Adsorbate effect on conductance quantization in metallic nanowires

C. Z. Li, H. Sha, and N. J. Tao*
Department of Physics, Florida International University, Miami, Florida 33199
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We have studied conductance quantization in metallic nanowires upon adsorption of molecules with different adsorption strengths. The conductance still changes in a step-wise fashion even in the presence of strong adsorption, and the average sharpness, length, and number of the conductance steps remain unchanged. However, the step positions deviate significantly from the integer values of the conductance quantum, $2e^2/h$. While the deviation may be attributed to the scattering of the ballistic electrons by the adsorbates, evidence shows that the adsorbates also affect conductance by changing the atomic configurations of the nanowires.
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It has been found for many years that the electrical conductivity of metals decreases upon adsorption of atoms and molecules because of the scattering of the conducting electrons by the adsorbates.[1–3] The studies, however, have been largely limited to nonballistic electron transport in which the electron mean free path is much smaller than the dimension of the metals. In the present paper, we study the adsorbate effect on ballistic electron transport in metallic nanowires. The conductance of the nanowires has been observed to vary in a stepwise fashion in which the steps occur at the integer values of conductance quantum, $G_0=2e^2/h$, when the wire width is decreased to the atomic scale.[4–11] We find that upon adsorption of molecules at the nanowires, the conductance steps are still well defined but the step positions deviate significantly from the integer values of G_0.

Metallic nanowires, in which electron transport ballistically, have been created by mechanically breaking a fine metal wire,[4] by separating a tip and a flat substrate,[5–10] or two macroscopic electrodes in contact,[11] by anodizing Al nanowires with an atomic force microscope,[12] and by electrochemical deposition.[13] In this paper, we use the tip-flat substrate setup in which a gold tip is placed over a gold film epitaxially grown on mica. Instead of vertically driving the tip into and out of the substrate,[5–10] we create the nanowires by sweeping the tip horizontally across the substrate surface with a modified scanning tunneling microscope (STM). The substrate is first roughened by scanning an area with a large tunneling current. A contact is made when the tip moves into a bump on the substrate, and pulling out of the contact results in the formation of a nanowire (Fig. 1). This method allows us to rapidly sample the conductance of the nanowires formed in different surface areas. The tip is swept at a rate of 100 nm/s and the bias voltage is typically set at 26 mV. The preamplifier was modified such that it could sustain a current load of tens of μA without affecting the bias voltage. We note that simply reducing the gain of a standard STM preamplifier usually results in a smaller bias voltage at large current, which shifts the conductance peaks in the histograms towards lower conductance values. The conductance vs time traces are recorded using a 200-MHz digital oscilloscope (Yokogawa) interfaced to a personal computer. The nonideal differential linearity of the oscilloscope is corrected in the data analysis. The tip and substrate are isolated from the rest of the setup using an environmental chamber (Molecular Imaging Co.) into which various species are introduced for adsorption. We have chosen three species, ethanol, pyridine, and 4-hydroxyl thiophenol (4 HTP) in this study because their adsorption strengths vary from weak physisorption ($<k_BT\sim0.025$ eV) to intermediate adsorption (~0.5 eV) and to very strong chemisorption (~2 eV). We compare the results with those in N_2. In order to maximize the chance of observing the adsorbate effect, we used saturated vapor in each of the cases. From the vapor concentrations, the average rate for molecules to directly collide with the narrowest portion of a nanowire is greater than 10^8/sec. The lifetime of the nanowire is in the order of many ms, during which the molecules can make more than 10^5 attempts to adsorb onto the nanowires. In addition, the molecules can first adsorb onto the thicker portion of the nanowire and then diffuse to the narrowest portion. For these reasons, we believe that the nanowire has a high probability to have molecules adsorbed onto its narrowest portion.

The conductance histograms of the nanowires in N_2, ethanol, pyridine, and 4HTP are shown in Fig. 2. Each histogram is constructed from $\sim$1000 traces. To ensure that 1000 traces provide reasonable statistics, we have performed three or more experiments in each case. Histograms of two typical 1000-trace experiments for N_2 are plotted in Figs. 2(a) and 2(b), which show good reproducibility of the histograms based on 1000 traces. The overall shape of the first three

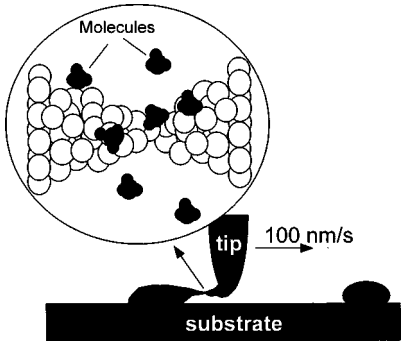

FIG. 1. Molecular adsorption at metallic nanowire formed pulling a gold STM tip away from a contact with a gold substrate horizontally.

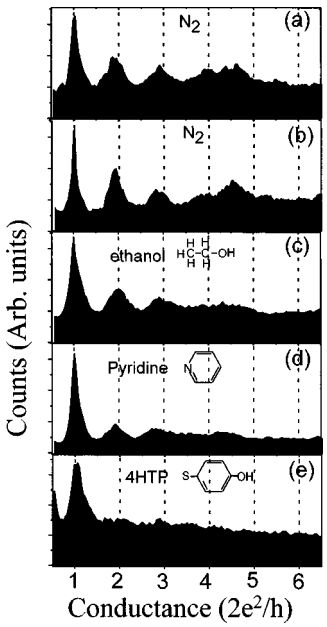

FIG. 2. Conductance histograms of gold nanowires in N_2 (a) and (b), vapors of ethanol (c), pyridine (d), and 4HTP (e). Each histogram is constructed from over a thousand traces.

peaks and the shift of the second and third peaks toward smaller conductance values are similar to the data obtained at liquid-helium temperature in vacuum.[14] Between $4G_0$ and $5G_0$, there is a broad peak that is observed in each of our nine separate measurements and in the histograms constructed from 10 000 traces using a gold-contact relay setup.[15] The origin of the broad peak is not yet understood. In the presence of ethanol vapor, the first three peaks are still visible, but the second and third peaks decrease relative to the first [Fig. 2(c)]. When replacing ethanol with pyridine, the second and third peaks decrease even more [Fig. 2(d)]. Finally, in 4HTP vapor, the second and third peaks are completely smeared out in the histogram and the first peak is also broadened considerably [Fig. 2(e)]. The degree of the adsorbate effect are consistent with the adsorption strengths of the three adsorbates.

The adsorbate-induced smearing-out of the peaks in the conductance histograms is not due to the disappearance of the conductance steps. Figure 3 shows two typical conductance traces in N_2 and in 4HTP vapor. In N_2 [Figs. 3(a) and 3(b)], well-defined conductance steps occur preferentially near the integer values of G_0. In the presence of 4HTP [Figs. 3(c) and 3(d)], the conductance steps are still well defined, but most steps deviate significantly from the integer values of G_0. The amount of deviation varies from trace to trace, which we will discuss later. The corresponding histogram (or derivative) of the trace yields peaks at noninteger values [Fig. 3(d)]. The steps in ethanol and pyridine vapors also tend to shift away from the integer values, but they occur less frequently than those in 4HTP.

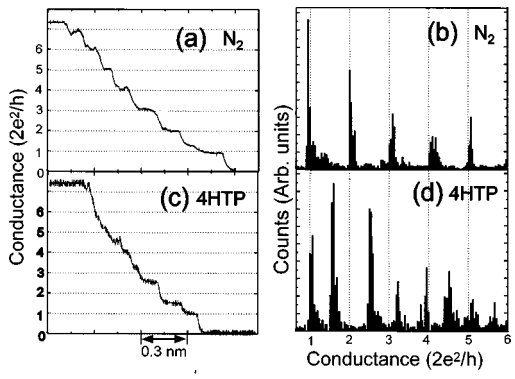

FIG. 3. Typical conductance traces recorded as the tip is pulled away from contacts with a gold substrate in N_2 (a) and in 4HTP (b).

TABLE I. Average number, length, and smoothness of conductance steps in N_2, vapors of ethanol, pyridine, and 4HTP, where the length is the distance over which a nanowire can be pulled before jumping to other conductance steps, and the smoothness is the full width at half maximum of each peak in the derivative of a conductance trace. The standard deviations of the averages are also given (after $\pm$ sign). To illustrate the reproducibility of the data, results from two separate experiments in N_2 and 4HTP are shown.

Adsorbate	Average number of steps	Average length per step (nm)	Average sharpness per step ($2e^2/h$)
N_2	5.9 ± 0.3	0.13 ± 0.01	0.1 ± 0.01
N_2	5.4 ± 0.3	0.12 ± 0.01	0.1 ± 0.01
Ethanol	5.9 ± 0.3	0.11 ± 0.01	0.1 ± 0.01
Pyridine	6.0 ± 0.3	0.12 ± 0.01	0.1 ± 0.01
4HTP	6.3 ± 0.3	0.12 ± 0.01	0.1 ± 0.01
4HTP	6.1 ± 0.3	0.13 ± 0.01	0.1 ± 0.01

The above observations based on the individual conductance traces are supported by a careful statistical analysis of the average length, smoothness, and number of the conductance steps between $0G_0$ and $6.5G_0$ (Table I). The average length is the average distance over which a nanowire can be pulled before the conductance jumps to a lower step. We calculate the average length from the average time duration of the steps and the rate that a nanowire is being pulled. The average length in each of the four cases is about 0.12 nm, which is in good agreement with the values reported in literature.[8,16] This value is independent of the pulling rate. We have varied the rate from 100 nm/s to 100 000 nm/s: the average step length stays the same. Note that the standard deviation in the length is as small as 0.01 nm, which indicates that the majority of the steps have lengths close to 0.12 nm. The average smoothness characterizes how well defined the conductance steps are, which is measured in terms of the full-width at half maximum of the peaks in the derivatives of the conductance traces [e.g., Figs. 3(b) and 3(d)]. The data show the steps in the four cases are about equally well defined and the standard deviation from the average is also fairly small. We determine the average number of the conductance steps by counting the number of peaks in the derivative of each conductance trace. In order to avoid miscounting noise as steps, we count only those peaks with corresponding steps longer than 0.04 nm and sharper than $0.3G_0$. Since the step lengths and smoothness are distributed within narrow ranges, the average number of steps are not very sensitive to the above criterion. What is more important is that the same criterion has been used for determining the average numbers of steps in N_2, ethanol, pyridine, and

4HTP. In all the four cases, we found that the average number is close to six, which means that the average separation between two adjacent steps is about G_0 even in the presence of strong adsorption.

Based on the statistical analysis described above, it is clear that the major adsorbate effect on the conductance of the nanowires is to shift the conductance steps away from the integer values of the conductance quantum. This may be understood from the scattering of the conduction electrons by the adsorbates. In the case of nonballistic electron transport, the scattering is known to lower the conductivity of metals, and microscopic theories have been successfully developed.[2,3] In ballistic electron transport, an appropriate theory is not yet available but electron scattering by a localized repulsive scatterer at a metallic nanowire and its effect on the conductance quantization has been modeled.[17] If considering adsorbate molecules as individual local scatterers, some of our observations can be explained based on this model. First, the model shows that the scattering can drastically shift the conductance steps from integer values. Second, the model predicts that the amount of deviation is sensitive to location of the scatterer, which explains the smearing out in the peaks in the conductance histograms because of the variation in the adsorption site in the experiment. However, the model predicts a smoothening in the conductance steps, which is not observed. Furthermore, the model shows all the conductance steps can be affected by the presence of the localized scatterer, while we observe that the lowest conductance step is largely unaffected. Evidence discussed below suggests that, in order to fully understand the experimental results, adsorbate effect on the atomic configurations of the nanowires has to be considered.

Because adsorbates affect the lowest conductance step far less than higher steps, it is of interest to analyze the effect on individual steps. We have extracted the occurrence frequency, length, and smoothness of the steps at various conductance values (Fig. 4). These plots provide more detailed information than the histograms (Fig. 2), which count the total number of data points occurs at each conductance value. In the case of N_2, the step occurrence and length have well-defined peaks around the integer values of conductance, which shows that the peaks in the conductance histograms in Fig. 2 are not only because the steps near the integer values occur more often but also because they last longer. In addition, the smoothness plots show that the conductance steps are more well defined near the integer values. In the presence of strong adsorption (4HTP), the steps still occur preferentially around $1G_0$, but their preference to occur at higher integers of G_0 is lost [Fig. 4(a)]. In the presence of weaker adsorption (ethanol and pyridine), the situations are somewhere in between. The length of the conductance step at $1G_0$ in the presence of adsorption is even longer than that in N_2, while the lengths of higher conductance steps are considerably shorter [Fig. 4(b)]. A previous study has directly shown that the occurrence of each conductance step is always associated with an abrupt rearrangement in the atomic configuration of a nanowire as the nanowire is being pulled.[8] Our observation shows that the adsorption at a nanowire can change the distance over which a nanowire can be pulled for each successive atomic rearrangement. This indicates that the adsorbates can affect the conductance of the nanowires not only by scattering the electrons but via affecting the stability of the atomic configurations of the nanowires. This observation is consistent with the recent experimental and theoretical works that show the importance of the interplay between the atomic configuration and conductance quantization.[8,18–19] While the adsorption affects the lengths of $1G_0$ step and high integer value steps in different ways, it changes little the step smoothness [Fig. 4(c)] of steps at various values.

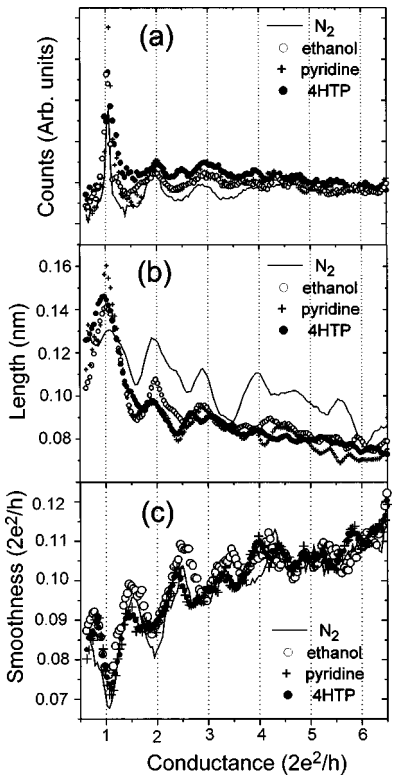

FIG. 4. Occurrence frequency (a), length (b), and smoothness (c) of the conductance steps at various conductance values.

In conclusion, we have studied quantum transport in gold nanowires in the presence of molecular adsorbates with different adsorption strengths. While the peak near the first integer value in the conductance histograms persists, the peaks at higher integer values smear out according to the strength of the adsorption. The smearing out is caused by the shift of the conductance steps away from the integer values and the conductance steps remain well defined. The shift in the conductance step may be attributed to the scattering of the conduction electrons by the adsorbates, but the adsorbates also affect the conductance by changing the stability of the atomic configurations.

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*Author to whom correspondence should be addressed. Electronic address: taon@fiu.edu

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