Electrochemical fabrication of atom-scale iron quantum wire combined with advanced lithography technique

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Abstract
A method to fabricate atom-scale iron quantum wire was described. The method included two steps. First, an Au nanogap was formed by a series of lithography process on Si substrate. Then the iron atoms were deposited into the gap to form stable iron quantum wire by a home-made electrochemically controlled system. By careful controlling the etching/deposition process, stepwise conductance behavior could be clearly observed. The I-V curve of the formed iron quantum wire showed the ohmic behavior with low bias voltage. The work is of great significance for molecular electronics, interface electrochemistry and sensing.

Keywords: Iron, quantum wire, electrochemistry, lithography, quantum conductance

1. 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, nano and molecular electronics, chemical and biological sensors [1-3]. During the past decade, quantum conductance phenomena of atom-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 $G_0 = \frac{2e^2}{h} \approx \frac{1}{12.9 K \Omega}$. $T_i$ 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. Recent studies [6-8] also showed that the electrical conductance step through an atom-scale metal wire often shifted away from the integer multiples of $G_0$ and changed to some fractional values. Although a theory for the quantum ballistic regime has not yet been fully established completely, a few models such as the existence of metastable configurations between the stable configurations [6], molecule and ion adsorbate scattering [7], structural defects [8] have been proposed to explain the behavior of fractional conductance. Conductance quantization in the metal junction has attracted much attention and been investigated in various systems.

2. Materials and Methods
All chemicals used were analytical reagent grade and all solutions were prepared with deionized water (18.2 MΩ.cm). The process of fabrication consisted of two parts. One is the preparation of Au nanogap, another is the preparation of iron quantum wire.

2.1 Preparation of gold nanogap
The Au nanogap was fabricated by microfabrication. Briefly, an Au microbridge was defined on a SiO$_2$/Si wafer using standard photolithography and lift-off techniques. Then a layer of SiN$_x$ was deposited by plasma-enhanced chemical vapor deposition (PECVD) as an insulating layer. A Cr mask was then deposited, and reactive ion etching was used to expose Au contact pads. The Cr layer was then removed with Cr etchant. In the final step focused ion beam milling was used to create an Au-Au electrode configuration with < 100 nm separation [6, 10].
2.2 Preparation of iron quantum wire

The experimental setup was the same with our previous work \cite{11, 12}, 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 (RE), a platinum slice counter electrode (CE) and the fabricated gold nanogap that served as a working electrode onto which the metal was etched or deposited. The electrolyte in the cell was 10 mM FeCl$_2$ aqueous solution. An AC voltage (15 mV, 10 Hz) for monitoring and a direct current (DC) voltage for deposition were applied simultaneously. Low frequencies for monitoring AC voltage were necessary to avoid shorting of the AC current. By controlling the deposition potential, the iron electrolytic bath and preserve sufficient measurement sensitivity. By controlling the deposition potential, the iron ion was deposited back to the gap. 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 increase sharply due to tunnel conductivity. Fig.1 showed a time evolution of the conductance across the electrodes during electrochemical deposition process. The quantum conductance increase was clearly observed under a time resolution of 200ms, as shown in the fig.1. These conductance plateaus indicated that the contact between the two electrodes consisted of a few iron atoms and are formed layer by layer in an atomic scale. These procedures 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 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. Usually, an iron quantum wire could be obtained. It must be mentioned that the conductance of formed iron quantum wire was often observed to deviate the preset conductance value. The main problem was with an atomic level study, the microscopic reaction will not always follow the controlled macroscopic parameter, which was consistent with the results reported by other group \cite{13}.

![Fig 1: Typical monitor current versus time curve during the deposition process. The stepwise changes were observed.](image1.png)

2.3 Iron quantum wire characterization

With our setup, iron growth was dendritic, and many iron 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 \cite{14, 15}.

A two-electrode system was used to characterize the current-voltage (I-V) behavior of the atom-scale nanowire. The potentiostat was changed into two-electrode system by shorting the counter and reference electrode. Fig.2 showed a clearly ohmic I-V curve for the quantum wire with different conductance value. With a low bias, the linear ohmic behavior was always observed for the metal quantum wire, which was consistent with the reported results \cite{16, 17}.

![Fig 2: Typical current-voltage characteristics of the iron quantum wire in an aqueous solution when it was scanned from -10mV to 10mV.](image2.png)

3. Conclusion

In this work, the Au nanogap was first formed by advanced lithography techniques, then stable iron quantum wire with atom-scale was successfully fabricated and electrically characterized with an electrochemical method in solution by a home-made electrochemically controlled system. By careful controlling the etching/deposition process, stepwise conductance behavior could be clearly observed. The I-V curve of the formed iron quantum wire showed the ohmic behavior with low bias voltage. The work is of great significance for molecular electronics, interface electrochemistry and sensing.

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5. Reference

1. Duan BK, Zhang JY, Bohn PW. Conductance-based chemical sensing in metallic nanowires and metal-semiconductor nanostructures, Anal Chem. 2012; 84(1):2-8.
2. Shi P, Bohn PW. Stable atom-scale junctions on silicon fabricated by kinetically controlled electrochemical deposition and dissolution, ACS Nano. 2008; 2(8):1581-1588.
3. Shi P, Bohn PW. Electrochemical control of stability and restructuring dynamics in Au-Ag-Au and Au-Cu-Au bimetallic atom-scale junctions, ACS Nano. 2010; 4(5):2946-2954.
4. Shi P, Zhang JY, Lin HY, Bohn PW. Effect of molecular adsorption on the electrical conductance of single Au nanowires fabricated by electron-beam lithography and focused ion beam etching. Small. 2015; 6(22):2598-2603.

5. Hwang TW, Branagan SP, Bohn PW. Chemical noise produced by equilibrium adsorption/desorption of surface pyridine at Au-Ag-Au bimetallic atom-scale junctions studied by fluctuation spectroscopy, J Am Chem Soc. 2013; 135(11):4522-4528.

6. He HX, Boussaad S, Xu BQ, Li CZ, Tao NJ. Electrochemical fabrication of atomically thin metallic wires and electrodes separated with molecular-scale gaps, J Electroanal Chem. 2002; 522(2):167-172.

7. Liu Z, Searson PC. Single nanoporous gold nanowire sensors, J Phys Chem B. 2006; 110(9):4318-4322.

8. Zhao JJ, Buia CL, Han J, Lu JP. Quantum transport properties of ultrathin silver nanowires, Nanotechnology. 2003; 14(5):501-504.

9. Hwang TW, Bohn PW. Robust Au-Ag-Au bimetallic atom-scale junctions fabricated by self-limited Ag electrodeposition at Au nanogaps, ACS Nano. 2011; 5(10):8434-8441.

10. Hwang TW, Bohn PW. Potential-dependent restructuring and chemical noise at Au-Ag-Au atomic scale junctions, ACS Nano. 2014; 8(2):1718-1727.

11. Dong XD, Liu JH, Zhang BL, Xia Y. Surface structural analysis of electrochemically fabricated Ag quantum wire by its interactions with NH₃ molecules in an aqueous environment, Electrochim Acta. 2012; 74:78-82.

12. Dong XD, Liu JH. Electrochemical fabrication of gold quantum wire with atomic-scale. Asian J Chem. 2013; 25(5):2641-2643.

13. Xiang J, Liu B, Liu B, Ren B, Tian ZQ. A self-terminated electrochemical fabrication of electrode pairs with angstrom-sized gaps, Electrochem Commun. 2006; 8(4):577-580.

14. Leroux YR, Fave C, Zigah D, Trippe-Allard G, Lacroix JC. Atomic contacts via electrochemistry in water/cyclodextrin media: A step toward protected atomic contacts, J Am Chem Soc. 2008; 130(40):13465-13470.

15. Molet P, Ghilane J, Martin P, Noel V, Randriamahazaka H, Pham MC et al. Electrochemical generation of stable copper nanowires with quantized conductance in DNA media, Electrochem Commun. 2010; 13(3):272-274.

16. Boussaad S, Tao NJ. Atom-size gaps and contacts between electrodes fabricated with a self-terminated electrochemical method, Appl PhysLett. 2002, 80(13):2398-2400.

17. Castle PJ, Bohn PW. Interfacial scattering at electrochemically fabricated atom-scale junctions between thin gold film electrodes in a microfluidic channel, Anal Chem. 2005; 77(1):243-249.