Quantized tunneling current in the metallic nanogaps formed by electrodeposition and etching

C. Z. Li, H. X. He, and N. J. Tao

Department of Physics, Florida International University, Miami, Florida 33199

(Received 16 August 2000; accepted for publication 23 October 2000)

We have studied electron tunneling across the gap between two electrodes as the gap is varied by electrodeposition and etching. The tunneling current tends to change in a stepwise fashion, corresponding to a discrete change of the gap width. The stepwise change is due to the discrete nature of atoms and a series of structural relaxations of the atoms at the electrodes between stable configurations upon deposition and etching. By stabilizing the tunneling current on various steps using a feedback loop, we have demonstrated that stable molecular-scale gaps can be fabricated with subangstrom precision. © 2000 American Institute of Physics.

As silicon-based microelectronics is heading towards the increasingly difficult road of nanometer scale, building electronic devices based on single molecules has been actively pursued in recent years as a promising alternative. Indeed, many molecules possess wonderful electronic properties, but a critical challenge is to find a practical method to connect them to the outside world. While impressive progress has been made to fabricate electrodes to connect macromolecules, such as nanotubes and DNA, it remains a challenge for most other interesting molecules that have much smaller dimensions. To meet the challenge, several methods have been attempted to make a gap between two electrodes smaller than the size of an atom. The tendency that the gap stabilizes at discrete steps of ~0.5 Å makes it possible to fabricate nanogaps with subangstrom precision for different molecules.

We used two setups in our experiments, a scanning tunneling microscope (STM) setup and microfabricated electrodes on oxidized Si. The STM setup was chosen because it allowed us to calibrate the gap width at a given tunneling current and to flexibly adjust the initial gap between the STM tip and a Au substrate (~100-nm-thick film evaporated on mica). The tip, made of Pt 0.8Ir 0.2 wire, was coated with Apiezon wax to reduce ionic conduction below ~1 pA. The tip–substrate gap was initially maintained at a fixed distance (1–50 nm), which was then closed by depositing Cu onto the tip electrode from an electrolyte solution containing 1 mM CuSO4 and 10 mM H2SO4. The tunneling current between the tip and substrate electrodes was continuously measured, allowing us to monitor the gap width and to control the process as a feedback signal. In order to fabricate long-term stable nanogaps, we replaced the STM setup with smaller than the size of an atom. The limit imposed by the discrete nature of atoms is much smaller than the size of an atom. The tendency that the gap stabilizes at discrete steps of ~0.5 Å makes it possible to fabricate nanogaps with subangstrom precision for different molecules.

In this letter, we demonstrate that a molecular-size gap between two electrodes can be fabricated with subangstrom precision by controlling electrochemical etching/deposition using the tunneling current between the electrodes as feedback (Fig. 1). By carefully insulating the electrodes, we were able to measure the tunneling current from pA to μA, allowing us to observe an interesting stepwise variation in the tunneling current during deposition and etching. The stepwise tunneling current is originated from the discrete nature of atoms, but the corresponding discrete change in the gap width is, typically, ~0.5 Å, due to atomic reconfiguration. So, the limit imposed by the discrete nature of atoms is much smaller than the size of an atom. The tendency that the gap stabilizes at discrete steps of ~0.5 Å makes it possible to fabricate nanogaps with subangstrom precision for different molecules.

FIG. 1. Schematics of the setup. Electrodeposition/etching of Cu onto the electrodes (WE1 and WE2) is controlled by the electrochemical potentials of WE1 and WE2 with respect to a reference electrode (RE) using a bipotentiostat [with the help of a counterelectrode (CE)]. The tunneling current across the gap between WE1 and WE2 is a sensitive function of the gap width, which is used as a feedback signal for controlling the deposition/etching. The inset shows a pair of facing electrodes fabricated on oxidized Si that is used in the experiment.
pairs of facing Au electrodes fabricated on oxidized Si chips at the Cornell Nanofabrication Facility and Motorola using e-beam lithography (Fig. 1, inset). The electrodes were covered with PMMA photoresist (Cornell) and SiO$_2$ (Motorola) in order to reduce ionic conduction (<0.1 nA at a bias of 26 mV), which is essential for measuring the tunneling current.

As expected, the tunneling current increases as the gap between the tip and substrate electrodes is reduced by Cu deposition onto the tip electrode (Fig. 2). What is interesting is that it changes in a stepwise fashion. The stepwise change is different from the conductance quantization observed in metallic nanowires because it is 3–4 orders of magnitude smaller and the step height increases exponentially with the current. We believe that the stepwise change is due to the discrete nature of atoms, leading to a discrete change in the current. We believe that the stepwise change is due to the discrete nature of atoms, leading to a discrete change in the current. We believe that the stepwise change is due to the discrete nature of atoms, leading to a discrete change in the current.

Knowing the tunneling current, the width of the gap can be determined using the relation $I_t \sim \exp(-ks)$, where $I_t$ is the tunneling current, $s$ is the gap width, and $k$ is a constant.

In order to extract the gap width, we determined the constant $k$ experimentally using the STM setup. In the experiment, we first deposited Cu onto the tip electrode, and then measured the tunneling current as the gap width was varied continuously with a piezoelectric transducer (inset, Fig. 2(a)). A $k$ value of $0.98 \pm 0.12 \text{Å}^{-1}$ was reproducibly obtained, which is somewhat smaller than the value in vacuum, and is in excellent agreement with the result reported in the literature.\cite{14}

Using the relation and the measured $k$, we found that a step in the tunneling current corresponded to a typical gap change of $\sim 0.5 \text{Å}$. This value is well below the interlayer spacing ($\sim 2 \text{Å}$) of Cu crystal, which means the growth at the end of the electrode is not a simple layer-by-layer process. This unexpected observation may be understood by the following considerations. When an atom is deposited onto the nanometer-scale electrode, instead of simply sitting on the surface of the electrode, the deposited atom and the other atoms at the very end of the electrode may undergo a structural relaxation to another stable configuration, which results in a smaller change in the gap than the interlayer spacing.\cite{15} Reconfiguration, as a spontaneous and energy-driven process, is common in reduced dimension systems. It is well known that nanoclusters (zero-dimensional) are stable only in the so-called magic configurations, and the corresponding change in diameter from one configuration to another is well below the size of the atoms.\cite{16} An extreme example is that of C$_{72}$, which contains 12 more atoms than C$_{60}$, but it is only slightly bigger. Another analogy is one-dimensional nanowires, which are found to switch abruptly from one magic configuration to another during elongation.\cite{17} A nanoelectrode, in the present case, represents a situation between the zero-dimensional nanoclusters and one-dimensional nanowires, and is expected to exhibit similar properties. Our results are also supported by a recent study of Cu nanoislands on a Au electrode during dissolution, which shows that the height change of the island can be smaller than the size of an atom.\cite{17}

The existence of stable (‘‘magic’’) configurations in the nanoelectrodes, as reflected in the stepwise change of the tunneling current, can be exploited to fabricate stable nanogaps by controlling the tunneling current at various stable steps. In order to control the gap width with a feedback loop, however, good reversibility is necessary. We have investigated the reversibility by first shrinking (deposition) the gap down to a preset value and then re-widening it (etching). The deposition and etching processes were switched on and off by adjusting the electrochemical potential. Figure 3 shows a series of such attempts. The tunneling current increases during deposition and stabilizes at various preset values, corresponding to gaps of 6.5, 5.5, and 5.0 Å. Re-widening the gaps by activating the etching process results in a stepwise decrease in the tunneling current, similar to the deposition process. In fact, the etching and deposition branches of the gap width versus time curves appear to be rather symmetric, which demonstrates good reversibility of the processes on the atomic scale, a property highly desirable for fabricating nanogaps in a controllable fashion. We note that good reversibility has also been observed in the mechanical fabrication of nanowires, where the compressive...
and tensile branches of the conductance curves of mechanically formed nanowires are quite symmetric.18,19

In order to test the long-term stability of the nanogaps, we used nanoelectrodes prefabricated on oxidized Si (inset, Fig. 1). A feedback loop was included to compare the measured tunneling current with the target value to determine whether to etch, deposit, or stop the electrochemical processes completely. Using the procedure, we have been able to routinely fabricate stable molecular-scale gaps with a precision of \( \sim 0.5 \) Å (Fig. 4). Similar to the results by the STM setup [inset, Fig. 2(b)], the gap width often fluctuates between plateaus with a typical height of \( \sim 0.5 \) Å (insets, Fig. 4). Fluctuations to higher plateaus were also observed, but much less frequently. We attribute the fluctuations to a dynamic equilibrium between deposition and etching that switches the atoms between two stable configurations. This explanation is supported by the observation that the fluctuations diminish by moving the nanoelectrodes out of the electrolyte after the formation of the nanogaps (Au-deposited nanoelectrodes). Another interesting observation is that gaps are quite stable even if a small (a few tens of mV) etching or deposition overpotential is applied to the electrodes. This surprising stability of the nanoelectrodes against further etching and deposition is highly favorable for applications and has been observed in other systems, but its mechanism is not yet completely understood.17,20

In summary, we have studied electron tunneling across two nanoelectrodes as the gap between the electrodes is varied by electrochemical deposition or etching. The tunneling current varies in a stepwise fashion, which reflects a discrete change in the gap due to the discrete nature of atoms. A typical stepwise change in the gap width is \( \sim 0.5 \) Å, which is much smaller than the size of an atom. We attribute the stepwise change to a series of structural relaxations as the atoms at the very end of the nanoelectrodes switch from one stable configuration to another upon deposition or etching of atoms. This work shows that the gap cannot be adjusted continuously because of the physical limit imposed by the discrete nature of atoms, but the limit is much smaller than the size of an atom due to the atomic reconfiguration. Another favorable consequence of the atomic reconfiguration is that the atoms at the nanoelectrodes have a strong tendency to lock into an energetically favorable configuration that enhances the stability of the fabricated nanogaps. Using this principle, we have fabricated stable molecular-scale gaps with subangstrom precision.

The authors would like to thank Dr. L. A. Nagahara, Dr. I. Amlani, and Dr. R. Tsui at Motorola for providing them with electrode chips and stimulating discussions, and AFOSR (F49620-99-1-0112) and NSF (CHE-9818073) for financial support. This work was performed in part at the Cornell Nanofabrication Facility (a member of the National Nanofabrication Users Network), which is supported by NSF (ECS-9319005), Cornell University, and industrial affiliates.