Atom-size gaps and contacts between electrodes fabricated with a self-terminated electrochemical method

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We describe a method to fabricate atomic-scale gaps and contacts between two metal electrodes. The method uses a directional electrodeposition process and has a built-in self-termination mechanism. The final gap width and contact size are preset by an external resistor ($R_{ext}$) that is connected in series to one of the electrodes. If $1/R_{ext}$ is chosen to be much smaller than the conductance quantum ($G_0=2e^2/h$), a small gap with conductance determined by electron tunneling is formed. If $1/R_{ext}$ is comparable or greater than $G_0$, a contact with conductance near a multiple of $G_0$ is fabricated.

Continued advances in nanoscience and nanotechnology demand methods to fabricate various nanostructured materials and devices. 1–3 This letter describes a self-terminated electrochemical method to fabricate atomic-scale contacts and gaps between two metallic electrodes. The conductance of the contacts varies in a stepwise fashion with a tendency to quantize near the integer multiples of the conductance quantum ($G_0$), a phenomenon that has been observed in metallic nanowires fabricated by both mechanical 4 and electrochemical methods. 5 The conductance of the gaps is determined by electron tunneling. Electrodes separated with such a gap may be used to connect a small molecule to the external world, but fabricating such electrodes is beyond the reach of conventional methods. 2 Several unconventional methods have been reported. 6–9

Unlike the previously reported electrochemical methods, 8,9 the present method is not only simpler but also has a built-in self-termination mechanism. The principle of this method is sketched in Fig. 1. It starts with a pair of electrodes separated with a relative large gap in an electrolyte or even pure water. When applying a bias voltage between two electrodes, metal atoms are etched off the anode and dissolved into the electrolyte as metal ions, which are then deposited onto the cathode. As we have found experimentally, the etching takes place all over the anode surface, but the dissolved metal ions are guided by the electric field and deposited onto the sharpest point of the cathode. Consequently, the gap decreases to the atomic scale and then completely closes as the two electrodes form a contact. In order to fabricate an atomic gap or contact in a controlled fashion, the etching and deposition processes must be terminated promptly once a desired gap or contact is formed.

We introduce a simple self-termination mechanism by connecting one electrode to an external resistor ($R_{ext}$). The effective voltage (or overpotential) for etching and deposition is given by

$$V_{gap} = \frac{R_{gap}}{R_{gap} + R_{ext}} V_0,$$

where $R_{gap}$ is the gap resistance between the two electrodes, and $V_0$ is the total applied bias voltage. $R_{gap}$ is determined by electron tunneling across the gap and by ionic conduction (leakage current) between the electrodes. Coating the electrodes with an insulating layer of epoxy can reduce the leakage current. The gap is initially large and the electron tunneling is negligible, so $R_{gap}>R_{ext}$, and $V_{gap} \sim V_0$, or the entire applied voltage is used for etching and deposition. Consequently, the etching and deposition processes take place at the maximum rates. As the gap narrows, the tunneling current rises exponentially and $R_{gap}$ decreases, which re-
results in a decrease in $V_{\text{gap}}$ [see Eq. (1)] and, therefore, a slowdown in the etching and deposition rates. Eventually, when $R_{\text{gap}}=R_{\text{ext}}$, $V_{\text{gap}} \sim 0$, which terminates the etching and deposition and results in a gap whose width depends on $R_{\text{ext}}$. If $R_{\text{ext}}$ is smaller than $\sim 12.7$ k$\Omega$, a contact between the electrodes is formed and the tunneling is replaced with ballistic transport.

The self-termination effect is further enhanced by the exponential dependence of the etching and deposition current density, $J$, on $V_{\text{gap}}$, according to

$$J(V_{\text{gap}}) \propto \exp(\alpha e V_{\text{gap}}/k_B T),$$

where $\alpha$ is usually around 0.5, $e$ is the electron charge, $k_B$ is the Boltzmann constant, and $T$ is temperature.

The starting electrodes in our experiment were prepared from a 25 $\mu$m Cu, Au, or Ag fibers (99.999%) coated with epoxy on a glass substrate. The initial gap between the electrodes was $10\sim20$ $\mu$m, created by carefully cutting the metal fibers. The electrodes were immediately covered by the etching/deposition solutions (e.g., pure water, KCl, HCl, and H$_2$SO$_4$). $R_{\text{ext}}$ tested in the experiment ranged from 1 k$\Omega$ to 1 G$\Omega$. The etching/deposition voltage was supplied with a function generator. The current was determined from the voltage across $R_{\text{ext}}$, which was monitored by an electrometer (Keithley, model 617).

Figure 1(b) shows a few snapshots of the formation of an atomic-scale contact. Applying a 1.2 V voltage ($V_0$) to the circuit, electrochemical deposition does not occur immediately. Instead, it takes some induction time (from tens of seconds to a few minutes) before the deposition becomes visible. Once the electrodeposition starts, it is rather fast and highly directional with its sharp growing front pointing to the anode. The growing front reaches the anode within a few minutes and the process then terminates itself, which is controlled by $R_{\text{ext}}$. We have systematically varied $R_{\text{ext}}$ in order to form contacts of different sizes and gaps of various widths, and monitored the conductance between the electrodes during the etching and deposition.

Figure 2(a) shows the conductance (normalized against $G_0$) between two Cu electrodes during electrochemical etching and deposition in water with $R_{\text{ext}}$ preset at 3 k$\Omega$ ($<12.7$ k$\Omega$). The initial conductance due to ionic conduction is negligibly small compared to $G_0$. A few minutes after applying a 1.2 V voltage, the conductance suddenly jumps to $\sim 2G_0$ and the deposition terminates itself as a contact is formed between the electrodes. However, the initial contact breaks within seconds and the conductance drops back to zero. The drop in the conductance reactivates the deposition process, and the contact with conductance near 1 $G_0$ is reformed a few seconds later. While the conductance tends to stabilize, a large noise (sharp spikes) in the conductance is clearly visible. Zooming in, the noise reveals stepwise fluctuations in the conductance between $\sim 1G_0$ and $\sim 0G_0$ [inset of Fig. 2(a)], corresponding to a constant breakdown and reforma-
tion of the contact. We believe that electromigration of the atoms near the contact causes the breakdown, which is then reformed by further deposition. Since electromigration depends sensitively on the applied voltage, we have studied the dependence of the noise on the applied voltage. Figure 2(b) shows an example of such studies. The conductance fluctuates violently when setting the voltage at 1.2 V, but the fluctuations are significantly smaller after reducing the bias voltage to 0.2 V, which supports the electromigration explanation.

We have formed a contact with conductance at a higher value by using a smaller $R_{\text{ext}}$. During the formation of the contact, the conductance varies in a stepwise fashion that can be recorded when the variation is slow enough [Fig. 2(c)]. We have measured the $I$–$V$ characteristics of the contacts. Figure 2(d) is an example of the $I$–$V$ curves for a contact with conductance near 1 $G_0$. The current is linearly proportional to the bias voltage, a simple Ohmic behavior.

By increasing $R_{\text{ext}}$ above 12.7 k$\Omega$, we have fabricated atomic-scale gaps between the electrodes. Figure 3(a) shows the conductance (normalized against $G_0$) in logarithmic scale during the etching and deposition processes ($R_{\text{ext}}=1$ M$\Omega$). The initial finite conductance is due to leakage current. Following the gradual increase in leakage is a jump in the conductance, which we attribute to the tunneling current that changes exponentially with the gap width. The conductance jump results in a sudden drop in the etching/deposition voltage and terminates the processes. The conductance, consequently, stabilizes at a finite value that depends on $R_{\text{ext}}$. Fluctuations in the conductance of the gaps are, in general, much less than those in atomic-scale contacts [e.g., Fig. 2(a)], but stepwise fluctuations are often observed [Fig. 2(a)].
3(b)]. Similar stepwise fluctuations have been observed by us previously and attributed to the etching and deposition of individual atoms.10

We have measured the $I – V_{\text{gap}}$ characteristics of the gaps [Fig. 3(c)]. The exponential dependence of the current on the bias is in sharp contrast to the simple Ohmic behavior of the atomic-scale contacts shown in Fig. 2(d). The current is also several orders of magnitude smaller than that for the atomic-scale contacts. Repeated cycling of the bias voltage does not show any hysteresis in the current, indicating that the current is not due to polarization or electrochemical reactions. Furthermore, the exponential dependence is in good agreement with electron tunneling across a square barrier. The above observations lead us to believe that the $I – V_{\text{gap}}$ characteristics of the gaps are due to electron tunneling.

We have varied $R_{\text{ext}}$ from 1 kΩ to 10 MΩ and found that the conductance of the terminal contact or gap decreases as $R_{\text{ext}}$ increases. Figure 4 plots the histogram of some of the measurements, which shows clearly the trend despite run-to-run variations. We have attempted to use $R_{\text{ext}}$ greater than 10 MΩ (e.g., 1 GΩ), but with less success because the tunneling current becomes comparable to the leakage current. This limit in $R_{\text{ext}}$ may be overcome by further reducing the leakage current using microfabricated metal electrodes that have smaller exposed electrode area.

In order to examine the possible effects of oxide formation, we have carried out the experiment with Cu electrodes in 0.5 M HCl and in 0.5 M H₂SO₄. The dependence of the final contact or gap conductance on $R_{\text{ext}}$ is similar, but the etching and deposition are significantly faster for a given applied voltage in the acid solutions. Although the increased etching and deposition rates can speed up the fabrication process, the increased ionic concentration results in a higher leakage current. We have also performed the experiment with Au and Ag electrodes. Unlike Cu and Ag that work in both electrolytes and pure water, Au cannot be etched easily in water and electrolytes such as 0.2 M HCl must be used.

In summary, we have demonstrated an electrochemical method to fabricate atomic-scale gaps and contacts between two metal electrodes. In contrast to the previously reported methods, the present method has a self-termination mechanism that allows us to quickly form a desired gap to fit a small molecule and an atom-size contact with quantized conductance.

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