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Confined Electrochemical Deposition in Sub-15 nm Space for Preparing Nanogap Electrodes

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Abstract

Electrode gaps with nanoscale separation offer great promise for molecular electronics and biosensing. Previous electrochemical methods to prepare nanogaps by depositing metal on pre-defined electrode tips have suffered from lack of control in the thickness direction and reproducible control of gap size. Here we report a new process wherein the electrochemical deposition is confined by a cavity to produce a nanogap with thickness smaller even than that of the initial electrodes. Using this process, we demonstrate controlled and reversible electrochemical deposition in a sub-15 nm space, to produce a nano-fluidic channel with finely tunable nanogap control electrodes for biosensing applications.

Introduction

There has been a high level of interest in fabricating nanogaps to be used in such applications as molecular electronics and biosensors. A nanogap consists of a nanoscale separation that matches the length scale of a single molecule between conducting electrodes, and a wide variety of techniques have been developed for creating gaps whose small size renders them challenging for conventional top-down lithographic methods (1). Popular approaches include: mechanical controllable break junction (MCBJ), first demonstrated in 1985 (2), by which gaps from angstrom scale to a few nanometers, as well as single-atom and metal-molecule-metal junctions have been fabricated (3,4); and electromigration (5,6,7), in which a high enough current through a thin enough metal wire will eventually result in a breakage of the wire to produce a gap of about 1 nm (6).

Another important strategy of preparing nanogaps is the use of electrochemical deposition to form nanogaps. In contrast to the previous two approaches, which begin from an intact wire and induce a breakage, this approach typically begins with a larger-scale gap that is narrowed by the electrochemical deposition of metal onto the electrode surfaces. The progress of the deposition can be monitored by tracking several different quantities, including current flow (8,9), potential difference (10), and coupling with external circuit elements (11). In particular, previous work has shown the promise of using the high-frequency impedance between the two electrodes in solution to control gap sizes from about 30 nm down to 1 nm (12,13). While electrochemical deposition has been successfully used to shrink down the lateral gap distances, the technique suffers from a lack of control in the height of the facing electrodes. Because the deposition process is isotropic, the final height

of the electrodes will be equal to the initial height plus half the starting distance between the electrodes. In practice, the final height is typically greater, because the deposition speed slows down at the tips due to increasing diffusion layer thickness as the electrodes get closer (14). For example, with starting electrode separations between 100 nm and 2 μm (15), this can result in electrode heights of more than 1 μm at the gap. More significantly, due to the complication in the geometry along the thickness direction, the deposition time and final shape of the gap are less controllable and irreproducible from sample to sample. This may also be the reason that although in principle all these methods are reversible, we have seen no successful demonstration of repeated opening and closing of the same nanogap with precise distance control.

To address these challenges, here we show that (1) the electrochemical deposition process can be effectively controlled in a confined nanoscale space with ac impedance as the feedback signal, and (2) when the thickness of the electrodes is limited to < 15 nm by the space confinement, the deposition process is more reproducible and the gap size can be reversibly decreased or increased reproducibly.

Experiment

Preparation of the Initial Electrode Gap Confined within a Nanoscale Cavity

As shown in Figure 1(a), starting electrode gaps were fabricated using standard photolithographic techniques. The starting substrate was a 170- μm thick glass slide with a 150 nm Si_3N_4 coating by plasma enhanced chemical vapor deposition (PECVD). Electrode pairs (2 nm Cr /30 – 50 nm Au) were fabricated with an initial separation of 1 μm by conventional photolithography (PL). A 4- μm wide sacrificial layer (15 nm Cr) was overlaid on the electrodes to fill the gap between them. Then a layer of 200 nm SiO_2 were deposited by sputtering to seal the surface of the whole device. A 20:1 dilution of buffered hydrofluoric acid was used to open windows in the SiO_2 using PL defined masks, through which the Cr sacrificial layer was additionally etched away using Cr etchant to create a cavity between the electrodes. This resulted in a 1 μm gap between the two electrode tips with a height constrained to sub-15 nm by the dielectric surfaces.

Electrochemical Deposition Setup

The system used for the electrochemical deposition is shown in Figure 1(b) and consists of two circuits: a two-electrode electrochemical cell for depositing and/or removing gold from the electrode tips and a monitor circuit for measuring the impedance between the two tips. The output from the monitor circuit is analyzed in real time by a program which serves as a feedback control for the electrochemical cell. The electrochemical cell establishes a potential difference between a grounded Ag/AgCl electrode serving as the counter electrode (CE) and the gold electrode tips serving as the working electrodes. The small currents involved in this geometry (< 1 nA) and the close distance between CE and WE allow us to neglect the polarization of the Ag/AgCl electrode. The electroplating solution used in this experiment consisted of 17.5 mM potassium gold cyanide, $\text{KAu}(\text{CN})_2$ and 186 mM potassium citrate, $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$. A pulsed deposition of gold onto the electrodes was performed by sending the gold WE a potential pulse with an amplitude of -0.9V and a width

of 2 – 20 ms, while removing gold from the electrodes was performed by giving the gold WE a similar potential pulse of +1.0 V in amplitude.

The AC Impedance Feedback Control Circuit

The monitor circuit, detailed in Figure 1(c), takes a 200 mV, 3kHz-20kHz AC signal from the reference channel of a lock-in amplifier and scales it down by a factor of 1/100 in two separate branches. In particular, one branch retains the same phase as the original signal, while the other branch inverts the phase. Each branch then passes through an equal-valued resistor R_b before connecting to one of the electrode tips. The signal from one branch is then amplified by 100X and sent back to the lock-in amplifier. The detected AC signal V_s depends on the original lock-in reference signal V_o , the bridge resistors, and the impedance between the two electrode tips as:

$$V_s = V_o (Z / (Z + 2R_b)) \quad [1]$$

In all our measurement, the capacitive impedance between the electrode tips is typically negligible due to the use of glass substrate and the very small parallel area of the electrodes. Therefore, the impedance Z can be considered as the resistive only. At large gap distances ($Z \gg R_b$), the output voltage equals the input voltage. As the gap shrinks, Z decreases, and the output voltage drops, with the greatest sensitivity coming at $Z = 2R_b$. The computer control collects the amplitude and phase of the AC signal at 20 kHz. Every 0.2 s, the computer analyzes the data from the previous cycle and sets the appropriate potential of the electrochemical cell for the next cycle, to keep depositing metal, maintain the gap size, or dissolve gold, based on the calculated threshold.

Results /Discussion

In a typical experiment, the impedance signal is recorded for 60–90 s before the electrochemical process starts such that a baseline for the open circuit value can be extracted from the data. Once the baseline has been calculated, reducing voltage pulses are applied between the WE and CE so that gold atoms will be plated onto the electrode surface. Depositing metal in pulses rather than at constant potential minimizes the diffusion polarization at the electrodes, and gives the control program more time to respond to changes in the gap impedance. Typical pulse width ranges from 2 ms–20 ms in a 200 ms cycle, meaning that active deposition is occurring only 1% – 10% of the time. As described in previous work (13), the impedance signal stays pretty much constant until the gap becomes $< \sim 30$ nm and a contact is about to be made between the two electrodes, at which point there is a rapid decrease as the gap shorts. When the program detects a short (conductance greater than the quantum conductance $G_0 = 2e^2/h = 77.5 \mu S$), the electrochemical cell can be directed to produce oxidizing potential pulses and dissolve gold from the electrodes. Through our automated program, the same electrode gap can be made to close and open repeatedly (Fig. 2(a)). Analysis of the conductance data captured during a shorting event (Fig. 2(b)) shows the conductance steadily increasing until it reaches G_0 , representing a quantum contact between the electrode tips. The conductance then jumps between multiples of G_0 as the deposition continues until eventually rising to complete

shorting. The “un-shortening” events, i.e. the breaking of the junction when pulse polarity is switched, demonstrate a slightly different behavior. Specifically, Fig. 2(c) and (d), and Fig. 2(e) and (f) compares two back-to-back shorting and un-shortening events, respectively. The shorting events typically showed a long dwelling time around G_0 . In contrast, as metal is removed from the junction, the measured conductance fluctuates but moves consistently downward to around $3\sim 4 G_0$. At this point, a single oxidizing potential pulse opens the gap. The explanation of such difference may need additional investigation, but the consistent behavior can be used as the “zero” point calibration for controlling the exact distance between the gaps, because the deposition and removal of the metal can be linearly tuned by the number and timing of the potential pulses. This is a very convenient way to reproducibly fabricate nanogaps of a required distance.

Figure 3 highlights the effects of confining the thickness of the gap. When there is no top SiO_2 coating to confine the thickness of the electrodes, the growth of metal is isotropic in three dimensions, so an initial gap size of around $1\text{ }\mu\text{m}$ (Fig. 3(a)) results in a final electrode height of about 500 nm (Fig. 3(b)). Significantly, there is no control of where the closest gap is formed in the thickness dimension. We have observed gap formation closer to the bottom (inset of Fig. 3(b)), as well as closer to the top, or even between laterally overlapping electrodes (data not shown). By sealing the electrodes, the metal growth is only allowed along the exposed side edges within the confined cavity, and the height of the gap is fixed by the thickness of the original sacrificial layer ($10 - 15\text{ nm}$), which is thinner than the grain size of deposited Au, leading to minimal roughness along the vertical direction. This results in a much faster deposition process with a consistent two-dimensional spread of the electrodes at a fixed sub-15 nm height. The contrast in the SEM image of Fig. 3(c) clearly shows the original electrodes which is 50 nm thick, and the newly grown metal film which is 10 nm. In addition, the lateral extension of the metal can be further minimized and the geometry of the gap optimized by reducing the initial gap distance between the electrodes. The final device will therefore feature a nanoscale fluidic channel completely aligned with a pair of control electrodes, which can have broad applications in nano-fluidic systems and single-molecule biosensing.

Conclusions

In summary, we have used electrochemical deposition of gold in a confined nanoscale cavity to fabricate nanogaps with tunable distance. We have demonstrated reproducible formation and breakage of the contacts between the electrodes and capture the quantized conductance behavior of close contacts, which can serve as the zero point for calibration of the gap size. Our approach can serve as a scalable platform to produce accurate nano-fluidic channels with metal nanogaps as control electrodes for single-molecule sensing.

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Figure 1. Schematics of the initial electrode gap, and the electrochemical deposition and feedback control circuit

(a) Cross-section schematic of initial gap preparation. In (1), the starting electrodes with a gap of $\sim 1 \mu\text{m}$ is deposited on the substrate. In (2), the Cr sacrificial layer between the electrodes and a top SiO_2 passivation layer over the whole surface are deposited. In (3), the sacrificial layer is etched away and a cavity is created between the electrodes and confined by the top SiO_2 and the substrate. (b) Deposition onto the electrodes inside the cavity is performed by a two-electrode electrochemical cell in which a Ag/AgCl electrode serves as the counter electrode and both nanogap tips are the working electrode. The impedance between the nanogap tips is monitored by an AC circuit, where the AC potential at one of the electrodes is analyzed by a lock-in amplifier so that a computer program can calculate the corresponding impedance between the electrodes, and use it to control the deposition in real time. (c) Circuit diagram for impedance measurement. The reference signal from a lock-in amplifier supplies the AC voltage, which is passed through an isolation amplifier (IA_1) and voltage follower (OA_1) before branching. The top branch goes through an inverting amplifier (OA_2) which reduces the signal amplitude to $1/100$ of its original value and shifts the phase by 180° . The bottom branch goes through a non-inverting amplifier (OA_3) which

reduces the signal amplitude to 1/100 of its original value while leaving the phase unchanged. Each branch passes through a bridge resistor R_b before connecting to the electrode gap, represented by impedance Z . The signal from the top branch is then amplified by a factor of 100 (OA_4) and passed through another isolation amplifier (IA_2) before being sent to a lock-in amplifier for analysis. The voltage V_s read by the circuit depends on the input voltage V_o and gap impedance Z and has its sensitivity tuned by the bridge resistance R_b .

Figure 2. Impedance data from electrochemical deposition

(a) Raw data from impedance monitor circuit showing shorting/un-shorting events. When the gap distance is large, an open circuit voltage (here about 6 V) is measured. When the gap is fully shorted, a short-circuit voltage (here about 0.5 V) depending on the total device resistance is measured. (b) Top: Gap conductance during shorting event. As the gap closes, the conductance rises until it reaches the quantum conductance G_0 . Afterwards, the conductance jumps between multiples of G_0 . Downward spikes may be caused by changes to the electric double layer induced by the reducing pulses. Bottom: Potential of WE vs. CE. (c)–(d) Back-to-back shorting and un-shorting events on a single electrode pair, respectively. (c) shows the conductance dwelling around G_0 before rapidly increasing, while (d) shows the conductance decreasing to around $3 G_0$ before dropping abruptly toward zero. (e)–(f) Another pair of shorting and unshorting events on the same electrode pair as (c) and (d), showing the same essential characteristics.

Figure 3. Scanning Electron Microscope (SEM) images

(a) Starting gap before electrochemical deposition. (b) Electrode pair after unconfined electrochemical deposition. Main image is taken at 45° tilt, revealing the height of the electrodes after unconfined deposition to be about 400 nm. Inset is a top view showing the formation of a 10-nm gap. (c) Electrode pair after confined electrochemical deposition. Contrast can be seen between (1) the original patterned electrodes (60 nm thick) at far left and right and (2) the electrochemically deposited gold (confined to 10 nm thick). Inset shows a ~20 nm gap.