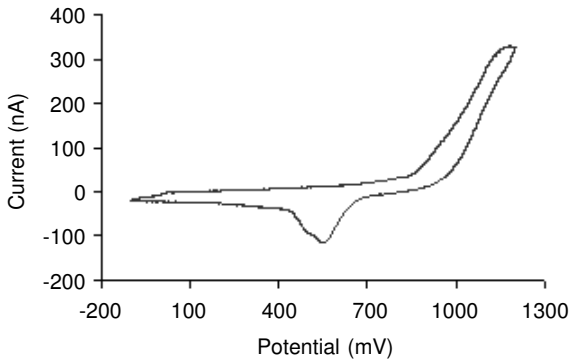

Fig. 2. Cyclic voltammogram of a thin gold wire in 0.5 mol/L KCl solution at a rate of 100 mV/s (*vs.* Ag/AgCl)

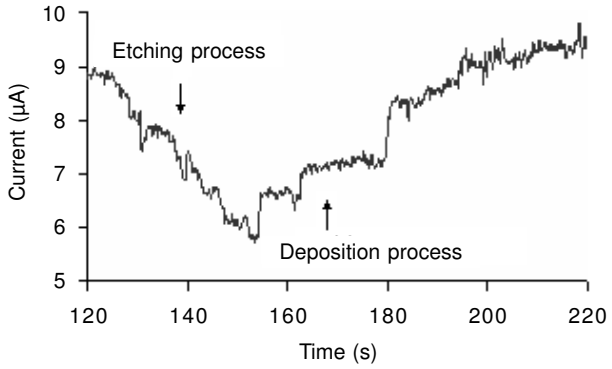

Fig. 3. Typical monitor current *versus* time curve during the etching/deposition process. The stepwise changes could be observed

mentioned above showed by carefully controlling the potential, the electrochemical etching/deposition process could be controlled so slowly that removal/deposition of a single atom could be observed. Therefore, when the AC monitor current reached the present current value, the programmed switch turned the dissolution/deposition off by cutting off the electrochemical dissolution/deposition current that flow between one of electrodes and the counter electrode. As a result, an gold quantum wire could be obtained. Then the formed gold quantum wire must be transferred into pure water in order to avoid the interference of other ions.

With the second preparation method, the gap resistance was initially very large, so the entire bias was used in the two-electrode system to etch gold from one electrode (anode) and to deposit to another electrode (cathode). The gap width decreased gradually because the etching took place all over the anode surface and the dissolved gold ions deposited onto the sharpest point of the cathode (called directional electrodeposition). As the gap narrowed, the tunneling probability across the gap increased and the gap resistance reduced. As a result, the divided voltage between the two electrodes also decreased, which terminated the etching and deposition process automatically. So the gold quantum wires with different conductance could be achieved by changing the value of external resistance R_{ext}.

It must be mentioned that the conductance of the formed gold quantum wire with the two methods was often observed to deviate more or less the preset conductance value. The main problem was when one carried out the study at an atomic level,

the microscopic reaction would not always follow the controlled macroscopic parameter, which was also observed by Castle and Bohn[11].

Characterization of gold quantum wire: A two-electrode system was used to characterize the current-voltage (I-V) behaviour of the atomic-scale nanowire. The potentiostat was changed into two-electrode system by shorting the counter and reference electrode. Fig. 4 showed a clearly ohmic I-V curve for the quantum wire. With a low bias, the linear ohmic behaviour was always observed for the metal quantum wire, which was consistent with the reported results[8,11]. We had also studied the characteristics of the quantum wire under higher bias. As the bias was increased at a rate of 10 mV/s, failure occurred at a threshold bias due to the effect of electromigration which had been studied previously to fabricate nanogap electrodes[12].

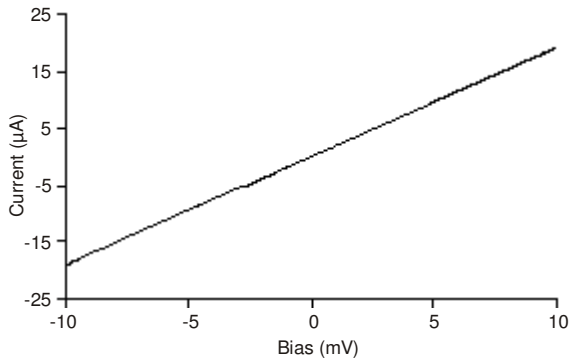

Fig. 4. Typical current-voltage characteristics of the gold quantum wire in an aqueous solution when it was scanned from -10 mV to 10 mV

Conclusion

In this work, we provided a complete description of the successful fabrication of gold quantum wire in solution using two kinds of electrochemical method. The gold quantum wire was not easy to be obtained by direct electrochemical etching of gold wire due to the mechanical stress. It's easy to control the process of electrochemical deposition on a preformed gold electrode pair as well as its reverse process-etching with addition of chloroauric acid in solution. The quantized conductance phenomenon was observed during etching and deposition process which showed the formed quantum wire was atomic-scale. The quantum wire was electrically characterized with two-electrode system. The work is of great significance for material science, interface electrochemistry and sensing.

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