Hydrogen-assisted distortion of gold nanowires

A. Halbritter, Sz. Csonka, and G. Mihály

Electron Transport Research Group of the Hungarian Academy of Science and Department of Physics, Budapest University of Technology and Economics, 1111 Budapest, Hungary

O.I. Shklyarevskii, S. Speller, and H. van Kempen
NSRIM, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, the Netherlands

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In this paper the influence of adsorbed hydrogen on the behavior of gold nanojunctions is investigated. It is found, that the hydrogen environment has a strong effect on the conductance of atomic-sized gold junctions, which is markedly reflected by the growth of an additional peak in the conductance histogram at 0.5 quantum unit, $2e^2/h$. The statistical analysis of the conductance traces implies that the new peak arises due to the hydrogen-assisted distortion of atomic gold chains.

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I. INTRODUCTION

The conductance histograms of different metals have been studied under various experimental conditions. It was found, that the peaks in the histogram arise due to the repeated establishment of some stable atomic configurations during the breaking process. Usually the general shape of the histogram is characteristic of the material, and it is not very sensitive to the experimental parameters, like the temperature or the magnitude of the bias voltage.

On the other hand, the interaction of adsorbates with the junction can influence the evolution of the nanocontact during the rupture and can cause drastic changes in the shape of the histogram. It was shown that the adsorption of some organic molecules on copper nanojunctions results in the appearance of new peaks around 0.5 and 1.5 quantum conductance unit, $G_0 = 2e^2/h$.

Similar phenomenon was observed using gold nanowires immersed in an electrochemical cell. By changing the potential on the nanoconstriction from positive to negative with respect to the reference electrode, the authors observed the appearance and growth of two new peaks, again at 0.5 and 1.5 $G_0$.

These studies have shown that the conductance histograms can serve as sensitive detectors of adsorbates. The new peaks in the histogram are assumably caused by the appearance of new, stable atomic arrangements in the modified environment. On the other hand, the conductance histograms alone cannot tell the microscopic background of the phenomenon. The above systems are rather complicated for theoretical calculations, so the origin of the observations has remained an open question.

In this paper we show that similar phenomenon can arise due to the adsorption of hydrogen molecules on gold nanowires. Hopefully, the simplicity of this system will open the opportunity for theoretical studies. We also show, that the detailed statistical investigation of the conductance traces supplies useful information about the nature of the new atomic configurations.

Quite recently, the influence of hydrogen molecules on platinum junctions was also studied. In this system the characteristic peak of platinum at 1.5 $G_0$ disappears, and a new peak grows in the histogram at 1 $G_0$. The detailed studies have shown, that the new peak is connected to the conduction through a $H_2$ bridge between the Pt electrodes. The comparison of these results with our observations is presented.

II. BASIC OBSERVATION: THE APPEARANCE OF A NEW PEAK IN THE CONDUCTANCE HISTOGRAM

We have performed our measurements on high-purity gold samples with the mechanically controllable break junction (MCBJ) technique. The experiments were done under cryogenic circumstances in the temperature range...
of 4.2 – 50 K. A typical conductance histogram of gold measured in ultra high vacuum at \( T = 20 \) K is presented in Fig. 1(a). It agrees with earlier reported data obtained under similar conditions.\(^4\) The most pronounced feature of this histogram is a sharp peak at 1 G\(_0\). The introduction of hydrogen into the vacuum pot resulted in the appearance of an additional peak positioned close to 0.5 G\(_0\), as shown in Fig. 1(b). In some cases a small peak at \( \sim 1.5 \) G\(_0\) was also visible, but due to its eventual occurrence we focus our attention on the peak at \( \sim 0.5 \) G\(_0\).

This basic observation was studied in detail by changing three experimental parameters: the temperature, the bias voltage and the amount of H\(_2\) near the contact. Even though the quantity of gas admitted into the vacuum pot was accurately determined, no reliable estimation for the H\(_2\) coverage of the junction can be given due to the presence of different materials and unavoidable temperature gradients in the sample holder. Fortunately, the results of the measurements were not sensitive to the precise amount. In contrast, the other two parameters played a rather crucial role and the new peak in the histogram was only observed in a restricted range of the temperature and the bias voltage.

The study of the temperature dependence showed that the fractional peak is only present in the range of approximately 10 – 30 K. The bias dependence of the conductance histograms measured at a fixed temperature (20 K) is shown in Fig. 2. At bias voltages \( \leq 100 \) mV the peaks of the histogram are superimposed on a large featureless background [Fig. 2(a)]. At higher bias, both the background and the relative amplitude of the peak at 0.5 G\(_0\) compared to the one at 1 G\(_0\) decrease [Fig. 2(b)]; and finally above \( \sim 200 \) mV the peak at 0.5 G\(_0\) completely disappears [Fig. 2(b)]. The absence of the new peak at elevated temperature or bias voltage is presumably caused by the desorption of hydrogen from the surface of the junction. These two effects can have the same origin: at elevated bias the voltage-induced heating of the junction causes the desorption. At low temperatures the vapor pressure of hydrogen is very small, so the amount of hydrogen near the contact is strongly reduced.

The same measurements were performed on silver and copper contacts. In high vacuum the histograms of these noble metals are resembling the one of gold.\(^5\) The inclusion of hydrogen resulted in a similar behavior with respect to the appearance of a featureless background at low bias voltage. On the other hand, in Ag and Cu no indication for the appearance of a new peak was observed.

III. THE NATURE OF THE CONDUCTANCE TRACES

In pure gold contacts the conductance plateau at 1 G\(_0\) is a robust feature. The conductance traces contain this plateau almost without exception. Furthermore, this is the last plateau, after which the contact breaks. This plateau is very flat, very long, and usually it is precisely positioned at 1 G\(_0\). These features are reflected by the exceptionally sharp peak in the conductance histogram [Fig. 1(a)]. There is some chance for having smaller conductance values down to 0.6 G\(_0\), but below that there are absolutely no counts in the histogram.

The appearance of a new peak around 0.5 G\(_0\) raises the question, how these strong features of the conductance traces of pure gold are modified in the presence of hydrogen. Naturally, the traces must contain plateaus both at 0.5 G\(_0\) and at 1 G\(_0\). However, the conductance histogram alone cannot tell how these plateaus are related to each other. Figure 3(a) shows a conductance trace extracted from the data set. It has plateaus at both...
conductance values: first the conductance stays at $1G_0$, then it jumps to $0.5G_0$, and finally the contact breaks. This kind of behavior was frequent, but not exclusive. Another two examples are presented in Fig. 3(b). These traces show a telegraph fluctuation between $0.5G_0$ and $1G_0$. This telegraph fluctuation implies that the contact can choose from two metastable atomic configurations. The one with unit conductance is assumably the cutaneous atomic arrangement of pure gold. The other one with $G = 0.5G_0$ is another – yet unknown – configuration which is only observable if hydrogen molecules are also present. It should be noted that plateaus at $0G_0$ are not typical. On the other hand, traces with plateau at $0.5G_0$ and no plateau at $1G_0$ were not typical.

The plateaus are not precisely placed at $1G_0$ and $0.5G_0$, which is indeed expected from the finite width of the peaks in the histogram. The peak at $0.5G_0$ grows above the interval $\sim 0.3 - 0.75G_0$, while the peak at $1G_0$ grows above $\sim 0.75 - 1.1G_0$. So all the plateaus in the first interval are regarded as plateaus near $0.5G_0$, while the plateaus in the second interval are taken as plateaus near $1G_0$.

Further on the lengths of these two types of plateaus are analyzed with statistical methods.

**IV. EXPLORING CORRELATIONS BETWEEN THE PEAKS IN THE HISTOGRAM**

As a first step, we investigate those traces for that the plateau at $0.5G_0$ is long. The length of this plateau was determined for each trace by counting the number of data points in the conductance interval $G/G_0 \in [0.3, 0.75]$. The data set of Fig. 1(b) contained 10000 conductance traces. From that those 3000 traces were selected, which have the longest plateau at $0.5G_0$. The histogram for these selected curves is shown in Fig. 4 by the area graph. This histogram is compared with the histogram for the whole data set, as shown by the dashed line. In order to have a good comparison, both histograms were normalized to the number of traces included.

For the selected curves the peak at $0.5G_0$ is significantly larger, which is a natural consequence of the selection. The interesting result of this comparison is the shrinking of the peak at $1G_0$ by more than $30\%$ due to the selection. The rest of the structures at higher conductance values are exactly the same on the two histograms.

This analysis shows that the traces with long plateaus at $0.5G_0$ have a smaller peak at $1G_0$ in the histogram; or in other words, if the plateau at $0.5G_0$ is longer than in average then the plateau at $1G_0$ is shorter than in average. This kind of anticorrelation implies that the summed length of the both plateaus is important, and the switching between them is probably a random process. This remark will have special importance in the next part, where the histograms for the plateau lengths are investigated.

**V. PLATEAU LENGTH HISTOGRAMS**

The measurements in a pure environment have shown, that a single atom gold contact has a single conductance channel with perfect transmission. Furthermore it was found that gold can form atomic chains with single atoms in a row and this chain also has a perfect transmission. The existence of these atomic chains was deduced from histograms plotted for the lengths of the last plateaus before break. These histograms revealed equidistant peaks, corresponding to the break of chains with different number of atoms. Therefore the question must be addressed, to what extent this chain formation is influenced by the presence of hydrogen.

As it was mentioned, even in hydrogen surrounding, a lot of traces just exhibit plateaus at $1G_0$ without
FIG. 5: Plateau length histograms for gold junctions in hydrogen environment. Panel (a) shows the plateau length histogram for the traces that do not have any plateau in the interval $G/G_0 \in [0.3, 0.75]$. The plateau length is determined by the number of data points in the interval $G/G_0 \in [0.75, 1.1]$. Panel (b) contains plateau length histograms for those traces that do have a plateau in the region $G/G_0 \in [0.3, 0.75]$. The dashed line shows the histogram for the lengths of the plateaus near 1 $G_0$. This is measured by the number of points in the interval $G/G_0 \in [0.75, 1.1]$. The area graph shows the histogram for the joint lengths of the plateaus around 1 and around 0.5 $G_0$. This length is given by the number of points in the interval $G/G_0 \in [0.3, 1.1]$

any additional plateau around 0.5 $G_0$. These traces can be regarded as “pure gold behavior”, and the plateau length histogram for these traces can serve as a reference [Fig. 5a]. This histogram shows two well-defined peaks. This means that the process of chain formation is present, but no really long chains are pulled. It should be noted, that in metals that cannot form chains the plateau length histogram shows only a single peak. The distance between the two peaks in Fig. 5a defines the Au-Au distance in the chain.

We can also plot the plateau length histogram for the traces that have a plateau around 0.5 $G_0$ as well. The anticorrelation demonstrated in the previous part implies that the summed length of the plateaus at 1 $G_0$ and at 0.5 $G_0$ is important. Therefore, as a first step the plateau length is measured for each trace by the number of data points in the conductance interval $G/G_0 \in [0.3, 1.1]$. The plateau length histogram built in this way is presented by the area graph in Fig. 5b. The position of the peaks coincides with the reference histogram. The plateau length histogram for the same traces can be plotted by measuring just the lengths of the plateaus at 1 $G_0$. (In this case the plateau length is the number of data points in the conductance interval $G/G_0 \in [0.75, 1.1]$) This analysis results in the histogram shown by the dashed line. In this histogram the peaks are smeared and considerably shifted compared to the reference histogram.

A plateau at 0.5 $G_0$ in a conductance trace is a clear sign, that the break of the nanojunction is influenced the hydrogen molecules. The two peaks in the plateau length histogram in Fig. 5b indicate that even in this case the chain formation of gold is preserved. Furthermore, a nice plateau length histogram is only obtained if the plateaus at 0.5 $G_0$ are also included in the plateau length. This indicates that the atomic configuration with $G = 0.5 G_0$ is a part of the chain formation.

VI. DISCUSSION OF THE OBSERVATIONS

Our measurements have shown, that the adsorption of hydrogen on gold junctions results in the appearance of a new peak at 0.5 $G_0$ in the conductance histogram. The same phenomenon was not observed in silver and copper junctions, which have conduction properties similar to gold. An important difference between the noble metals is the striking property that gold can form atomic chains while Ag and Cu cannot. It has already implied that the new peak at 0.5 $G_0$ is somehow connected to the chain formation of gold. This assumption was further supported by the investigation of plateau length histograms. This analysis has shown that the configuration with $G = 0.5 G_0$ is indeed a part of the chain formation.

Local density functional simulations have shown that a small increase in the interatomic distance in a Au chain causes a considerable reduction of the conductance. This implies, that the configuration with perfect transmission is the usual gold chain, while the conductance value of $G = 0.5 G_0$ corresponds to a distorted chain with slightly increased Au-Au distance.

This distortion can be an intrinsic property of gold, which is just aided by the hydrogen environment. It was shown that stretched atomic chains have a tendency for spontaneous dimerization. Calculations of the conductance through a short chain of gold atoms with a dimer yield values from 0.58 $G_0$ to 0.4 $G_0$. Such dimers have never been observed in high vacuum, but the adhesive hydrogen environment might stabilize this configuration. A crucial problem with this interpretation is the following. In a process called “dimerization” at least three atoms should be included in the chain. In our measurements the occurrence of such long chains was not frequent (see the plateau length histograms in Fig. 5b), so a plausible explanation should also account for the distortion of a chain with two atoms.

As another possibility, the binding of the hydrogen molecule on the chain itself might cause the distortion. The precise nature of such process cannot be predicted without microscopic model calculations. The possibility of the chemical reaction of H$_2$ with the gold chain also cannot be excluded.
The measurements on hydrogen covered platinum junctions have demonstrated that the new peak in the histogram is connected to the conductance through a hydrogen molecule. In gold the plateau length histograms strongly indicate that the conductance values near 0.5 $G_0$ are related to chains of gold atoms; therefore, the same explanation is not supported. A similar analysis of the plateau length histograms can also be performed on platinum, which has the tendency of chain formation as well. Our measurements have shown that in Pt the chain formation is completely destroyed in the presence of hydrogen.

In conclusion, we have shown that a new stable atomic configuration appears in gold nanojunctions due to the adsorption of hydrogen. The analysis of the results implies that this configuration is related to a distorted chain of gold atoms. Presently, the experimental observations cannot provide more information about the nature of this configuration. Hopefully, the simplicity of the gold-hydrogen adsorbate system will stimulate extensive theoretical investigations, which will lead to a better understanding of the details of molecular adsorption on nanowires.

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