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A Controllable Electrochemical Fabrication of Metallic Electrodes with a Nanometer/Angstrom-Sized Gap Using an Electric Double Layer as Feedback**

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A pair of facing electrodes with a desired gap width ranging from several angstroms to several nanometers is a key structure in the domain of nanoscience and nanotechnology.[1–10] For example, such a structure supported on a microchip provides a means to interface individual molecules or nanocrystals in integrated circuits.[2–5] The fabricated gap should have a width that is controllable and can be set to meet the specific needs of the target molecules (0.5–2 nm scale) or nanocrystals (1–10 nm scale) whose electron-transport properties can be characterized in detail.[6–10]

In the past few years, three methods have been developed for fabricating electrode pairs with nano-sized or angstrom-sized gaps for device applications.[10–18] The first one, referred to as "break junction", is based on the mechanical breaking of a metal wire into two electrodes with a certain gap.[10,11] The involvement of mechanical forces in the fabrication procedure seems unlikely to be promising for manufacturing microchips, and, moreover, does not have the precision and flexibility to give the desired gap width. The second approach is based on electromigration of metal atoms, which is realized by passing a large electrical current through, and eventually breaking, a gold nanowire.[12,13] This process can yield a stable electrode separation of 1 nm with high efficiency. The above two methods, however, have certain limitations in applicability. The metal nanowire to be broken on a chip should be very thin, around 20 nm, and nanowires of this diameter can only be fabricated by electron-beam lithography, which is not commonly available.

The third method, which is based on the principle of electrodeposition or electrodissolution, can overcome the above-mentioned disadvantages.[14–19] By electrodepositing metal atoms onto a specific face of electrodes, one can sequentially narrow the gap from the original micrometer scale down to the domain of a few angstroms, or even connect

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two electrodes to form a quantum contact.[14–19] This electrochemical method is more versatile than the break-junction and electromigration methods mentioned above, especially as the process can be reversed in the electrodissolution mode for controlled etching of metal atoms from a wire to solution, thus widening the gap from angstrom up to sub-micrometer scales. The most important feature of the electrochemical method is the use of a feedback system to precisely control the resultant gap width. Several experimental parameters, such as electrochemical current and electrolyte conductance, are critically dependent on the gap between two facing electrodes, especially when the gap is narrowed to below the sub-micrometer scale. The electrodeposition process can be stopped by switching off the potentiostat when the conductance reaches a preset value, which provides an accurate and reproducible way to control the gap width between 20 and 3 nm.[16–19] Recently, Tao and co-workers developed a new method to fabricate a molecular-sized gap by using the tunneling current as feedback to precisely monitor electrochemical deposition/etching.[15] When the gap is narrowed below 1 nm, a tunneling current occurs and increases exponentially with a further reduction in the gap width. They observed an interesting stepwise variation in the tunneling current during deposition and etching, which makes it possible to fabricate gaps with sub-angstrom precision. This method affords a great advantage in that it achieves a snug fitting of different molecules, which is an important feature in the fabrication of molecular electronics.[2,20] However, this very promising method seems to have two insurmountable limitations. First of all, it is much more suitable for making a small gap (below 1 nm). Secondly, the four-electrode bipotentiostat to monitoring the tunneling-current feedback is custom-made to a special design and is not commercially available.

In view of the above limitations, it is desirable to develop a simpler and more versatile electrochemical method. Firstly, the method should be able to create gaps ranging from several angstroms to 10 nm, since this is the best scale for fitting designed molecules or growing a nanodot (nanocrystal) of semiconductors or other materials in-between the two electrodes in nanodevices. Secondly, the method should also have a much simpler feedback system that allows the adaptation of a commonly used electrochemical instrument, as this may persuade many research groups to use the method. We report here a chronopotentiometric method that readily allows the electrochemical fabrication of pairs of metallic electrodes with defined gap widths that range from several nanometers down to several angstroms. In this new approach, gap widths are fabricated for the first time by using both the electrode potential and also a universally available three-electrode potentiostat as feedback indicators. The process is simple, controllable, reproducible, and robust, and enables the rapid fabrication of a wide range of nanogaps without the need for any sophisticated instrumentation.

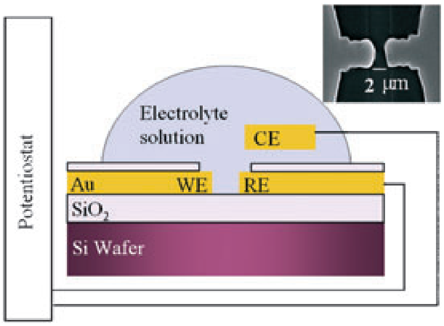

Figure 1. Schematic representation of the experimental setup. The inset shows a pair of facing gold electrodes fabricated on, and covered with, SiO_2, which allows only a small area of both electrodes to be exposed to a solution containing gold ions.

The fabrication involves two major steps—lithography and electrodeposition. First, a pair of facing gold electrodes supported on a SiO_2 chip is prepared with an electrode gap of about 2 µm by a conventional lithography technique (see inset of Figure 1). The wide electrode separation at this stage is not critical. The second step is to narrow the gap down to the nanometer scale by electrodepositing Au atoms onto the working electrode. In comparison with previous methods[14–19] the present method has two major differences, namely, the electrode configuration and the feedback mode (see Figure 1). In our new design, the pair of facing electrodes serve as the working electrode (WE) and reference electrode (RE), respectively. This configuration differs from the conductance-feedback and current-feedback modes, which use both facing electrodes as WEs.[14–19] Experiments were carried out on this unique electrode arrangement by applying a controlled current between the WE and the CE with a current source (a galvanostat).[21] Metal atoms were deposited layer by layer on the WE face at a chosen constant current (I_{dep}) so as to narrow the gap width between the WE and the RE. The operation is controllable and the coating uniform. The potential difference between the WE and the RE (V_{gap}) was monitored continuously during the electrodeposition process, and was plotted as the chronopotentiometric curve shown in Figure 2a. The monitored V_{gap} was about -0.55 V at a deposition current (I_{dep}) of 0.1 mA cm^{-2}, and remained constant until the gap was narrowed below a certain value. The value of V_{gap} decreased irregularly with time, and finally approached zero, thus indicating that the WE and RE electrodes had become connected. This observation clearly demonstrates that V_{gap} can be used as a feedback to control the gap width. It was of special interest to examine the evolution of the gap when V_{gap} started to decrease according to the chronopotential response shown in Figure 2a. Figure 2b and 2c show SEM images of the gap at a preset chronopotential value of $V_{gap} = -0.55$ V (at the initial changing stage) and $V_{gap} = -0.01$ V (near the final stage) as indicated by the potential feedback, respectively. The gap width in the former is approximately 4.5 nm, while the latter shows the gap to be very small and beyond the resolution of SEM. Alternatively, the width of the gap can be estimated from the formula $I \propto V\exp(-ks)$, where I is the tunneling current, V the bias potential, s the gap width, and k a constant. Therefore, if we measure the I–V curve experimentally for the case shown in Figure 2c, and with a known k value, we can calculate s. The linear I–V curve for the gap in air (Figure 2d)

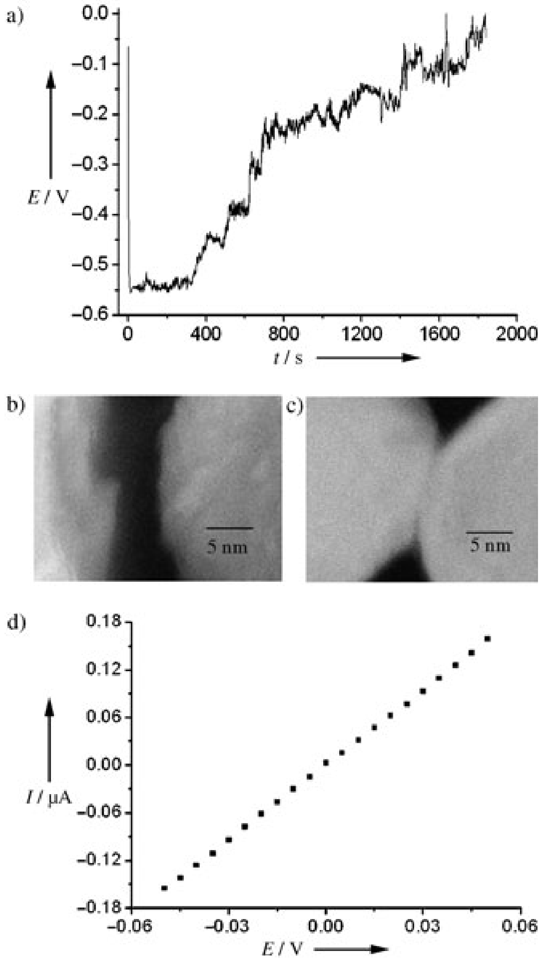

Figure 2. a) A chronopotential response curve during the whole electrodeposition process as Au is deposited on the WE. b) An SEM image of the gap at the preset V_{gap} of −0.55 V. c) An SEM image of the gap at the preset V_{gap} of −0.01 V. d) The corresponding *I–V* curve of the gap in (c).

enabled us to substitute *k* with an average of its values in vacuo[22] and in solution,[23] and calculate the gap width to be approximately 1.5 Å.

We then performed a set of experiments by presetting 12 potentials from −0.55 to −0.01 V as the feedback to control the nanogap fabrication, and then measured their *I–V* values.

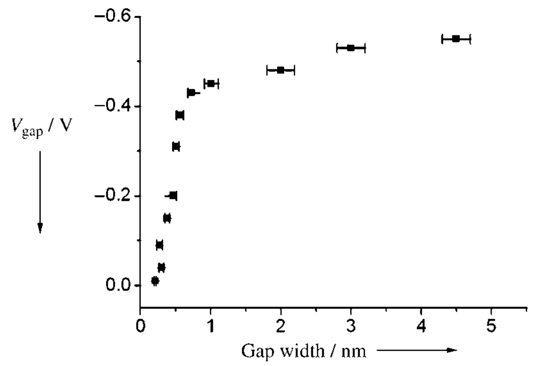

Figure 3. Correlation of the monitored gap width versus V_{gap}.

The value of V_{gap} is plotted against the gap width in Figure 3, which shows that the gap can be fabricated in a controlled manner over a range from 4.5 nm to 2 Å. This systematic experiment demonstrates that an electrode separation ranging from several angstroms to several nanometers can be constructed simply by choosing a preset potential. By measuring the potential difference between the WE and the RE, we are able to monitor the gap distance in a range smaller than 4.5 nm and perform a controlled deposition with subnanometer resolution.

Why, under the present electrode configuration, does V_{gap} start to decrease when the gap is narrowed down to around 5 nm (Figure 3)? This trend most probably results from the pattern of potential drops in the electrical double-layer. According to the Guoy–Chapman–Stern (GCS) model,[24] a double layer consists of a compact layer (CL) with a sharp potential drop and a diffuse layer (DL) with a slow potential drop (Figure 4a). Since no potential drop occurs beyond the double-layer region when the gap is narrowed down to around the double-layer thickness, the RE (awhich acts as the potential probe) can be considered to penetrate into the double-layer region of the WE (Figure 4b). This arrangement provides a guide for presetting the V_{gap} value so that the termination of the electrodeposition process produces a desired gap width.

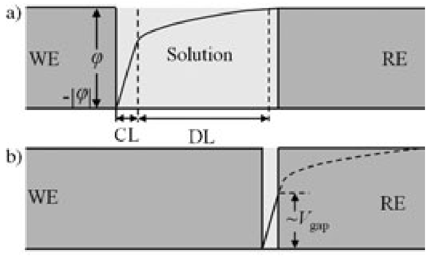

Figure 4. Representation of the working electrochemical principle when fabricating nano/angstrom-gap electrodes. The double layer consists of a compact layer (CL) and a diffuse layer (DL).

The electrolyte concentration can also critically influence the double-layer structure,[24] which is another factor that contributes to the V_{gap} versus gap-width relationship. Since the fabrication of the largest gap width by our method is mainly determined by the double-layer structure, namely, the potential distribution and the layer thickness, one could also control the width by adjusting the electrolyte concentration. Figure 5 shows that when the concentration of the plating solution is diluted by 100 times and the potential is set at −0.6 V, the accessible gap width can be extended to 10 nm (Figure 5b). It should be noted that the potential distribution in the nanogap is much more complicated than that shown in Figure 4 because of many factors. For example, the double layer of the RE has not been taken into account in our preliminary model. A systematic investigation of this unique double layer is needed to gain a more-detailed picture.

In summary, we have demonstrated a simple potential-feedback system with a hitherto-untried electrode configuration to fabricate metallic electrodes with controlled gap

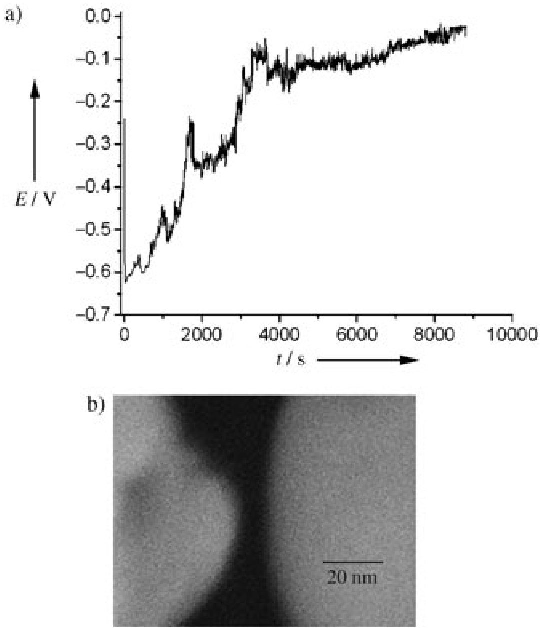

Figure 5. a) A chronopotential response curve during the whole electrodeposition process as Au is deposited on the WE. $I_{dep}=0.1$ mA cm^{-2}; the electroplating solution contains 0.15 μM KAu(CN)$_2$, 3 μM $K_3C_6H_5O_7$, and 3 μM KH_2PO_4. b) An SEM image of the gap at the preset V_{gap} of -0.6 V.

widths over a wide range from about 10 nm down to several angstroms. The working principle is based on the potential distribution in the electric double-layer. The process is simple, controllable, and reproducible, and allows the rapid fabrication of electrode pairs with conventional equipment, which may persuade more research groups to use the method. This method has the potential of leading to three techniques for future studies in nanodevices, surface-enhanced Raman scattering (SERS), and electrochemical double-layers. A nanocrystal of various materials could be grown electrochemically to fuse the gap by simply changing the electroplating solution.[25] It could also be used to study SERS of molecules located at the junction of two nanotips to determine which exhibits the highest activity.[26] More importantly, one could use this controllable nanogap to investigate the double-layer structure in detail, which has been a key issue in electrochemistry for a long time.

Experimental Section

The electrode pair and nanogap fabrication: The pair of facing Au (99.99%) electrodes were fabricated by an optical-lithography technique on an n-type Si wafer of <111> orientation that was covered with 2-μm, thermally oxidized silicon layer. The initial separation was typically 2 μm. The electrochemical fabrication of the nanogap electrodes was realized by using a CHI631A electrochemical workstation (CHI Co., USA). The deposition current in chronopotentiometry was 0.1 mA cm^{-2}. The electroplating solution was 15 μM KAu(CN)$_2$, with 0.3 mM $K_3C_6H_5O_7$ and 0.3 mM KH_2PO_4 as supporting electrolytes. These optimized experimental parameters, especially the current density, ensure that the Au deposits in a uniform and compact manner, which ensures a reasonably good stability of the fabricated nanogap in both solution and air. When the electroplating solution was diluted by a factor of 100, that is, the electroplating solution was 0.15 μM KAu(CN)$_2$ with 3 μM $K_3C_6H_5O_7$ and 3 μM KH_2PO_4, the largest fabricated gap width was about 10 nm. All solutions were prepared with analytical grade reagents and Milli-Q water. The nanogap electrodes with a gap larger than 1 nm were characterized with a LEO1530 scanning electron microscope (LEO Co., Germany). The nanogap electrodes with gaps smaller than 1 nm were characterized with a Keithley 4200 semiconductor characterization system to measure the corresponding *I–V* curve of the gap.

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