Fractional Conductance Quantization in Metallic Nanoconstrictions under Electrochemical Potential Control

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We study the electrical conductance of gold nanoconstrictions by controlling the electrochemical potential. At positive potentials, the conductance is quantized near integer multiples of $G_0 (2e^2/h)$ as shown by well-defined peaks in the conductance histogram. Below a certain potential, however, additional peaks near $0.5G_0$ and $1.5G_0$ appear in the histogram. The fractional conductance steps are as stable and well defined as the integer steps. The experimental data are discussed in terms of electrochemical-potential-induced defect scattering and Fermi energy shift, but a complete theory of the phenomenon is yet to be developed.

The electrical conductance through a narrow constriction with a width of the order of the electron wavelength is quantized in units of $G_0 = 2e^2/h$, where the factor 2 comes from spin degeneracy. This interesting phenomenon has been observed in semiconductor devices containing a two-dimensional electron gas in which the width of the constriction is controlled by applying a voltage to the gate electrode [1,2]. In three dimensions a similar stepwise change in conductance has also been observed in atomic scale metal contacts or nanoconstrictions. These nanoconstrictions are created by mechanically separating two conductors in contact [3–5] and by electrochemically etching macroscopic wires down to atomic scale [6].

In this paper, we control the electrochemical potential of the nanoconstrictions relative to a reference electrode in electrolyte (Fig. 1) [7]. This is in analogy to the gate electrode potential in semiconductor devices, which changes the carrier density of the region underneath the gate electrode. By controlling the electrochemical potential, the charge of the nanoconstrictions can be varied [8]. For example, lowering the potential raises the Fermi energy level of the nanoconstrictions, corresponding to a negative charge or excessive electrons in the nanoconstrictions. The negative charge is balanced by cations near the nanoconstriction in the electrolyte. For a macroscopic metal wire, the excessive electrons give rise to an increase in the density of electrons over only a distance of a few Å from the surface. For a nanoconstriction made of a single or a few atoms, the density changes over a significant volume of the nanoconstriction and it may, therefore, on the other hand, have a greater impact on the conductance. At positive potentials, we observed well-defined peaks near integer multiples of G_0 in the conductance histograms, which are similar to those in vacuum and in air [9]. However, as the potential decreases, peaks near half multiples of G_0 become increasingly pronounced and coexist with the peaks at integer multiples of G_0. The unexpected findings are discussed in terms of different models.

The nanoconstrictions in this work were created by driving a scanning tunneling microscopy (STM) tip into and out of contact with a gold substrate at a typical rate of 40 nm/s in an electrochemical cell. The time response of a STM I/V converter is about 10 kHz. The tip was made of gold (99.999%, diameter ~0.25 mm) wire, which was coated with Apiezon wax to eliminate ionic conduction. The gold substrate was a gold thin film evaporated on mica in a UHV chamber. The experiment was performed in an electrochemical cell mounted in a chamber that was filled with high purity N_2 gas to reduce contamination. The electrochemical potential of the nanoconstrictions was controlled using a bipotentiostat (Pico-Stat, Molecular Imaging Co.) with respect to a Ag wire (0.5 mm diameter) quasireference electrode that was placed ~1 mm from the nanoconstriction. The potential is, however, quoted in terms of the widely used Ag/AgCl reference electrode, whose scale is ~-4.63 V [10] below the vacuum scale in solid state physics. Thus, the Fermi energy of the nanoconstriction, $E_F = -4.63$ eV $- eE_{AgCl}$, where E_{AgCl} is the electrochemical potential of the nanoconstriction in terms of Ag/AgCl scale. A 0.25-mm-diam Pt wire
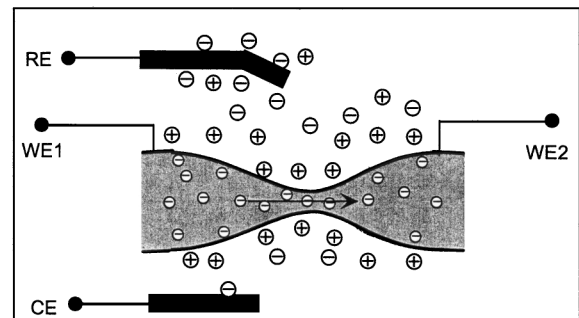

FIG. 1. Schematics of a nanoconstriction under electrochemical-potential control. The potential is controlled with respect to a reference electrode (RE) in the electrolyte. The potential difference between the two ends (WE1 and WE2) of the nanoconstriction is maintained constant (52 mV) during the experiment. A counter electrode (CE) was also used as in a standard electrochemical setup. In comparison to a field effect transistor, the RE, WE1, and WE2 electrodes are analogous to the gate, source, and drain electrodes.

was used as a counterelectrode. The electrolyte was 0.1 M $NaClO_4$ prepared from high purity chemicals and nanopure water. The fractional conductance steps were also observed in 0.1 M $HClO_4$ electrolyte. The transient conductance traces were recorded using a 100 MHz digital oscilloscope (Yokogawa) with a sampling rate of 100 kHz. The nonideal differential linearity of the oscilloscope was corrected in the data analysis.

Figure 2(a) shows the conductance histograms at various potentials. At positive potentials, well-defined peaks appear near integer multiples of the G_0. These peaks persist even when the potential is raised to ~ 1 V, where oxidation of gold begins to take place. By decreasing the potential to -0.5 V, a peak appears near $0.5G_0$, which increases rapidly in height and even surpasses the peak near $1G_0$ below -0.8 V. The fractional conductance peak is about as sharp as the $1G_0$ peak in the histograms. Carefully examining the histograms below -0.5 V reveals a small peak near $1.5G_0$ (arrows). de Heer *et al.* have observed fractional conductance near $G = \frac{1}{2}G_0, \frac{2}{3}G_0, \frac{3}{4}G_0, \ldots$ as weak peaks superimposed on pronounced integer peaks in the histograms [11]. The fractional conductance peaks in this work are different in several ways: They occur only near half multiples of G_0, and they are as pronounced as the integer peaks and are electrochemical-potential dependent. The electrochemical-potential-dependent fractional conductance quantization is illustrated more clearly by the correlation histograms [Fig. 2(b)] which show the proba-

bility of each conductance step *in the presence* of the $0.5G_0$ step. The correlation histograms are constructed by selectively counting the conductance traces that have steps near $0.5G_0$. These histograms clearly show that the fractional and integer conductance steps have a high probability to appear simultaneously in each of the conductance measurements. Therefore, the occurrence of the fractional conductance steps is not due to a simple shift of the integer steps by $0.5G_0$ (see also inset of Fig. 3). Instead, the conductance appears to be quantized with a spacing of $0.5G_0$.

The fractional conductance steps do not show up in every conductance trace, but their population increases rapidly when decreasing the potential below -0.5 V. This trend is demonstrated in Fig. 3 which plots the ratio of the fractional step population to the integer step population from several experiments. Although there is a large fluctuation, due to a limited number of samples, from run to run, the general trend of rapid increase in the population of the fractional steps below -0.5 V is reproducible.

In order to quantify how well defined the fractional conductance steps are, we have extracted the step length and smoothness (Fig. 4) [12]. The step length measures the distance over which a nanoconstriction can be elongated before its conductance jumps to another step. Because each conductance jump corresponds to a rearrangement in the atomic configuration of the nanoconstriction, this quantity provides information about the stability of each atomic configuration upon elongation. The step length is obtained from the time duration of a conductance step and the elongation rate is controlled by the STM piezoelectric transducer. At positive potentials, the step length exhibits well-defined peaks near integer multiples of G_0 [Fig. 4(a)], demonstrating that the atomic configurations with integer values of conductance not only occur more frequently but
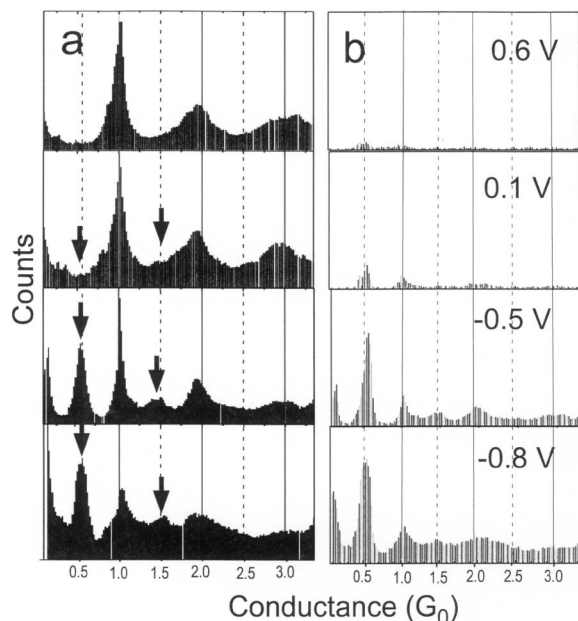

FIG. 2. (a) Conductance histograms of gold nanoconstrictions at various potentials. Each histogram was obtained from over one thousand conductance traces. (b) Correlation histograms that show the occurrence of steps at various conductance values in the presence of a step near $0.5G_0$. The correlation histograms were constructed from those conductance traces that have a step near $0.5G_0$.
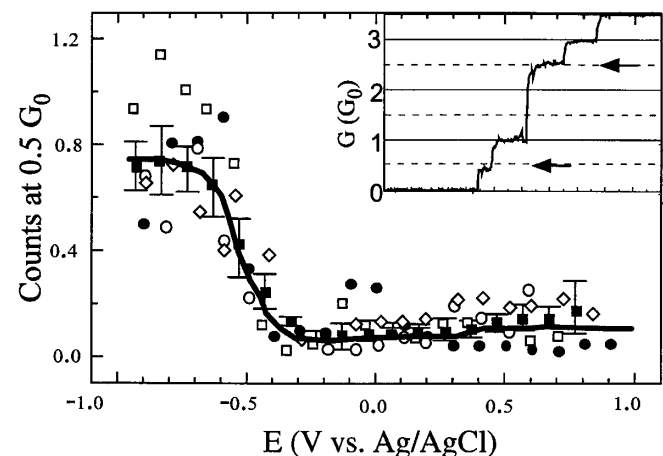

FIG. 3. The ratio of the number of steps near $0.5G_0$ to that near $1G_0$ as a function of the electrochemical potential. Different symbols represent data points obtained in several different experiments. The solid line is a guide for the eye. Inset: a typical conductance trace that shows both fractional and integer conductance steps.
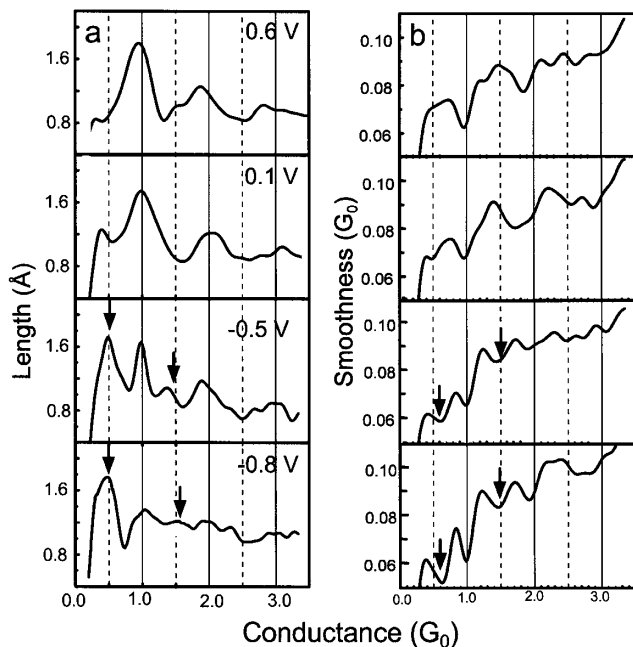
FIG. 4. (a) Step length distribution as a function of the potential. (b) Step smoothness distribution as a function of the potential.

also last longer upon elongation than an arbitrary configuration. Lowering the potential to −0.5 V, additional peaks at the fractional values begin to appear. Therefore, the atomic configurations corresponding to fractional conductance steps also last longer upon elongation than an arbitrary atomic configuration.

The smoothness measures how well defined each step is. The quantity is defined as the full width at half maximum of the peaks in the derivatives of the conductance traces. At positive potentials, well-defined dips appear near the integers, which shows that the steps near integer multiples of G_0 are more well defined than a step with an arbitrary conductance [Fig. 4(b)]. By decreasing the potential, however, dips at $0.5G_0$ and $1.5G_0$ begin to appear, showing clearly that the fractional conductance steps are also better defined.

Our observations can be summarized as follows: (1) The repeated conductance measurements of gold nanoconstrictions under electrochemical-potential control contain traces with conductance steps near half multiples of G_0. (2) The percentage of the traces with the fractional steps increases rapidly as the electrochemical potential of the nanoconstrictions is lowered below −0.5 V. (3) The fractional conductance steps are as well defined as those integer steps. (4) The atomic configurations of the nanoconstrictions with the fractional conductance values appear to be more stable upon elongation than those with arbitrary conductance values. Below we discuss the origin of the experimental observations.

Given the pronounced peaks at multiples of $0.5G_0$, it is tempting to interpret the data in terms of a lift in spin degeneracy. However, this is unlikely because gold is nonmagnetic and the experiment was carried out in the absence of external magnetic field. A recent theory predicted that nanowires of simple nonmagnetic metals undergo a transition to a spin-polarized magnetic state at critical radii [13]. Even if the transition occurs in the gold nanoconstrictions, the magnetic domains at both sides of a nanoconstriction are expected to be random in the absence of external magnetic field. This would mean a transmission between 0 and 1, which cannot explain the conductance steps near multiples of $0.5G_0$. Furthermore, this model fails to explain why the spontaneous spin polarization depends on the electrochemical potential. A successful model must be able to explain the dependence of the fractional conductance on the electrochemical potential. To a first order approximation of a metal-electrolyte interface, the electrolyte is considered as a continuous medium, and the electrochemical potential changes the charge and Fermi energy of the nanoconstriction [8]. A more accurate picture must include the redistribution of the discrete ions surrounding the nanoconstriction as a function of the electrochemical potential. Each picture is considered below to explain the electrochemical-potential-induced fractional conductance.

We first consider the change of the Fermi energy and charge of the nanoconstriction in terms of a microscopic model [14] that relates the conductance to the microscopic parameters of atoms at the nanoconstriction. The model predicts a direct link between valence orbitals and the number of conduction channels in one-atom contacts, which has been confirmed by recent experimental work for both monovalent and multivalent atoms [15]. For monovalent metals, such as Au, Na, and Ag, the theory predicts well-defined quantum steps at integer multiples of G_0 because of the existence of resonant states. The conductance through a resonant state is given by [16]

$$ G = G_0 \frac{4\Delta_L \Delta_R}{(E_F - \varepsilon_a)^2 + (\Delta_L + \Delta_R)^2}, \qquad (1) $$

where E_F is the Fermi energy level, ε_a is the position of the resonant state, and Δ_L and Δ_R describe couplings between the atom at the nanoconstriction and the leads. The requirement of charge neutrality at the nanoconstriction keeps the Fermi energy at the center of the resonant state or $E_F = \varepsilon_a$, and results in a half-filled resonant state. G for the half-filled state is near G_0 even for a very asymmetric coupling (e.g., when $\Delta_L/\Delta_R = 2$). By changing the electrochemical potential, charge neutrality no longer holds and the Fermi energy level shifts away from the center of the resonant state, which leads to fractional conductance steps. This model provides a natural explanation of the fractional steps at negative potentials. However, if one considers that the electrochemical potential was changed gradually in the experiment, one would expect a continuous shift in the conductance step position. This is contrary to the experimental observation that only peak heights in the conductance histogram change, but not the positions.

We now turn to the effect of electrochemical-potential-induced counterion redistribution surrounding the nanoconstriction on the conductance. At negative electrochemical potentials, cations, such as Na^+ in $NaClO_4$ and H^+ (H_3O^+) in $HClO_4$, are expected to accumulate on the nanoconstriction, and they may act as disorders to scatter the conduction electrons and thus change the conductance of the nanoconstriction. The effect of disorders in the conductance quantization has been treated in a number of theoretical works [17–19].

Brandbyge *et al.* [19] have calculated electron transport in metallic nanoconstrictions in the presence of both localized scatterers and corrugated boundary using a jelliumlike model. They concluded that, depending on their locations, localized scatterers smear and downshift the conductance steps selectively, but we observed no smearing-out in the steps. In the case of a corrugated boundary, they found that, depending on the length scale of the corrugation, the conductance steps might be substantially downshifted without suffering from severe smearing. This model has two difficulties: (1) The conductance steps are shifted to nearly half multiples of G_0 while the model predicts arbitrary shifts, depending on the degree of disorder. (2) Well-defined integer steps remain unchanged in the presence of the pronounced fractional steps.

By using a tight-binding approximation, Garcia-Mochales and Serena have found that disorders in a nanoconstriction give rise to an effective resistance in series to the nanoconstriction [18]. Consequently, each peak in the conductance histogram shifts to a lower conductance value by an amount that increases as the conductance increases, which is, however, not what was observed here.

de Heer *et al.* [11] have shown that the elastic scattering of the electrons by the disorders in the nanoconstrictions can lead to an effective conductance of $nmG_0/(n + m)$, where n and m are integers. The result is equivalent to the breakdown of a nanoconstriction into two nanoconstrictions in series. This model was first used by them to explain weak peaks near $1/2G_0$, $2/3G_0$, $3/4G_0$, etc., in their carefully measured conductance histogram. If we assume a symmetric distribution of the counterions, then m is equal to n, and the model leads to conductance peaks near $0.5G_0$ and $1.5G_0$, which explains the observation here. Of course, because the effect of disorder in conductance quantization is model dependent, one cannot yet claim that a complete understanding of the fractional conductance observed here has been reached, and further studies are clearly needed.

In summary, we have studied quantum transport through Au nanoconstrictions under electrochemical-potential control. At positive potentials, the conductance is quantized near the integers even if the potential approaches the oxidation potential of Au. However, by decreasing the potential towards -0.5 V, fractional conductance steps appear in coexistence with the integer steps. The fractional steps are as stable and well defined as the integer steps. We have discussed the observation in terms of Fermi energy shift and electron scattering by disorders, but a complete theory is yet to be developed.

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