

Molecular detection based on conductance quantization of nanowires

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We have studied molecular adsorption onto stable metallic nanowires fabricated with an electrochemical method. Upon the adsorption, the quantized conductance decreases, typically, to a fractional value, which may be attributed to the scattering of the conduction electrons by the adsorbates. The further conductance change occurs when the nanowire is exposed to another molecule that has stronger adsorption strength. Because the quantized conductance is determined by a few atoms at the narrowest portion of each nanowire, adsorption of a molecule onto the portion is enough to change the conductance, which may be used for chemical sensors. © 2000 American Institute of Physics. [S0003-6951(00)01610-7]

As materials shrink to the nanometer scale, interesting quantum phenomena emerge, which may lead to novel applications.¹ In this letter, we describe a molecular detection method based on the conductance quantization in metallic nanowires. The phenomenon of conductance quantization occurs when the diameter of the wire is comparable to the electron Fermi wavelength.² At the lowest conductance step ($G=2e^2/h$), the narrowest portion of the wire has been shown to be as small as a few atoms.³ Because the few atoms dictate the conductance of the entire wire, adsorption of even a single molecule onto them may drastically change the conductance, which is the basis of molecular detection explored here.

For a practical device, the nanowires must have long term stability and be producible in large quantities. The widely used mechanical methods² that involve bringing two metallic wires in and out of contact are not suitable. In the present work, we fabricate highly stable nanowires by electrochemically etching a metal wire down to the atomic scale,^{4,5} and demonstrate that the conductance changes in the stable nanowires upon adsorptions of various molecules may be used for molecular detection.

We fabricated stable nanowires using pairs of Au micro-electrodes supported on oxidized Si substrates as the starting point (Fig. 1). These electrodes were fabricated at Cornell Nanofabrication Facility by combining photolithography and focused ion beam techniques. They were covered with a Si_3N_4 insulation layer to eliminate ionic conduction in the etching/deposition electrolyte (CuSO_4). The two electrodes in each pair were separated with a small gap (~ 100 nm) created with a focused ion beam (1a), which was bridged by electrochemical deposition of Cu into the gap (1b). We note that a similar method was applied to fabricate facing electrodes with atomic scale gaps.⁶ The deposition was monitored continuously by measuring the conductance between the electrodes and controlled until a desired conductance was reached with a feedback circuit. When the nanowire was over grown, the feedback circuit switched on the etching process to decrease the conductance back to the desired value. Once a stable nanowire was formed, sample molecules

were injected to the solution and the subsequent conductance was monitored and recorded with a DL2700 digital oscilloscope (Yokogawa, 1c). We used Cu nanowire to bridge the Au electrodes because it can be easily etched away without damaging the Au electrodes in case of an overgrown wire. Cu is also more reactive than Au and, therefore, more suitable for molecular detection.

By carefully controlling the deposition/etching potential and electrolyte concentration, we have been able to reproducibly stabilize the conductance of a nanowire at an integer for many hours [Fig. 2(b)]. Thermal instability due to temperature fluctuations was minimized by immersing the nanowire chip in aqueous solution. Possible instability due to the electromigration effect was reduced by using a small bias

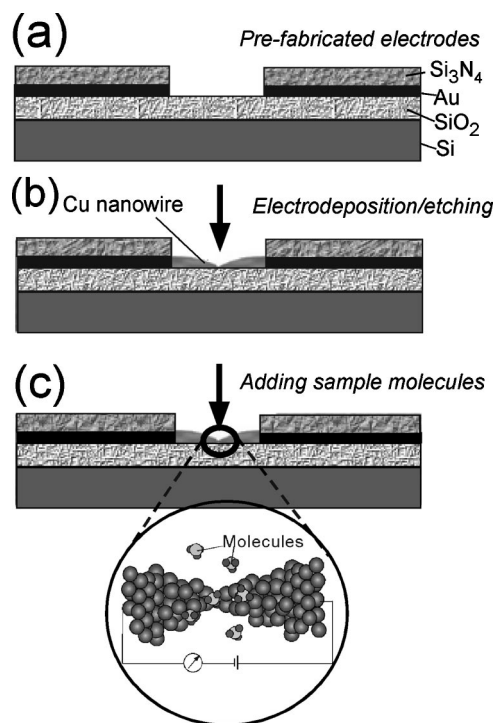


FIG. 1. Schematic procedure for making stable Cu nanowires and then using it to sense molecules adsorbed onto them. A pair of Au electrodes facing each other with a gap of ~ 100 nm is fabricated on a Si/SiO₂ substrate (a). The gap is bridged to form a nanowire with a desirable conductance by electrochemically depositing Cu on the ends of the electrodes (b). Molecular adsorption on the nanowire is reflected by a change in the conductance (c).

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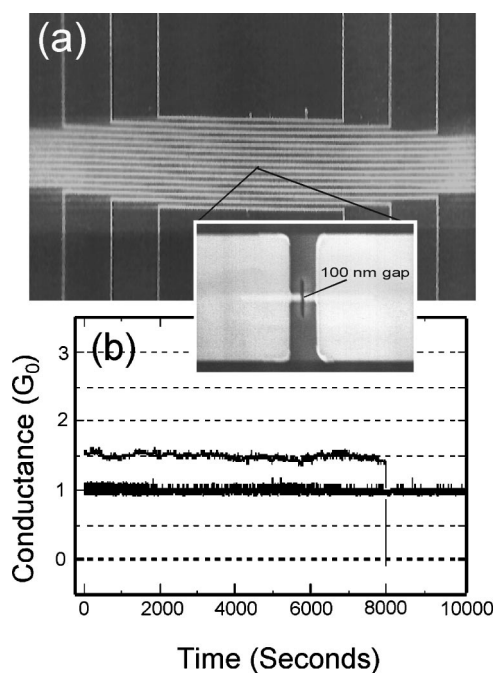


FIG. 2. Top: Scanning electron microscopy images of an array of Au electrode pairs on Si/SiO₂ substrate fabricated by combining conventional photolithography and focused ion beam techniques. Bottom: The conductance of the Cu nanowires can be stabilized at an integer or fractional multiples of G_0 for hours.

voltage (<26 mV). The eventual breakdown of the nanowires came likely from drift in the deposition-etching potential due to electrical noises and variations in the electrolyte concentration. The conductance can also be held at fractional multiples of G_0 for hours [Fig. 2(b)]. Note that the conductance histograms constructed from repeated transient measurements of both mechanically² or electrochemically^{4,5} formed nanowires have shown clear preference for the conductance to take integer multiples of G_0 . The fact that the conductance can be kept at a fractional value for hours indicates the existence of metastable configurations between the stable configurations that give rise to integer conductance values.²

We have studied three molecules, 2,2'-bipyridine (22BPY), adenine, and mercaptopropionic acid (MPA) because their adsorption strengths vary from weak (22BPY) to very strong chemical adsorption (MPA). We started the experiment by holding a nanowire at a quantum step and then switch off the feedback circuit. After the nanowire was stabilized at the quantum step, we then added a drop of solution containing a sample molecule into the solution cell and monitored the subsequent change in the conductance continuously. Upon introduction of 22BPY, the conductance changes instantly and then stabilizes to, typically, a lower value. An example is shown in Fig. 3(a), where the conductance decreases from $1G_0$ to $\sim 0.5G_0$ upon adsorption of 22BPY. The decrease in the conductance may be attributed to the scattering of the conduction electrons in the nanowires by the adsorbates, as predicted by a recent simulation.⁷ The final conductance tends to stabilize near a half multiple of G_0 . In order to confirm this observation, we performed a transient experiment using a scanning tunneling microscope (STM) setup.² In the experiment, a large number of nano-

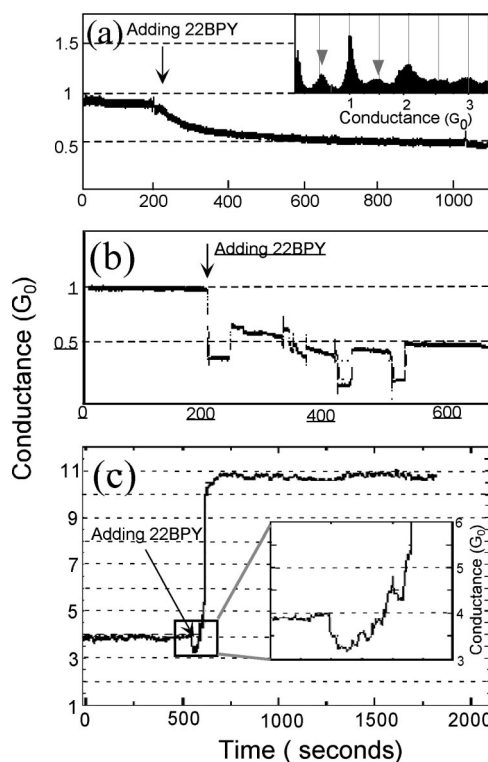


FIG. 3. Response of the quantized conductance of Cu nanowires to the adsorption of 22BPY. Upon molecular adsorption, the conductance typically decreases to a fractional value [(a) and (b)], but sometimes the decrease is followed by an increase due to a change in the atomic configuration of the nanowire. The inset in (a) shows the conductance histogram constructed from over a thousand measurements using a STM setup.

wires were repeatedly created by moving the STM tip in and out of the contact with a substrate, which allowed us to construct conductance histograms with and without the molecules in the solution cell. In the presence of the molecules, the histogram shows increased counts near half multiples of G_0 , which is consistent with the observation on the stable nanowires [inset of Fig. 3(a)]. The peaks at the integers are still pronounced, which is likely because each nanowire in the transient experiment lasted too short (<1 ms) to allow the molecules to adsorb every time. We note that conductance steps near half integers appear even without the presence of molecules, especially at very low electrochemical potentials,⁸ but the molecular adsorption increases the probability of the occurrence.

Before stabilizing at a lower value, the conductance sometimes fluctuates up and down upon the adsorption of 22BPY [see Fig. 3(b)]. The fluctuations are not due to mechanical disturbance associated with the introduction of the molecules into the sample cell because we found no changes in the conductance when repeatedly adding blank electrolyte solution into the sample cell. We attribute the fluctuations to transient adsorption processes involving the movements of individual adsorbed molecules as well as rearrangement of the metal atoms in the nanowire.

The conductance sometimes decreases initially upon molecular adsorption and then increases to a higher value. While the initial decrease may be attributed to adsorbate scattering, the later increase is likely due to a rearrangement in the atomic configuration of the nanowires induced by the adsorption.^{9,10} It is common that strong adsorption of mol-

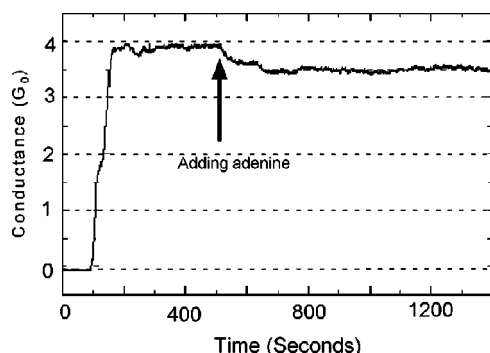


FIG. 4. Exposing a Cu nanowire that is covered with preadsorbed 22BPY to stronger adsorbate (adenine) causes an additional slow change in the conductance, which reflects the replacement of 22BPY by adenine.

ecules onto a surface can change the binding among the surface atoms and results in surface reconstruction.¹¹ We have recently found that adsorbates significantly alter the distances over which a nanowire can be elongated before it switches to the next stable atomic configuration.⁹ Further evidence comes from an *ab initio* local density functional simulation that shows the adsorption of methylthiol changes dramatically the atomic configuration of a four-atom gold chain.¹⁰

Upon adsorption of adenine, the conductance also tends to shift to a lower fractional step. This is consistent with the fact that both adenine and 22BPY are structurally similar and they bind to metal surfaces via the two N atoms linked to the aromatic rings.^{11,12} When exposing the nanowire to MPA, the conductance often drops to zero, corresponding to the breakdown of the nanowire. The thiol group in MPA is well known to bind strongly to Cu and Au¹³ which have been observed to weaken the metallic binding between the metal atoms and make the surface atoms mobile.¹⁴ A large change in the atomic configuration of the nanowire upon adsorption of MPA is expected.

In addition to molecular adsorption on fresh nanowires, we have studied the nanowires that were first exposed to a chemical species. Shown in Fig. 4 is the conductance of a nanowire that has been pre-exposed to 22BPY. When exposing the nanowire to adenine solution, further decrease in the conductance occurs, which indicates replacement of 22BPY by adenine. The changes, however, takes place at a much slower rate than that of a fresh nanowire. Interestingly, reversing the order by exposing a nanowire to MPA first then to adenine or 22BPY, for example, leads to no further changes in the conductance. This reflects precisely the relative adsorption strengths of the molecules to Cu, which may be used to improve the specificity in chemical sensor applications.

A good chemical sensor must have high sensitivity, good specificity, and fast response time. The sensitivity of the nanowire-based sensor is excellent because the quantized conductance is determined by a few atoms at the narrowest portion of each nanowire and adsorption of molecules onto the atoms causes a large change in the conductance. A simple macroscopic analogy of the sensor that has been used for many years is to detect O₂ with a glowing W filament. Recently, surface conductivity was shown to provide a sensitive detection of alkanethiol adsorption onto Au films.¹⁵

The response time is limited by how fast molecules can diffuse and adsorb onto a nanowire and can be sped up by using a large array of nanowires. Our current setup allows us to fabricate 15 nanowires on each chip, but the method can be used to fabricate larger arrays. The ultimate specificity for molecular identification depends on the mechanism for the adsorbate-induced changes in the conductance, which is not yet fully understood. It appears that adsorbates can change the quantized conductance by scattering the conduction electrons in the nanowires or by changing the atomic configurations of the nanowires. Both mechanisms depend on the molecule-nanowire interactions, so the conductance changes should be specific for different adsorptions. The specificity can be improved if the nanowires are preadsorbed with functionalized molecules because a specific interaction of a sample molecule with the functionalized molecules provides identity information about the sample molecule. This strategy has been widely used to improve the specificity of other chemical sensors, such as the microcantilever based sensors.¹⁶

In summary, we have fabricated stable Cu nanowire arrays using an automated electrochemical method and studied changes in the quantized conductance of the nanowires upon adsorption of molecules in aqueous solutions. The dependence of the conductance on molecule adsorption may be used for chemical sensor applications.

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