Fractional Conductance in Hydrogen-Embedded Gold Nanowires

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Interaction of the physically adsorbed molecular hydrogen with a breaking gold nanowire results in additional stable atomic configurations in few atom contacts and appearance of fractional peaks in the conductance histogram. This effect is explained by peculiar dynamic evolution of the hydrogen-embedded nanoconstriction due to competition between tensile and capillary forces. Dimerization within the atomic wire and hydrogen-assisted stabilization of gold dimers results in preferable atomic arrangements with conductivity close to 0.5 and 1.5 of quantum conductance unit $G_0 = 2e^2/h$.

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Conductance traces of a breaking nanowire show a stepwise behavior with plateaus corresponding to stable atomic configurations and sudden jumps due to force relaxation accompanied by transition to the next stable arrangement of atoms in the contact [1]. The conductance histogram technique, developed for statistical analysis of inherently irreproducible individual conductance curves, has proven to be an extremely useful tool for investigation of structural, mechanical, and transport properties of few atom contacts [2–4]. Peaks in the conductance histograms are related to statistically more probable atomic configurations emerging in the process of breaking. For every metal the number, position, shape, and amplitude of peaks are unique. Moderate shift of conductance peaks, variations in their shape, and relative intensity are caused by scattering on impurities/lattice defects [5,6] or by elevated bias voltage [7–9]. Even at extreme conditions the conductance histogram remains recognizable. In contrast, additional peaks in conductance histograms can emerge only as a result of new stable atomic arrangements or of a drastic change in conductance of the original ones.

It was recently shown that the weak adsorption of organic molecules (2, 2′ bipyridine or adenine) on a copper nanowire results in fractional peaks at approximately 0.5 and 1.5 quantum units of conductance $G_0 = 2e^2/h$ ($1/G_0 \approx 12.9\ \mathrm{k}\Omega$) [10]. Although peak positions in the conductance histograms of noble metals do not coincide with multiple integers of G_0(except of the first one), in the following we refer to these peaks as integer and to the additional ones as fractional. The most extensive study of fractional conductance was made using gold nanowires immersed in an electrochemical cell filled with 0.1 M $NaClO_4$ and $HClO_4$ electrolytes [11]. By changing the potential on the nanoconstriction from positive to negative with respect to the reference electrode, the authors observed appearance and growth of fractional peaks. They discussed a number of models for this phenomenon and found that none of them was consistent with the experimental observation. The model proposed in [12]—several quantized conductors in series—is not conclusive. The conductance quantization effect can be considered only as a second order correction to the effect caused by atomic rearrangement. At the same time, adsorption of molecules on nanowires certainly results in a drastic change of conductivity of quantum contacts. The most important question, however, remains unanswered: What is the origin of fractional conductivity?

In order to address this question, in this Letter we present results of our studies of the fractional conductance phenomenon in gold nanocontacts caused by the physically adsorbed molecular hydrogen H_2. We show that dimerization within the atomic wire accompanied by H_2-assisted stabilization of gold dimers is at the origin of this effect.

Conductance histograms were measured in a temperature range of 10–30 K with the standard mechanically controllable break junction (MCBJ) technique described elsewhere [3]. Well-annealed polycrystalline gold, copper, and silver wires (99.99%–99.999% purity) were used as the sample material. The temperature inside the vacuum pot was maintained to within ± 0.01 K. We found that a small amount of He exchange gas does not affect any of our results. Moreover, it reduces the temperature gradients and improves the accuracy of the temperature measurement. Individual conductance traces $G(z)$ were measured with two current to voltage converters with a gain of 0.1 and 1 $\mathrm{V}/\mu\mathrm{A}$, respectively, in different ranges of the bias voltage. An AT-MIO-16XE-50 National Instruments data acquisition board was used for accumulating the data at a sampling rate of 10–20 kHz.

Experimental histograms depend primarily on the temperature of the nanowire T and on the bias voltage V_b. The influence of the local shape of the electrodes was minimized by acquiring more than 10^4 individual conductance traces for each histogram. Another relatively

uncertain parameter in our experiments is the hydrogen coverage of the electrode surfaces Θ. Even though the amount of gas admitted into the vacuum pot was accurately determined, the presence of different materials and unavoidable temperature gradients introduce a large uncertainty in Θ. Fortunately, the effect of fractional conductance can be observed in a wide Θ interval ranging from a few to $\approx 10^2$ monolayers of H_2.

A typical conductance histogram for gold measured in ultrahigh vacuum (UHV) at 20 K is presented in Fig. 1(a). It practically coincides with earlier reported data obtained under similar conditions [4] as well as with detailed measurements carried out at 4.2 K [13]. Significant deviations from this picture, including the appearance of additional peaks at $0.5G_0$ and $1.5G_0$, are expected only at extremely high bias voltages $eV_b \sim 0.4\varepsilon_F$, where ε_F is the Fermi energy [14]. Introduction of ultrahigh purity (99.9999%) hydrogen into the vacuum pot at 10–30 K resulted in additional peaks with maxima located at $\sim 0.55G_0$ and $\sim 1.45G_0$ [Fig. 1(b)]. The bias dependence of conductance histograms measured at a fixed temperature (20 K) and at an estimated coverage of a few monolayers of H_2 is shown in Fig. 2. At $V_b < 100$ mV only two first integer and fractional peaks superimposed on a featureless background were observed [Fig. 2(a)]. We attribute the large background at low conductivity to the capillary forces between electrodes embedded in adsorbed hydrogen. Interaction of H_2 molecules with the surface of electrodes and with each other results in different dynamics of the breaking process. Additional elastic deformation of electrodes caused by the capillary forces smooths abrupt changes in the atomic arrangement, results in quasicontinuous conductance traces, and increases the relative intensity of low-conductance peaks. On many occasions we observed stepwise behavior of the tunnel conductivity [inset of Fig. 2(a)]. This means that atomic rearrangement in the electrodes is continued and is mediated by adsorbed H_2. Curve 2 shows that, while the electrodes were pulled apart for more than 1 nm, the distance between the two foremost gold atoms (derived from changes in the tunnel conductivity) stays within ± 0.02 nm. This unexpected stability is explained by elongation of the periphery of the nanoconstriction due to the capillary forces. From the tunneling data it is seen that the capillary and tensile forces are on the same order of magnitude. Competition between these forces might result in additional stable atomic arrangements as compared to clean contacts.

At a higher bias, both the background and the relative amplitude of fractional peaks gradually decrease [Fig. 1(b)]. The fractional peaks completely disappear at $V_b \approx 220$–240 mV [Fig. 2(b)]. At lower/higher concentrations of hydrogen or at different temperatures, the overall picture remains essentially the same. Disappearance of fractional peaks at elevated V_b is caused by desorption of hydrogen from the surface of the nanoconstriction. This is most probably not only due to the applied potential; rather, the overheating of the contact area via power dissipation in the electrodes plays a role [15].

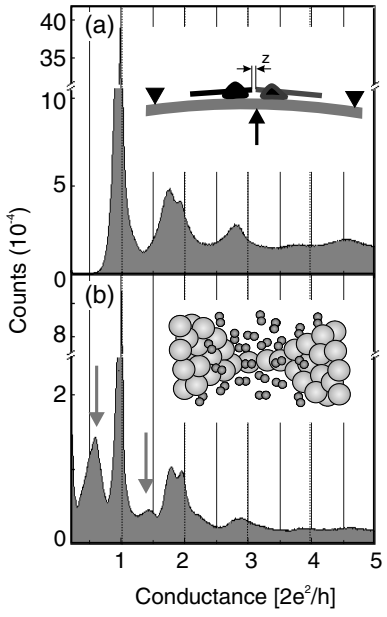

FIG. 1. Conductance histograms (raw data) for Au measured at 20 K in UHV (a) and in the presence of adsorbed H_2 (b). These histograms are based on 50 000 and 10 000 individual conductance traces, respectively. The bias voltage was 129 mV. Insets: schematic of the sample mounting (a) and H_2-embedded constriction (b).

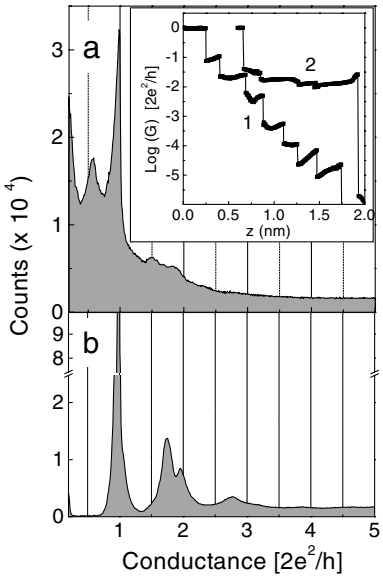

FIG. 2. Bias dependence of conductance histograms measured at 20 K. The bias voltages are 65 mV (a) and 240 mV (b). Inset: two stepwise conductance traces measured in the tunneling regime.

To analyze the experimental data we built up correlation histograms selecting curves with either the first [Fig. 3(a)] or the second [Fig. 3(b)] fractional conductance plateaus (using $\approx 30\%$ of traces with the longest plateaus). We also calculated correlation matrices $r_{i,j} = \langle (l_i - \langle l_i \rangle)(l_j - \langle l_j \rangle) \rangle / \sigma_i \sigma_j$, where $l_{i,j}$ is the plateau length around $i, j = 0.5G_0$, $1G_0$, $1.5G_0$, $2G_0$ and $\sigma_{i,j}$ is the standard deviation of $l_{i,j}$ (inset of Fig. 3). No correlation between fractional peaks was found. The value of the corresponding coefficient was always small, $|r_{0.5,1.5}| \leq 0.02$. In contrast, anticorrelation between fractional and corresponding integer peaks was observed. For the plateaus at $0.5G_0$ and $1G_0$ we found $r_{0.5,1} \approx -0.25$. In other words, the one- or two-atom gold contacts are occasionally replaced by atomic arrangements with fractional conductivity. Moreover, the occurrence of each of these atomic arrangements is an independent event. The average length of the fractional plateaus is approximately 3 times shorter than that of the integer ones, implying considerably worse mechanical stability of such arrangements. Current-voltage characteristics for contacts with fractional conductance also indicate that these atomic arrangements can sustain significantly less current. While *I-V* curves of one-atom gold contact are linear, are reproducible, and can routinely be measured up to 500–600 mV, the contacts with fractional conductance demonstrate nonlinear, asymmetric, and irreproducible behavior. The break of these contacts or transition to a contact with an integer conductivity usually occurs at $\lesssim$ 200 mV(inset of Fig. 4), which is in agreement with the bias dependence of conductance histograms. The above implies that atomic configuration with fractional conductivity can be viewed as a lattice defect placed at the point of the highest current density. Electron wind forces and increase of the constriction temperature associated with scattering of electrons by such a defect result in electrical instability of the contact. Individual conductance traces presented in Fig. 4(a) show that transitions between fractional and integer plateaus may occur in the course of breaking. We also found that for a steady-state one-atom contact (stretched to a certain degree) the conductivity switches between the integer and fractional conductance levels in a random way at a time scale from tens of milliseconds to a few seconds [Fig. 4(b)]. Therefore, in the process of formation and disappearance of atomic arrangements with fractional conductance, no strong bonds are formed.

Conductance histograms of Cu and Ag show no indication of fractional peaks due to the physically adsorbed H_2. This implies that the fractional conductance effect originates from properties that distinguish gold quantum contacts from silver and copper ones. The most distinct feature of gold nanocontacts is the possibility to form an amazingly stable single-atom chain while stretched [16,17]. It was also shown that stretched single-atom chains have a strong tendency to spontaneous

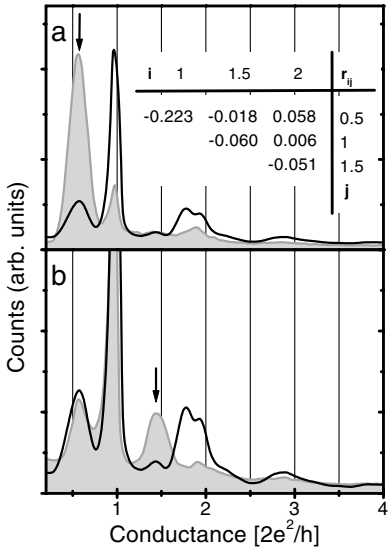

FIG. 3. Correlation histograms (area graphs) based on selected conductance traces with long plateaus at $\sim 0.6G_0$ (a) and $\sim 1.45G_0$ (b). Raw data were smoothed using a $0.05G_0$ window. Line graphs represent the histogram for the original, unselected data set. The histograms are scaled such that the amplitudes of the concerned fractional peak in the correlation histogram and the corresponding integer peak in the original one are the same. Inset: correlation matrix for the same data set.

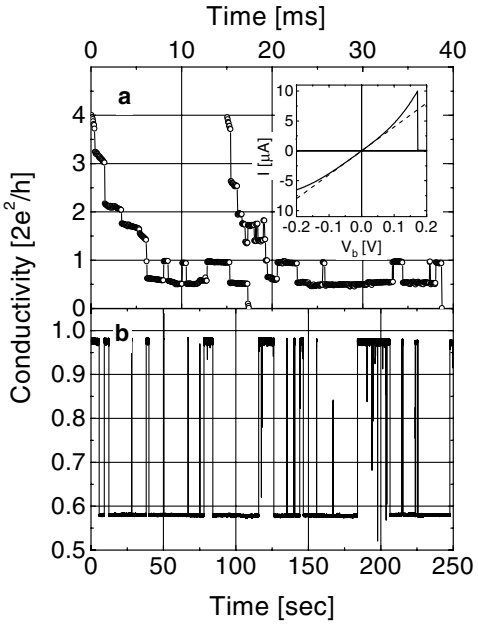

FIG. 4. Conductance traces demonstrating reversible transition between fractional and integer plateaus (a). Time trace for a stretched single-atom chain demonstrating spontaneous transition between normal ($\approx 1G_0$) and dimerized ($\approx 0.6G_0$) atomic configurations (b). Inset: a typical *I-V* curve for a contact with zero-bias conductivity $\sim 0.52G_0$.

dimerization—a predecessor for Pierls transition in extended 1D systems [18–21]. Calculations of conductance through a short chain of gold atoms with a dimer yield values ranging from $0.58G_0$ [20] (in good agreement with the first fractional peak in our histogram) to $0.4G_0$ [19]. However, the dimerization effect has never been observed in conductance histograms measured in vacuum due to the intrinsic instability of such structures during the breakage process.

Our results suggest that the effect of fractional conductance can be explained by formation of stable gold dimers at the last stage of breakage. The configuration with dimers is preserved assuming that the elongation of the hydrogen-embedded nanowire occurs at the expense of its periphery due to the capillary forces. This maintains unchanged or even decreased interatomic spacings in the thinnest part of the constriction. Concerning the peak at $1.5G_0$ we note that, because of the irregularity of electrode surfaces, a two-atom contact can be represented by two parallel and spatially separated contacts [15]: an ordinary one-atom contact plus a dimerized chain. Since the probability of such a configuration is small, the observed intensity of this peak is rather low.

At this point, we briefly discuss the difference between our results and those very recently presented in Ref. [22]. In the latter case, the conductance through a bridge of two hydrogen atoms adsorbed on the surface of chemically active platinum was measured. In contrast, fractional peaks in our experiment arise solely due to the different dynamical behavior of the Au nanowire in inert media with van der Waals interaction between metal and molecular hydrogen only.

In conclusion, we observed additional fractional peaks in conductance histograms of gold MCBJ in the presence of physically adsorbed H_2. Corresponding atomic arrangements with fractional conductance emerge independently from each other and are found to be considerably less stable against nanowire stretching and the electrical current. All experimental observations are in agreement with the assumption that dimerization of atomic wires occurs during the final stage of breakage. The interaction between the Au dimers and H_2 and competition between the tensile and capillary forces in a hydrogen-embedded nanoconstriction stabilize these dimers for a sufficiently long time. More details of the interaction between molecular hydrogen and gold surface are expected to emerge as a result of further studies of the tunnel characteristics of MCBJ. Finally, the simplicity of a metal-hydrogen adsorbate system makes it an attractive object for extensive theoretical investigations.

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