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Molecular Adsorption onto Metallic Quantum Wires

Albert Bogozi,[†] Osvaldo Lam,[†] Huixin He,[†] Chunzeng Li,[†] Nongjian J. Tao,*,[†]
Larry A. Nagahara,[‡] Islamshah Amlani,[‡] and Raymond Tsui[‡]

Contribution from the Department of Physics, Florida International University, Miami, Florida 33199, and Physical Sciences Research Laboratories, Motorola Labs, 7700 South River Parkway, Tempe, Arizona 85284

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Abstract: We have studied the adsorption of mercaptopropionic acid, 2,2′-bipyridine, and dopamine onto electrochemically fabricated Cu nanowires. The nanowires are atomically thin with conductance quantized near integer multiples of $2e^2/h$. Upon molecular adsorption, the quantized conductance decreases to a fractional value, due to the scattering of the conduction electrons by the adsorbates. The decrease is as high as 50% for the thinnest nanowires whose conductance is at the lowest quantum step, and smaller for thicker nanowires with conductance at higher quantum steps. The adsorbate-induced conductance changes depend on the binding strengths of the molecules to the nanowires, which are in the order of mercaptopropionic acid, 2,2′-bipyridine, and dopamine, from strongest to weakest. The sensitive dependence of the quantized conductance on molecular adsorption may be used for molecular detection.

Introduction

The quest for ever-increasing miniaturization of semiconductor devices has triggered a surge of interest in nanomaterials in recent years. On the nanometer scale, interesting new phenomena, such as single-electron charging effect[1−4] and conductance quantization,[5−9] become important. These phenomena may lead to novel applications from electronic and optical devices to chemical and biological sensors.[10−13] For example, Smith has demonstrated digital switches based on quantum point contact,[10] and Brousseau et al. have explored chemical sensing applications based on the single-electron charging effect in metallic nanoparticles.[13] This paper reports an attempt to utilize conductance quantization in metallic nanowires for molecular detections.

In a classical (macroscopic) metallic wire, the conduction electrons experience multiple diffusive scatterings when they traverse through the wire. The conductance of the wire is proportional to the cross-sectional area and inversely proportional to the length of the wire. When the length is decreased below the electron mean free path (∼30 nm for Cu at room temperature), the electron transport is ballistic (i.e., without any collisions). If, in addition, the diameter of the wire is shrunk to the order of the electron wavelength (a few angstroms for Cu), the electrons in the transverse direction form well-defined quantum modes or standing waves. The conductance, G, is described by the Landauer formula,[14] $G = G_0\sum_{i=1}^{N}T_i$, where $G_0 = 2e^2/h \approx 1/13\ \mathrm{k}\Omega$ is the conductance quantum, T_i is the transmission coefficient of each mode, and the summation is over all the quantum modes. For many metals, such as Au, Cu, and Ag, T_i is close to 1, so the conductance is given by NG_0, where $N = 1, 2, 3....$ However, recent experimental evidence shows that T_i depends on the chemical valence of the metal and may significantly deviate from 1, so each quantum step may not be exactly $1G_0$.[15]

This phenomenon was first clearly demonstrated in semiconductor devices containing a two-dimensional electron gas confined in a narrow constriction by the gate voltage.[5,6] A similar quantized change in conductance has also been observed in three-dimensional metallic nanowires created by mechanically breaking a fine metal wire[16] or separating two electrodes in contact.[8,17−20] Since the wavelength of conduction electrons in a typical metal is only a few angstroms, comparable to the size of an atom, a metallic nanowire with conductance quantized at the lowest steps must be atomically thin. This conclusion has

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[†] Florida International University.

[‡] Motorola Labs.

(1) Averin, D. V.; Likharev, K. K. In *Mesoscopic phenomena in solids*; Altshuler, B. L., Lee, P. A., Webb, R. A., Eds.; Elsevier: Amsterdam, 1991.

(2) Ingram, R. S.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Whetten, R. L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. *J. Am. Chem. Soc.* **1997**, *119*, 9279−9280.

(3) Keating, C. D.; Feldheim, D. L. *Chem. Soc. Rev.* **1998**, *26*, 1.

(4) Fan, F.-R. F.; Bard, A. J. *Science* **1997**, *277*, 1791−1793.

(5) Wharam, D. A.; Thornton, T. J.; Newbury, R.; Pepper, M.; Ahmed, H.; Frost, J. E. F.; Hasko, D. G.; Peacock, D. C.; Ritchie, D. A.; Jones, G. A. C. *J. Phys. C* **1988**, *21*, 209−214.

(6) Wees, B. J. v.; Houten, H. v.; Beenakker, C. W. J.; Williams, J. G.; Kouwenhowen, L. P.; Marel, D. v. d.; Foxon, C. T. *Phys. Rev. Lett.* **1988**, *60*, 848−850.

(7) Landman, U.; Luedtke, W. D.; Burnham, N. A.; Colton, R. J. *Science* **1990**, *248*, 454−457.

(8) Gimzewski, J. K.; Moller, R. *Phys. Rev. B* **1987**, *36*, 1284−1287.

(9) Krans, J. M.; Muller, C. J.; Yanson, I. K.; Govaert, T. C. M.; Hesper, R.; Ruitenbeek, J. M. v. *Phys. Rev. B* **1993**, *48*, 14721−14724.

(10) Smith, D. P. E. *Science* **1995**, *269*, 371−373.

(11) Gittins, D. I.; Bethell, D.; Schiffrin, D. J.; Nichols, R. J. *Nature* **2000**, *408*, 67−69.

(12) Li, C. Z.; Bogozi, A.; Huang, W.; Tao, N. J. *Nanotechnology* **1999**, *10*, 221−223.

(13) Brousseau, L. C., III; Zhao, Q.; Shultz, D. A.; Feldheim, D. L. *J. Am. Chem. Soc.* **1998**, *120*, 7645.

(14) Landauer, R. *IBM J. Res. Dev.* **1957**, *1*, 223−231.

(15) Scheer, E.; Agrait, N.; Cuevas, J. C.; Yeyati, A. L.; Ludoph, B.; Martin-Rodero, A.; Bollinger, G. R.; van Ruitenbeek, J. M.; Urbina, C. *Nature* **1998**, *394*, 154−157.

(16) Krans, J. M.; Ruitenbeek, J. M. v.; Fisun, V. V.; Yanson, I. K.; Jongh, L. J. d. *Nature* **1995**, *375*, 767−769.

(17) Pascual, J. I.; Mendez, J.; Gomez-Herrero, J.; Baro, A. M.; Garcia, N.; Binh, V. T. *Phys. Rev. Lett.* **1993**, *71*, 1852−1855.

(18) Olesen, L.; Lægsgaard, E.; Stensgaad, I.; Besenbacher, F.; Schiotz, J.; Stoltze, P.; Jacobsen, K. W.; Norskov, J. K. *Phys. Rev. Lett.* **1994**, *72*, 2251−2254.

(19) Costa-Kramer, J. L.; Garcia, N.; Garcia-Mochales, P.; Serena, P. A. *Surf. Sci.* **1995**, *342*, L1144.

(20) Yasuda, H.; Sakai, A. *Phys. Rev. B* **1997**, *56*, 1069−1072.

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been directly confirmed by high-resolution transmission electron microscopy.[21] We have recently demonstrated an electrochemical etching/deposition method for fabricating metallic nanowires with quantized conductance.[12,22] In contrast to the mechanical methods, the electrochemical method makes it possible to fabricate arrays of stable nanowires. We have observed that the conductance quantization is sensitive to molecular adsorption.[23,24] We report in this paper a systematic study of adsorbate-induced conductance change in metallic nanowires with conductance quantized at various steps for several different molecules.

Principle

The principle is based on the phenomenon that a conductor changes its conductance upon molecular adsorption onto its surface.[25−27] This phenomenon has been known for decades in the classical regime in which diffusive scattering of electrons determines the conductance. It has attracted renewed interest in recent years because of its direct relevance in chemical sensing and surface frictions.[28] Zhang et al. have recently shown that the self-assembly of thiol compounds onto a Au film can be easily detected by measuring the conductance of the Au film.[29] Several groups have studied the conductance changes of thin-film electrodes due to electrochemically controlled molecular and anion adsorptions.[30−33]

It is widely accepted that the adsorbate-induced conductance change is due to the scattering of the conduction electrons by the adsorbates as the electrons impinge on the surface.[28,34] In some systems, a reduction in the conduction electron density by adsorbates is also believed to play a role.[26,31] For metal films thicker than a few nanometers, the semiclassical models of Fuchs[35] and Sondheimer[36] have been frequently used. Ishida has developed a microscopic theory that allows one to evaluate the conductance change in terms of adsorbate−substrate bonding length and adsorbate−adsorbate distance.[34] Recently, Persson has extended the semiclassical models and developed a simple relation between the adsorbate-induced conductance change and the density of states of the adsorbed molecules, $\rho_a(\epsilon_F)$, at the Fermi energy of the conductor.[28] According to his theory, the conductance change per adsorbate molecule is

$$\frac{\Delta G}{G} \propto -\frac{\Gamma \rho_a(\epsilon_F)}{d} \tag{1}$$

where d is the thickness of the metal film and Γ is the width of $\rho_a(\epsilon)$ that has usually a bell shape. Since different molecules have different $\rho_a(\epsilon_F)$, the conductance change should be specific for each adsorbate, which has been confirmed for classical conductors.[26,28] Equation 1 also shows that the adsorbate-induced conductance change is inversely proportional to the thickness of the film. So, in terms of sensor applications, thinner films mean higher sensitivity.

Based on the above argument, we expect that the atomically thin nanowires give the highest sensitivity. As we have discussed in the Introduction, the conductance of such wires is quantized, and the diffusive electron transport picture used in Persson's theory no longer holds. A theory for the quantum ballistic regime has not yet been fully developed, but the adsorbate scattering is also expected to be an important mechanism. A number of theoretical attempts have been made to calculate the effects of defects in/on metallic nanowires on the quantized conductance.[37−39] Bradbyge et al. have treated a defect by an effective potential superimposed on an otherwise smooth wall of the nanowire.[39] Their numerical calculations as well as tight binding method-based calculations[38] show that the scattering by defects lowers the nanowire conductance, as found in the classical theories. Consequently the conductance steps shift away from the integer multiples of G_0 to fractional values.

Since the nanowire in the last quantum steps consists of only a few atoms,[21] a microscopic theory that treats the individual atoms and adsorbate molecules seems necessary. Landman et al. have simulated the adsorption of a methyl thiol onto a gold nanowire made of a chain of four Au atoms between two well-defined electrodes.[40] They found that the molecule binds strongly to the gold atoms and becomes a part of the nanowire. The final conductance of the molecule−gold nanowire can be even greater than that of the gold nanowire. Using a self-consistent scheme, Lang has calculated the conductance through a chain of three Al atoms connected to Jellium electrodes.[41] Substituting one of the Al atoms with a sulfur atom decreases the conductance. The theoretical works mentioned above predict an adsorbate-induced conductance change, which is the basis of the molecular detection applications of nanowires. However, it is also apparent that a satisfactory theory is far from complete, and experimental data in this area should stimulate further theoretical efforts.

Experiments

The Cu nanowires were fabricated using an electrochemical method that was first demonstrated by us with a scanning tunneling microscope (STM).[22] To fabricate nanowires with long-term stability, the STM setup was replaced with the following two setups. In the first one, a thin Cu wire (diameter of 5−25 μm) was attached to the bottom surface of a solution cell made of Plexiglas (Figure 1a).[12] The wire was coated with a layer of insulation (wax), except for a region of a few micrometers wide near the center. The central region was then exposed to 1 mM $CuSO_4$ + 100 mM H_2SO_4 for electrochemical etching, which was controlled by the electrochemical potential of the wire. The potential was controlled with a home-made bipotentiostat using a Cu quasi reference electrode and a Pt counter electrode. The etching process was monitored by measuring the current through the wire while maintaining a fixed bias voltage (26 mV) between the two ends of the wire. This method does not require sophisticated equipment, but it can

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(21) Ohnishi, H.; Kondo, Y.; Takayanagi, K. *Nature* **1998**, *395*, 780−783.

(22) Li, C. Z.; Tao, N. J. *Appl. Phys. Lett.* **1998**, *72*, 894−897.

(23) Li, C. Z.; Sha, H.; Tao, N. J. *Phys. Rev. B* **1998**, *58*, 6775−6778.

(24) Li, C. Z.; He, H. X.; Bogozi, A.; Bunch, J. S.; Tao, N. J. *Appl. Phys. Lett.* **2000**, *76*, 1333−1336.

(25) Schumacher, D. In *Surface Scattering Experiments with Conduction Electrons*; Hohler, G., Ed.; Springer: New York, 1993; Vol. 128.

(26) Krastev, E. T.; Kuhl, D. E.; Tobin, R. G. *Surf. Sci.* **1997**, *387*, L1051−L1056.

(27) Rauh, M.; Heping, B.; Wissmann, P. *Appl. Phys. A* **1995**, *61*, 587−590.

(28) Persson, B. N. J. *J. Chem. Phys.* **1993**, *98*, 1659−1672.

(29) Zhang, Y.; Terrill, R. H.; Bohn, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 9969.

(30) Tucceri, R. I.; Posadas, D. *J. Electroanal. Chem.* **1985**, *191*, 387−399.

(31) Tucceri, R. I.; Posadas, D. *J. Electroanal. Chem.* **1990**, *283*, 159−166.

(32) Korwer, D.; Schumacher, D.; Otto, A. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1484−1488.

(33) Hanewinkel, C.; Otto, A.; Wandlowski, T. *Surf. Sci.* **1999**, *429*, 255−259.

(34) Ishida, H. *Phys. Rev. B* **1995**, *52*, 10819.

(35) Fuchs, K. *Proc. Cambridge Philos. Soc.* **1938**, *34*, 100.

(36) Sondheimer, E. H. *Adv. Phys.* **1952**, *1*, 1.

(37) Nikolic, K.; MacKinno, A. *Phys. Rev. B* **1994**, *50*, 11 008.

(38) Garcia-Mochales, P.; Serena, P. A. *Phys. Rev. Lett.* **1997**, *79*, 2316.

(39) Bradbyge, M.; Jacobsen, K. W.; Norskov, J. K. *Phys. Rev. B* **1997**, *55*, 2637−2650.

(40) Hakkinen, H.; Barnett, R. N.; Landman, U. *J. Phys. Chem.* **1999**, *103*, 8814−8817.

(41) Lang, N. D. *Phys. Rev. B* **1995**, *52*, 5335−5342.

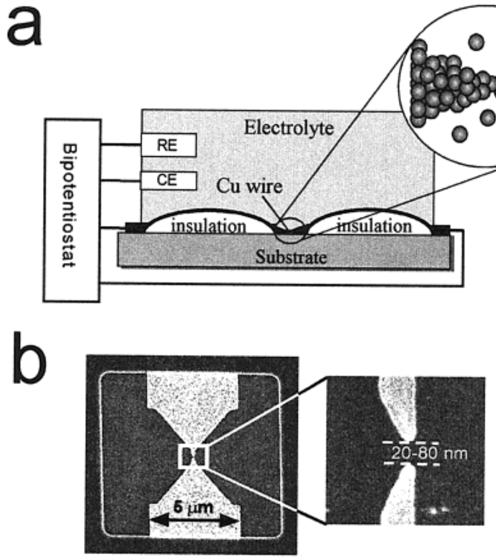

Figure 1. Schematic drawing of the experimental setups. (a) A Cu wire is attached to the bottom surface of a Plexiglas solution cell. The wire is coated with wax, except for a small section that is exposed to 1 mM $CuSO_4$ + 100 mM H_2SO_4 for etching. The electrochemical potential of the wire is controlled by a bipotentiostat with Cu as reference electrode (RE) and Pt as counter electrode (CE). (b) Replacing the setup in (a) with an array of microfabricated Au nanoelectrode pairs. The scanning electron microscopy of one pair of such nanoelectrodes is shown.

be tedious to lay down each wire onto the surface with minimal mechanical stress and then coat the wire with a proper insulation layer.

In the second setup, the starting step was to fabricate an array of Au nanoelectrode pairs on an oxidized Si substrate by electron beam lithography (EBL) and optical lithography (Figure 1b). The nanoelectrodes with spacing from 20 to 80 nm between each pair were patterned in poly(methyl methacrylate) by a Leica VB6 EBL system using a kinetic energy of 100 kV. Trilayer metal (30 Å Ti/ 50 Å Pt/ 500 Å Au) was then evaporated and lifted off; Pt was used as a barrier layer to prevent interdiffusion of Ti and Au in the subsequent processing steps. The nanoelectrodes were connected to the bonding pads via Au lines on the substrate patterned by optical lithography. Finally, the whole substrate was covered with SiN, and small windows of sizes 5×5 μm^2 and 10×10 μm^2 were etched into the SiN around the ends of the nanoelectrodes. This was done to ensure that the exposed surface area of the electrodes is small and the corresponding ionic current is minimal during electrodeposition and etching. The setup is similar to the one used to fabricate nanogaps by Morpurgo et al., except that we coated the electrodes with SiN insulation.[42] A nanowire was formed by electrochemically depositing Cu onto the nanoelectrodes. The thickness of the nanowire was monitored continuously by measuring the conductance of the nanowire and controlled by the electrochemical potential of the wire.

Three molecules, dopamine (Sigma), 2,2′-bipyridine (22BPy) (Aldrich), and mercaptopropionic acid (MPA) (Fluka), were studied in this work. These molecules have different binding strengths to Cu electrodes. Dopamine is an important neurotransmitter, which is expected to weakly adsorb onto Cu (binding strength < ~0.6 kcal/mol).[43] MPA adsorbs onto the electrodes via the strong sulfur−metal bond (binding strength ~44 kcal/mol).[43−45] 22BPY binds to metal electrodes via N−metal interaction (binding strength ~8.4 kcal/mol),[46] which allows individual 22BPY molecules to stand vertically on Au[47,48] and Cu electrodes,[49] as shown directly by STM. The 22BPY binding strength to Cu electrodes is stronger than that of dopamine, but weaker than that of MPA. A 1 mM concentration of each molecule dissolved in the electrolyte was used in the experiment, which was prepared using water from a bioresearch-grade Nanopure system (Barnstead) fed with distilled water.

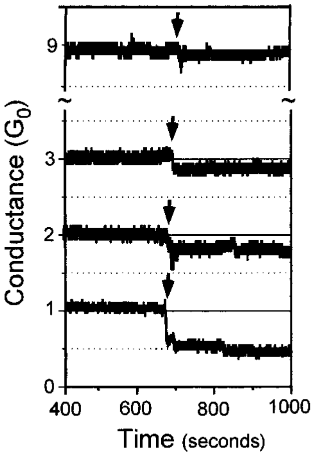

Figure 2. Conductance change of Cu nanowires with conductance quantized at $1G_0$, $2G_0$, $3G_0$, ..., $9G_0$ upon dopamine adsorption from the electrolyte.

Results and Discussions

Using the deposition/etching method described above, we have been able to stabilize a nanowire at a quantized conductance step for many hours. Once a nanowire was stabilized at a chosen quantum step, sample molecules were injected into the solution with a syringe, and the subsequent conductance was monitored and recorded with a DL1520 digital oscilloscope (Yokogawa).

Figure 2 shows the conductance of Cu nanowires quantized at various steps upon introduction of dopamine into the solution cell. For the nanowire with conductance at the lowest quantum step ($1G_0$), the conductance decreased drastically a few seconds after the introduction of a drop of dopamine, and it then stabilized at ~$0.5G_0$. The decrease in the conductance supports the scattering of the conduction electrons by the adsorbates as the dominant mechanism. Adding another drop of dopamine caused no further change, which indicates no further adsorption once the nanowires are covered with the molecules. We have repeated the measurement and found that the time lapse between the introduction of dopamine and the change in the conductance varied from run to run. This is probably because the diffusion of a few molecules onto the nanowire was not well controlled in the experiment.

The observed conductance change is not due to mechanical disturbance during the injection of the sample solution into the cell. We minimized the mechanical disturbance by fixing the syringe to a support and inserted the needle of the syringe into the solution at a spot far away (~1 cm) from the nanowire. To ensure that the mechanical disturbance was indeed minimal, we added blank electrolyte into the cell in the same way and found no visible change in the quantized conductance.

We have studied the nanowires with conductance stabilized at higher quantum steps in a similar way. For a nanowire at the

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(42) Morpurgo, A. F.; Marcus, C. M.; Robinson, D. B. *Appl. Phys. Lett.* **1999**, *14*, 2082.

(43) Giz, M. J.; Duong, B.; Tao, N. J. *J. Electroanal. Chem.* **1999**, *465*, 72−79.

(44) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437−463.

(45) Widrig, C. A.; Alves, C. A.; Porter, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 2805−2809.

(46) Yang, D.; Bizzotto, D.; Lipkowski, J.; Pettinger, B.; Mirwald, S. *J. Phys. Chem.* **1994**, *98*, 7083−7089.

(47) Cunha, F.; Tao, N. J. *Phys. Rev. Lett.* **1995**, *75*, 2376.

(48) Cunha, F.; Tao, N. J.; Wang, X. W.; Jin, Q.; Duong, B.; D'Agnese, J. *Langmuir* **1996**, *12*, 6410.

(49) Tao, N. J.; Li, C. Z., unpublished.

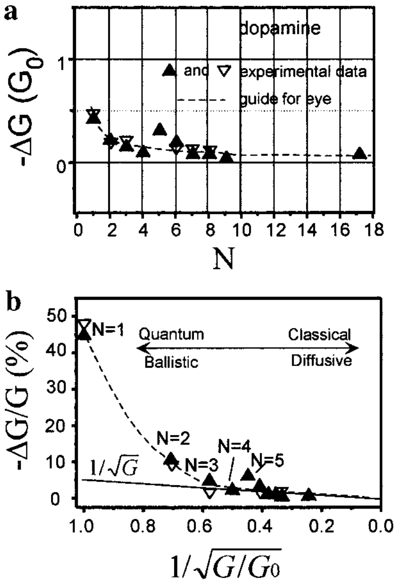

Figure 3. (a) Dopamine-induced conductance change ($-\Delta G$) vs number of conductance step (N). (b) The relative change, $-\Delta G/G$ vs $1/G^{1/2}$, for various quantum steps (N). The solid line marks the limit of the semiclassical theories for diffusive scattering. The slope of the solid line is ~0.05, which reflects the binding strength between dopamine and the Cu nanowires. Note that the conductance change is negative.

second step ($2G_0$), dopamine adsorption caused also a sharp decrease in the conductance, but the net change is about $0.25G_0$, much smaller than that of the first quantum step. For a nanowire at the third step ($3G_0$), the decrease is even smaller. At the 17th conductance step, the decrease becomes too small to be accurately measured with our current setup. We found that stabilizing a nanowire at a high conductance step precisely was more difficult than that at a low quantum step. This is consistent with the previous statistical analysis of mechanically formed nanowires, which shows well-defined peaks in the conductance histograms only for the first 5 or 6 steps.[16,17]

We summarize the above observation by plotting the conductance change, ΔG, versus the quantum step, N, in Figure 3a (note that the change is negative). Some repeated data are also plotted in the figure as open triangles to illustrate the reproducibility of the measurement (we will return to this later). A more meaningful quantity is the relative conductance change, $-\Delta G/G$, which is plotted in Figure 3b. The relative change is as high as 50% for the first conductance step, but it decreases rapidly at higher steps as the quantum regime is eventually replaced by the classical diffusive scattering regime. So, in terms of chemical sensor applications, a nanowire with conductance at the lowest quantum step gives the highest sensitivity.

The observation that the adsorbate-induced conductance change increases as the diameter (d) of the nanowire decreases is not surprising according to eq 1, from the semiclassical Persson's theory.[28] Because the number of the quantum modes is proportional to the square of the nanowire diameter, we have $G = NG_0 \sim d^2$ or $d \sim G^{1/2}$. Substituting this relation into eq 1, we have

$$-\frac{\Delta G}{G} \sim \Gamma\rho(E_f)\,\frac{1}{G^{1/2}} \tag{2}$$

The dependence of the conductance change on the nanowire thickness can also be understood from a simple geometric surface-to-volume ratio argument. Assuming a cylindrical nanowire of length L, the surface area and volume are $2\pi dL$ and πd^2L, respectively, which leads to $\Delta G/G \sim 2\pi dL/\pi d^2L \sim 1/d$, the same thickness dependence as in eq 1. To examine the above relation, we plotted $-\Delta G/G$ versus $1/G^{1/2}$ in Figure 3b. A solid straight line in the figure marks the simple dependence by eq 2. The slope of the straight line is proportional to $\Gamma\rho_s(E_F)$, which depends on the electronic states of the adsorbate. For high-conductance steps that correspond to thicker nanowires, the experimental data can be roughly described by the simple dependence with a slope of ~0.05. However, for the conductance at the lowest few steps, $-\Delta G/G$ increases much faster than $1/G^{1/2}$ as G decreases. The failure of the semiclassical theories and the geometrical argument may be attributed to the following reasons. A nanowire with a conductance at the lowest quantum steps is determined by only a few atoms, so virtually every atom is a surface atom and the nanowire cannot be simply treated as a cylinder with a smooth wall. As found by the molecular dynamics simulations, the adsorbate molecules may get incorporated into the nanowires.[40]

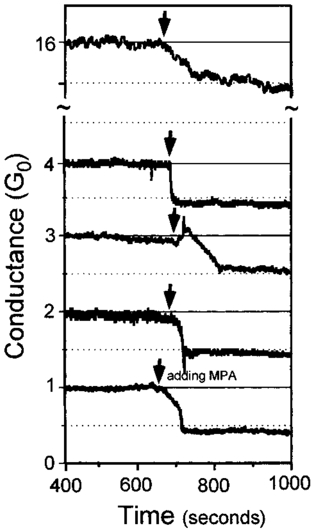

Figure 4. Conductance change of Cu nanowires with conductance quantized at $1G_0$, $2G_0$, $3G_0$, $4G_0$, ..., $16G_0$ upon MPA adsorption from the electrolyte.

Figure 4 shows the conductance change due to the adsorption of MPA onto Cu nanowires stabilized at various conductance steps. At the first quantum step ($1G_0$), the adsorption induces a decrease in the conductance by ~$0.6G_0$, which is somewhat greater than that of dopamine. At higher quantum steps, the MPA-induced conductance change stays more or less the same. This observation is in sharp contrast to the dopamine-induced change that diminishes quickly as the conductance increases to higher quantum steps. In fact, a change of ~$0.5G_0$ was observed even for a nanowire with conductance at $16G_0$. The effect of MPA adsorption on the quantized conductance is much greater than that of dopamine, which is consistent with the relative binding strengths of the two molecules to Cu electrodes.

We plotted the conductance change as a function of the quantum step in Figure 5a. The plot shows clearly that the MPA-induced conductance change depends only slightly on the number of the quantum step. The relative change of the conductance, $-\Delta G/G$, is plotted versus $1/G^{1/2}$ in Figure 5b. Similar to what we found for dopamine, $-\Delta G/G$ increases as G decreases, and the increase follows the $1/G^{1/2}$ dependence (the straight solid line) only for high-conductance steps. The slope of the straight line is about 0.25, much greater than that of dopamine. Below $5G_0$, $-\Delta G/G$ increases much faster than $1/G^{1/2}$.

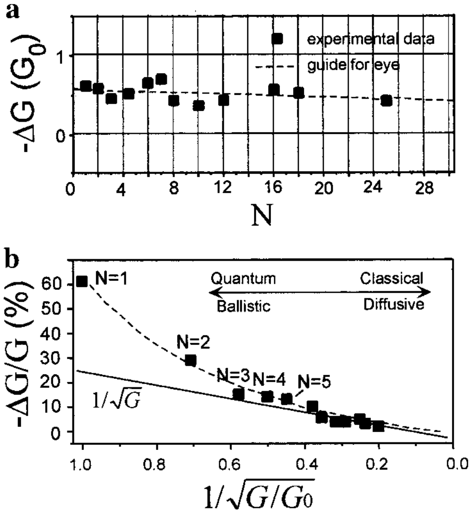

Figure 5. (a) MPA-induced conductance change ($-\Delta G$) vs number of conductance step (N). (b) The relative change, $-\Delta G/G$ vs $1/G^{1/2}$, for various quantum steps (N). The solid line marks the limit of the semiclassical theories for diffusive scattering. The slope of the solid line is ~0.25, reflecting a stronger binding of MPA to Cu than that of dopamine.

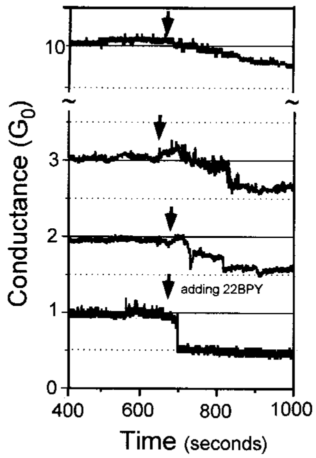

Figure 6. Conductance change of Cu nanowires with conductance quantized at $1G_0$, $2G_0$, $3G_0$, ..., $10G_0$ upon 22BPY adsorption from the electrolyte.

Upon the adsorption of 22BPY, the conductance of Cu nanowires also shifts to lower values (Figure 6). Similar to the case with dopamine, the 22BPY-induced conductance change diminishes as the conductance increases to higher steps, but it diminishes more slowly than the dopamine-induced change (Figure 7a). For example, the conductance change for 22BPY is measurable even at $30G_0$, where the change for dopamine diminishes almost completely. The relative conductance change, $-\Delta G/G$, changes linearly with $1/G^{1/2}$ for large G, but much faster than $1/G^{1/2}$ for G below $5G_0$ (Figure 7b). These observations are similar to those with dopamine and MPA, except that the slope for large G is about 0.1, smaller than that with MPA but greater than that with dopamine.

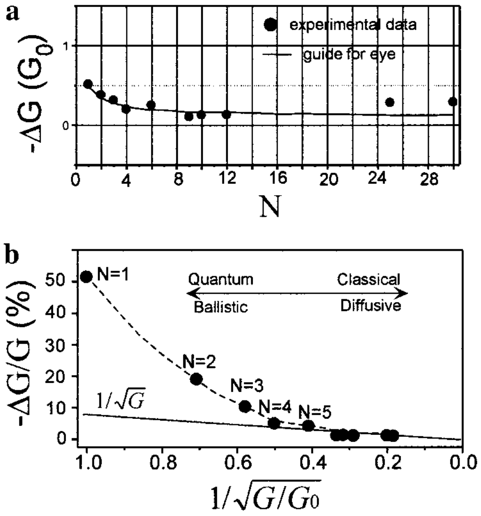

Figure 7. (a) 22BPY-induced conductance change ($-\Delta G$) vs number of conductance step (N). (b) The relative change, $-\Delta G/G$ vs $1/G^{1/2}$, for various quantum steps (N). The solid line marks the limit of the semiclassical theories for diffusive scattering. The slope of the solid line is ~0.1, reflecting a 22BPY binding stronger than that of dopamine but weaker than that of MPA.

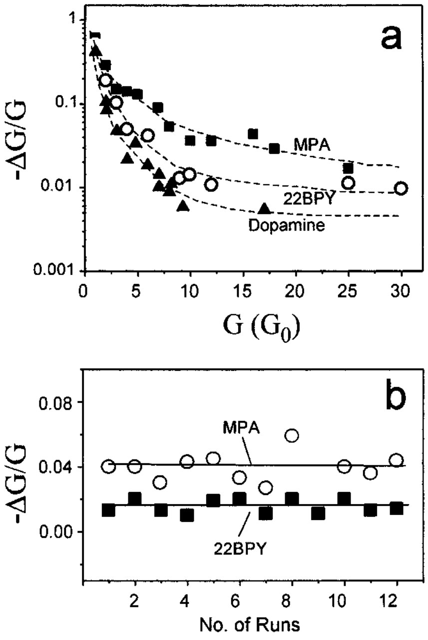

Figure 8. (a) Comparison of dopamine-, MPA-, and 22BPY-induced conductance changes of a Cu nanowire with conductance at various quantum steps. The changes are consistent with the relative binding strengths of the three molecules. Due to the rapid decay in the changes, a logarithmic scale is used. (b) Repeated measurements of MPA- and 22BPY-induced conductance changes of nanowires quantized at $10G_0$. Each data point was obtained from a freshly fabricated nanowire from different chips in order to minimize contaminations.

As we have pointed out, the slope of the classical $1/G^{1/2}$ dependence reflects the binding properties of the molecules to the nanowires, which is consistent with the relative strengths of binding of the three molecules to Cu electrodes. Figure 8a compares the relative conductance changes, $-\Delta G/G$, versus G for the three molecules. Despite large fluctuations in the data, it is clear that they all decrease as G increases, which is fully expected. The figure shows also that MPA induces the greatest change, dopamine the least, and 22BPY in between, which is again in accordance with the relative binding strengths of the three molecules. Figure 8b plots data from 11 independent measurements, which shows that the differences between different molecules are not due to experimental errors.

After introducing molecules into the solution, we frequently observed fluctuations in the conductance (Figure 9a). These fluctuations tend to be stepwise and may be attributed to the rearrangement of the adsorbed molecules or the Cu atoms in the nanowires. The latter is expected because the strong binding

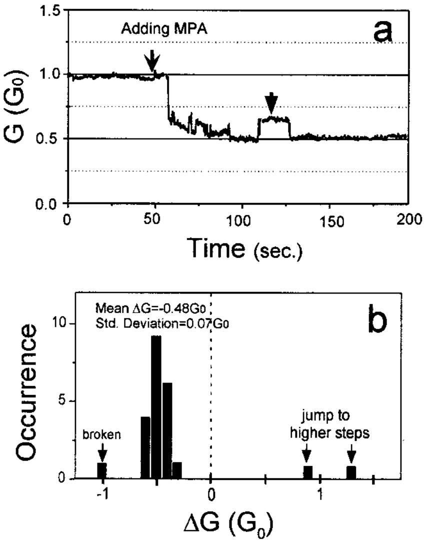

Figure 9. (a) Stepwise fluctuations (arrows) are frequently observed in the adsorbate-induced conductance change. (b) A histogram of 22BPY-induced conductance changes in nanowires quantized at $1G_0$. Each data point was obtained from a freshly fabricated nanowire from different chips in order to minimize contaminations.

between the molecules and metal atoms weakens the binding between metal atoms and thus leads to rearrangement in the atomic configuration of the nanowires. The conductance can sometimes fluctuate to a higher conductance step and stabilize on the step for a long time. This may be attributed to the fact that the metal atoms settle down to a new atomic configuration of a higher conductance step after adsorbate-induced rearrangement. This fluctuation is a source of run-to-run deviations in conductance changes (Figure 9b).

The conductance is dominated by the narrowest portion of the quantum wire, which has been revealed to be a chain of 2−4 atoms at the lowest quantum step.[21] Even for a wire with conductance quantized at the 10th step, it is still only a few atoms thick. Given the dimensions of the wires and molecules, it is likely that only one or a few molecules are able to adsorb onto the quantum wire. So, the conductance changes in the wires at the lowest quantum steps may be triggered by a single molecule. In terms of sensor applications, a single molecule may be detectable from the conductance changes. However, the response time depends on how quickly an analyte molecule finds a quantum wire, which is clearly a function of analyte concentration. This is in sharp contrast to most conventional sensors that detect a large ensemble of molecules, and in which the analyte concentration is proportional to the detected signal. The conventional sensitivity defined by an analyte concentration for a detectable change of signal is thus not applicable here. Improvement in the response time (or sensitivity in the conventional sense) can be achieved by using a large array of nanowires and by forcing analyte-containing solution to flow through the nanowire region. Molecular adsorption changes the conductance via scattering of conduction electrons, which depends on the adsorbate electronic states and is, therefore, expected to be specific. Our experiments show different conductance changes for different molecules. One way to improve specificity is to measure the conductance more accurately using a bridge method. Another way is to take advantage of molecular recognition by coating the nanowire with receptor molecules. The binding of a target molecule to the receptor molecules causes a change in the conductance of the nanowire and can be detected. We will explore these possibilities in the future.

Summary

We have fabricated Cu nanowires with conductance quantized at various integer steps using an electrochemical etching and deposition method. We have studied the change in the quantized conductance upon adsorption of dopamine, MPA, and 22BPY. The conductance decreases as the molecules adsorb onto the nanowires, which is attributed to the scattering of the conduction electrons by the adsorbates. The relative conductance change is as large as ∼50% for the nanowires with conductance quantized at the lowest step, $1G_0$, but it diminishes at higher conductance steps, where classical diffusive scattering eventually takes over. This observation shows that the highest sensitivity is found with the nanowires at low quantum steps, corresponding to a few atoms in thickness. While the thickness-dependent sensitivity is expected from the semiclassical theory as well as the simple surface-to-volume ratio argument, these theories deviate significantly from the experimental data for the thinnest nanowires. The adsorbate-induced conductance change depends on the strengths of absorption of the molecules to the nanowires. MPA induces the largest change, dopamine the least, and 22BPY in between, consistent with the relative strengths of binding of the three molecules to Cu electrodes.

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