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Effect of hydrogen Evolution Reaction on conductance quantization of Au, Ag, Cu nano contacts

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Abstract

We have mechanically fabricated Au, Ag, and Cu nano contacts in solution under the electrochemical potential control. At the hydrogen evolution potential, fractional conductance peaks appeared near $0.5 G_0$ ($G_0=2e^2/h$) in the conductance histogram of Au and Cu. This fractional conductance peak was not observed in the conductance histogram of Ag. In the case of Au nano contacts in 50 mM H₂SO₄ solution, a $0.1 G_0$ peak appeared in the conductance histogram, as well as the $0.5 G_0$ peak. The origin of the fractional conductance peak and its metal dependence were discussed based on previously reported values of metal-hydrogen binding energy, which was estimated by the exchange current density for the hydrogen evolution reaction.

1. Introduction

Electrical conductance through an atomic scale metal nano contact is expressed by $G = 2e^2/h \sum T_i$ where T_i is the transmission probability of the i -th conductance channel, e is the electron charge, and h is Plank's constant [1]. The value of $G_0 = 2e^2/h$ is a unit of the quantized conductance. Conductance quantization depends not only on the atomic structure of the metal nano contact but also on inherent properties of the metal. In the case of noble metals, the conduction channel is a single s channel with

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$T = 1$, and thus, the conductance is quantized in units of G_0 . Quantized conductance behavior of noble metals has been studied using various techniques, such as a scanning tunneling microscope (STM) [2,3] and mechanically controllable break junctions (MCBJ) [4]. The conductance histogram of Au shows a well-defined peaks near 1, 2, 3 G_0 . For Cu and Ag, the conductance histograms have a dominant peak at 1 G_0 [1-4]. The quantized conductance behavior is well investigated and understood for clean noble metals especially in ultra-high vacuum at low temperature.

On the basis of the understanding of the clean metal nano contacts, the influence of adsorbed molecules on quantized conductance behavior has been studied for noble metal nano contacts [5-9]. In ultra high vacuum (UHV) at ultra low temperature, the conductance of Au, Ag, Cu nano contacts was investigated in the presence of H_2 [5,6], O_2 [7] or CO [8]. A broad fractional conductance feature appeared near 0.5 G_0 in the conductance histogram of Au under hydrogen dosing. The fractional conductance feature was not observed for the Ag or Cu nano contacts under hydrogen dosing [5]. On the other hand, oxygen dosing affects the Ag nano contacts [7]. A broad feature was observed below 1 G_0 in the conductance histogram of Ag under oxygen dosing. It is noteworthy that a 2 nm long Ag atomic chain could be created in the presence of oxygen, while clean Ag forms only short chain [1,7]. The molecular adsorption on the metal nano contact affects the conductance and structure of the contacts fabricated in UHV.

Recently, the influence of molecules was investigated for the noble metal nano contacts in several electrochemical systems. Li *et al.* reported a decrease in the conductance of the Cu nano contacts due to adsorbates in solution [9]. The decrease in conductance was attributed to adsorbate scattering of electrons in the Cu nano contact and rearrangement in the atomic configuration of the nano contact induced by molecular adsorption. Under hydrogen evolution reaction, a well defined fractional conductance peak appeared near 0.5 G_0 in the conductance histogram of Au [2,3]. The intensity of the fractional conductance peak could be larger than that of 1 G_0 peak, while the intensity of the broad fractional feature was much smaller than that of 1 G_0 peak in UHV [5,6]. In the electrochemical system, the bonding strength between the metal atoms, and the interaction of the metals with molecules of surrounding medium could be controlled by the electrochemical potential. These facts make possible to fabricate very stable metal nano contacts, which has not been

prepared in UHV [10-13]. At the present stage, it was revealed that a Au nano contact showing conductance of $0.5 G_0$ can be stabilized under hydrogen evolution reaction, but it is not clear whether other structures showing fractional conductance values other than $0.5 G_0$ can be stabilized in solution. In addition, the effect of the hydrogen is not clear for the Ag and Cu nano contacts.

In the present study, we have mechanically fabricated Au, Ag and Cu nano contacts under the electrochemical potential control. The effect of the hydrogen evolution reaction on the quantized conductance behavior was investigated for the Au, Ag, Cu nano contacts in detail. The origin of the fractional conductance peak is discussed by comparing former documented values of theoretical conductance calculations and experimental results in UHV [5,6].

2. Experimental

The experiments have been performed with the modified STM system in an electrochemical cell mounted in a chamber that was filled with high purity N_2 gas to avoid effect of oxygen in air. (see Ref [11-13] for a detailed description). The STM tip was made of a Au wire (diameter ~ 0.25 mm, >99 %) coated with wax to eliminate ionic conduction. The substrate of Au(111) was prepared by a flame annealing and quenching method [14]. Figure 1 shows the schematic view of the experimental setup. The electrochemical potential (Φ_0) of the Au tip and substrate was controlled using a potentiostat (Pico-Stat, Molecular Imaging Co.) with a Ag/AgCl reference electrode. A 0.50 mm diameter Pt wire was used as a counter electrode. The electrolyte was 0.1M Na_2SO_4 or 50 mM H_2SO_4 in the study of the Au nano contacts. In the study of the Cu and Ag nano contacts, the electrolytes were 1 mM $CuSO_4 + 50mM H_2SO_4$, and 1 mM $Ag_2SO_4 + 50$ mM H_2SO_4 , respectively. In the following discussion, the electrolytes are referred to as the Cu solution and Ag solution. The metal nano contacts were created by driving a STM tip into and out of contact with a substrate at a typical rate of 50 nm/s in the electrochemical cell. Separation of the contact resulted in the formation of the metal nano contact between the tip and substrate. To fabricate the Cu or Ag nano contacts, the electrochemical potential of both the STM tip and substrate were maintained at lower than the potential where bulk deposition proceeds (Cu: $\Phi_0=0mV$, Ag $\Phi_0= 400mV$) [15,16]. After sufficient deposition of the

metals onto the surfaces of the STM tip and the substrate, the tip was driven into and out of contact with the substrate. Conductance of the metal nano contact was measured during the breaking process under an applied bias of 20 mV between the tip and substrate.

3. Results

Figure 2 (a,b) shows the cyclic voltammogram (CV) of the Au electrode in 0.1 M Na₂SO₄ and 50 mM H₂SO₄. Hydrogen evolution proceeded when the electrochemical potential of the Au electrodes was maintained at more negative than $\Phi_0 = -700$ mV in 0.1 M Na₂SO₄, and $\Phi_0 = -250$ mV in 0.1 M H₂SO₄. Figure 3 shows the cyclic voltammogram of the Au electrode in the Cu or Ag solution. In the Cu solution, Cu deposition and hydrogen evolution proceeded at more negative than $\Phi_0 = 0$ mV and $\Phi_0 = -500$ mV, respectively. In the Ag solution, Ag deposition and hydrogen evolution proceeded at more negative than $\Phi_0 = 400$ mV and $\Phi_0 = -450$ mV, respectively.

Figure 4 shows the conductance traces and histograms of the Au nano contacts in 0.1 M Na₂SO₄ and 50 mM H₂SO₄. The stretch length was obtained by the distance between the STM tip and the substrate. The zero point was defined as the point at which the contact broke. When the electrochemical potential of the Au nano contact was maintained at $\Phi_0 = 500$ mV in 0.1 M Na₂SO₄, the plateau of 1 G_0 was observed in the conductance trace (Fig. 4(a)). The corresponding histogram shows a peak at 1 G_0 (Fig. 4(b)). As the potential was scanned from $\Phi_0 = 500$ mV to the hydrogen evolution potential ($\Phi_0 = -1000$ mV), reversible transition of the conductance between 1 G_0 and 0.5-0.7 G_0 was observed in the conductance trace as shown in Fig. 4(c). This conductance fluctuation resulted in the fractional conductance peak near 0.5 G_0 in the conductance histogram (see Fig. 4 (d)), as reported in our previous study [3]. At the hydrogen evolution potential ($\Phi_0 = -300$ mV) in 50 mM H₂SO₄, the plateau of 0.1 G_0 was observed in the conductance trace (see Fig. 4(e)) as well as the plateau of 0.5 G_0 and 1 G_0 . Corresponding conductance histogram shows peaks near 0.1 G_0 , 0.5 G_0 and 1 G_0 as shown in Fig. 4(f). Here, we briefly comment on the length of the plateau in the conductance trace. Relatively long plateau 1 nm in length was observed in the conductance trace, indicating that a mono atomic contact could be stretched up to 1 nm. In UHV at room temperature, a clean Au mono

atomic contact cannot be stretched more than 0.2 nm [1]. Improvement in the stability of the Au mono atomic contact in electrochemical system can be explained by adsorption of the anion or hydrogen on the surface of the Au mono atomic contact [3].

Figure 5 shows the conductance trace and histogram of the Cu nano contacts at double layer ($\Phi_0=-100$ mV) and hydrogen evolution potential ($\Phi_0=-550$ mV). At double layer potential, a plateau of $1 G_0$ was observed in the conductance trace (Fig. 5(a)) and a clear $1 G_0$ peak was observed in the conductance histogram (Fig. 5(b)), as is the case with the Au nano contact. At the hydrogen evolution potential, a plateau of $0.5 G_0$ appeared in the conductance trace, leading to the appearance of a $0.5 G_0$ peak in the conductance histogram (Fig. 5(d)). Figure 6 shows the conductance trace and histogram of the Ag nano contacts at double layer ($\Phi_0=0$ mV) and hydrogen evolution potential ($\Phi_0=-550$ mV). Compared with the Au and Cu nano contacts, the Ag contact was quickly broken as shown in Fig. 6(a). At the double layer potential, there was no clear feature in the conductance histogram (Fig. 6(b)). As the potential was scanned to the hydrogen evolution potential, a plateau of $1 G_0$ appeared in the conductance trace (Fig. 6(c)) and a $1 G_0$ peak appeared in the conductance histogram of the Ag nano contact (Fig. 6 (d)).

4. Discussion

At the double layer potential, clear $1 G_0$ peaks were observed in the conductance histograms of Au and Cu, while there was no appreciable feature in the conductance histogram of Ag. Since the conductance of a mono atomic contact is $1 G_0$ for noble metals [1], the present results indicated that the Au and Cu mono atomic contacts could be fabricated in solution, but the stable Ag mono atomic contact could not be fabricated. The Ag mono atomic contact would be mechanically or chemically unstable in solution. The mechanical stability of metal nano contacts could be discussed considering the melting point. The melting point is 1340 K for Au, 1265 K for Ag and 1360 K for Cu [17]. The melting point of Ag is the lowest among the noble metals, suggesting stronger effect of the thermal fluctuation at the Ag nano contacts. The large thermal fluctuation may prevent the long-term stability of the Ag mono atomic contact, resulting in the featureless conductance histogram. The instability of the Ag nano contact is suggested by the conductance

trace, in which the contact quickly broken (see Fig. 6(a)).

At the hydrogen evolution potential, fractional conductance peaks were observed in the conductance histogram of Au and Cu. This characteristic result in solution can be compared with the results in UHV. In UHV, a weak $0.5 G_0$ feature appeared in the conductance histogram of the Au nano contacts under hydrogen dosing [5,6]. However, the feature was broad and the intensity of the $0.5 G_0$ feature was much smaller than that of the $1 G_0$ peak. In the case of Ag and Cu nano contacts, the fractional conductance feature has not been reported in UHV. In solution, a clear $0.5 G_0$ peak appeared for the Au nano contacts under the hydrogen evolution reaction. In 50 mM H_2SO_4 , the intensity of the $0.5 G_0$ peak could be larger than that of the $1 G_0$ peak. In addition to the $0.5 G_0$ peak, a $0.1 G_0$ peak appeared in 50 mM H_2SO_4 . In the case of Cu nano contacts, a $0.5 G_0$ peak appeared in the conductance histogram at hydrogen evolution potential. In solution, electrochemical potential can precisely control the molecular adsorption on the metal nano contacts and the potential energy of the electrons in the contacts, which would make possible to fabricate the stable metal nano structures which has not been prepared in UHV.

There are several possibilities which can be considered as the origin of the fractional conductance peak. One of the possibilities is the spin-dependent conductance quantization. If the properties of the Au nano contact might change into ferromagnetic via adsorbed hydrogen, the system would show spin-dependent conductance quantization in the units of $0.5 G_0$ [18]. However, the fractional value in the present result appeared as the reversible transition between integer and fractional conductance, rather than the appearance of stable plateau at the fractional value (Fig. 4(c)). This result may exclude the possibility of the spin-dependent conductance, because the transition from a single atom contact ($0.5 G_0$) to a two atoms contact ($1 G_0$) should be a rare event in pulling the nano contact at room temperature. Another possibility is the hydrogen incorporated Au nano contact. The atomic structure and conductance were calculated for the Au mono atomic wire with a hydrogen molecule [19,20]. While a hydrogen molecule does not dissociate on the surface of bulk Au, the atomic hydrogen was found to energetically prefer to get incorporated into the wire by the calculation [19]. Reduced dimensionality of the nano wire would induce this high reactivity. The incorporated hydrogen shifts the metal orbital to lower energy. This energy shift results in a reduction of

density of states (DOS) at Fermi level of Au atoms for the mono atomic wire [20]. Since the conductance of the Au mono atomic wire depends on the DOS at Fermi level, the incorporated hydrogen reduces the conductance of the Au wire. The reduction of the conductance by the incorporated hydrogen has been observed for Pt mono atomic wire [21]. The conductance of the Au wire depends on the local structure of the wire, and it varies from 1 to $0.05 G_0$. In the present study, the fractional conductance peaks were observed in the conductance histogram of Au under the hydrogen evolution reaction. The theoretical calculation results indicate that the fractional conductance peaks originate from the hydrogen incorporated Au nano contact. In 50 mM H_2SO_4 solution, both $0.1 G_0$ and $0.5 G_0$ peaks appeared in the conductance histogram. The difference of the conductance of the fractional conductance peak could be explained by the atomic configuration of the Au nano contact. The number of incorporated hydrogen atom could be larger for the contact showing $0.1 G_0$. The hydrogen incorporated Cu nano contact would also be formed in solution at the hydrogen evolution potential. Although the theoretical calculation results explain the decrease in the conductance of the Au nano contacts, they do not show any energetically favorable atomic configurations showing $0.5 G_0$. This result is consistent with the results obtained in UHV, in which a broad feature appeared in the conductance histogram of Au. In solution, on the other hand, a clear peak appeared in the conductance histogram under the hydrogen evolution reaction. Certain atomic configuration showing a fixed conductance value could be preferentially stabilized under the electrochemical potential control, although the stabilization mechanism is not completely understood yet.

Finally, we discuss the reason why the fractional conductance feature was not observed for Ag, while fractional peaks appeared in the conductance histogram of Au and Cu. The metal-hydrogen (M-H) binding energy was investigated by the exchange current density for the hydrogen evolution reaction [22]. The M-H binding energy is 45 kcal for Au, 43 kcal for Cu and 38 kcal for Ag. The M-H binding energy is smallest for Ag. Due to the weak interaction, the conductance value of the Ag nano contact would not be affected by hydrogen, and thus, the fractional conductance peak did not appear in the conductance histogram of Ag. While the conductance of the Ag nano contact was close to that of the clean Ag nano contact, the stability of the Ag nano contact would be affected by hydrogen. Under hydrogen evolution reaction, a $1 G_0$ plateau

appeared in the conductance trace and a clear $1 G_0$ peak appeared in the conductance histogram. Hydrogen would stabilize the Ag atomic contact showing the conductance of $1 G_0$. Similar stabilization of the atomic contact was observed for Fe, Co, Ni and Pd nano contacts [11-13]. It is noteworthy that the binding energy of the Cu-H, Ag-H and Au-H bond decreases in that order in UHV. The hydrogen desorption temperature is 170 K for Au, 180 K for Ag and 300 K for Cu [23]. The M-H binding energy in UHV is different from that in solution under the hydrogen evolution reaction. This difference would be the origin of the difference of the quantized conductance behavior of the noble metal nano contacts between in UHV and in solution.

5. Conclusion

We have studied the quantum conductance behavior of Au, Ag and Cu nano contacts under the electrochemical potential control. As well as $1 G_0$ peak, fractional conductance peaks appeared near $0.1 G_0$ and $0.5 G_0$ in the conductance histogram of Au at the hydrogen evolution potential. The fractional conductance peak was also observed for the Cu nano contacts at the hydrogen evolution potential. In the case of the Ag nano contacts, feature less conductance histogram was observed at the double layer potential, while a $1 G_0$ peak appeared at the hydrogen evolution potential. The dependence of the quantized conductance behavior on metal and electrochemical potential was discussed based on previously reported values of metal-hydrogen binding energy, which was estimated by the exchange current density for the hydrogen evolution reaction, and previous theoretical calculation results.

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Figures

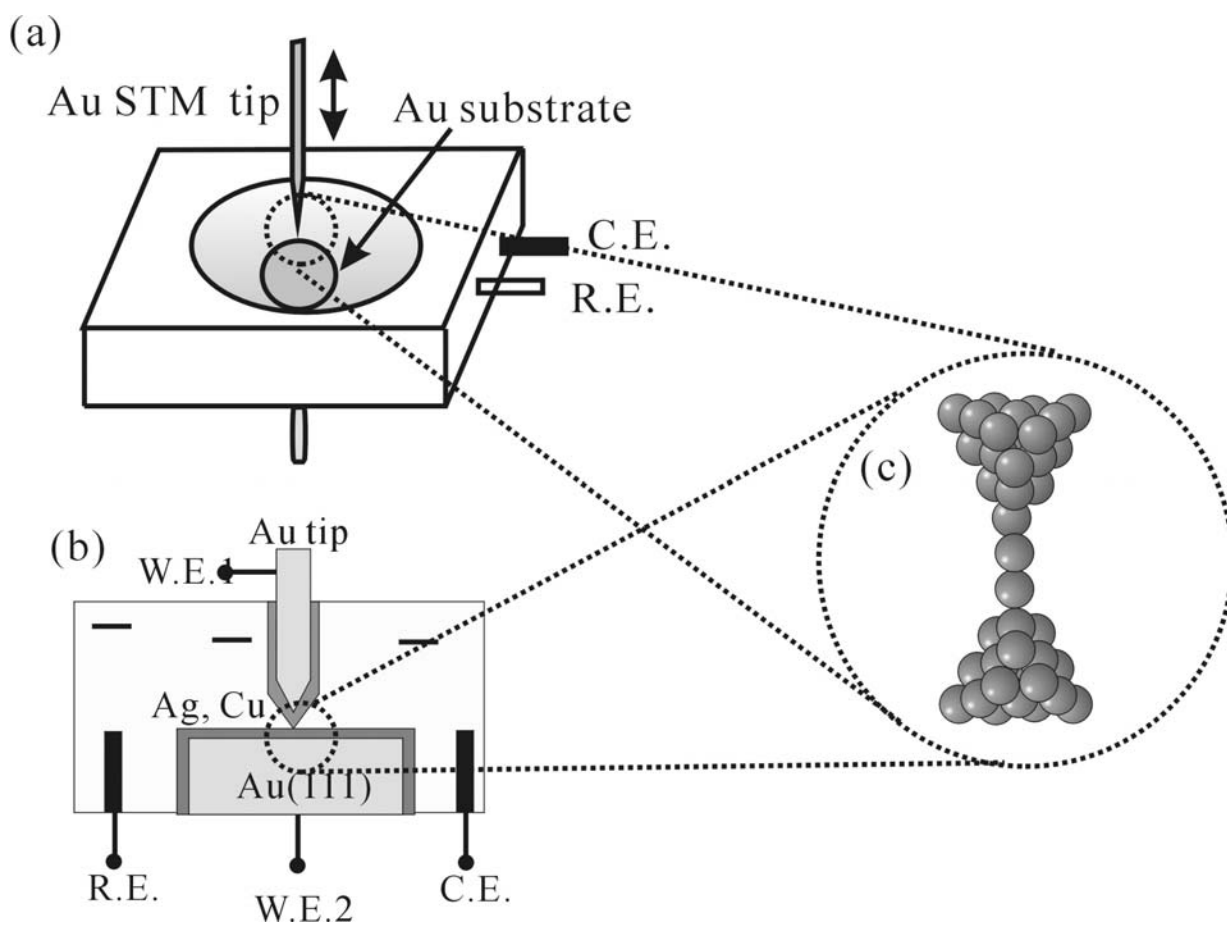


Fig. 1: (a, b) Schematics view of the experimental setup. (b) Ag or Cu was deposited on the Au single crystal substrate and STM tip. (c) A metal nano contact was fabricated between the substrate and STM tip. R.E. : reference electrode, W.E. : working electrode, C.E. : counter electrode.

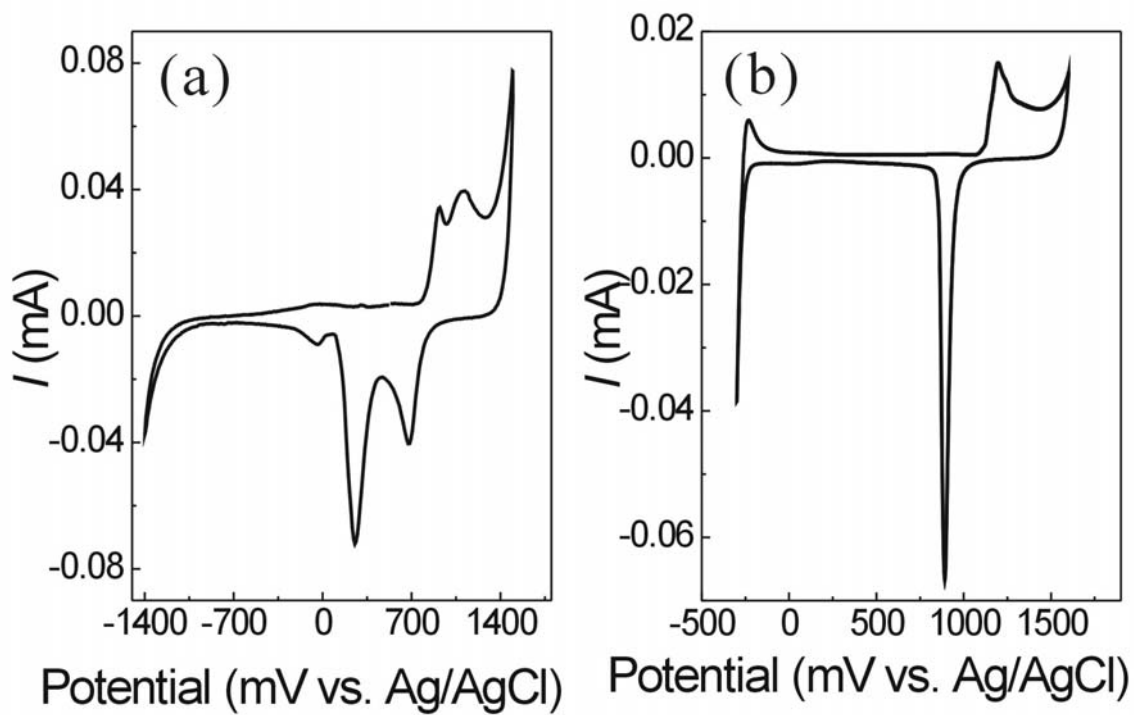


Fig. 2: Cyclic voltammogram of a polycrystalline Au electrode in (a) 0.1 M Na_2SO_4 , (b) 0.05 M H_2SO_4 .

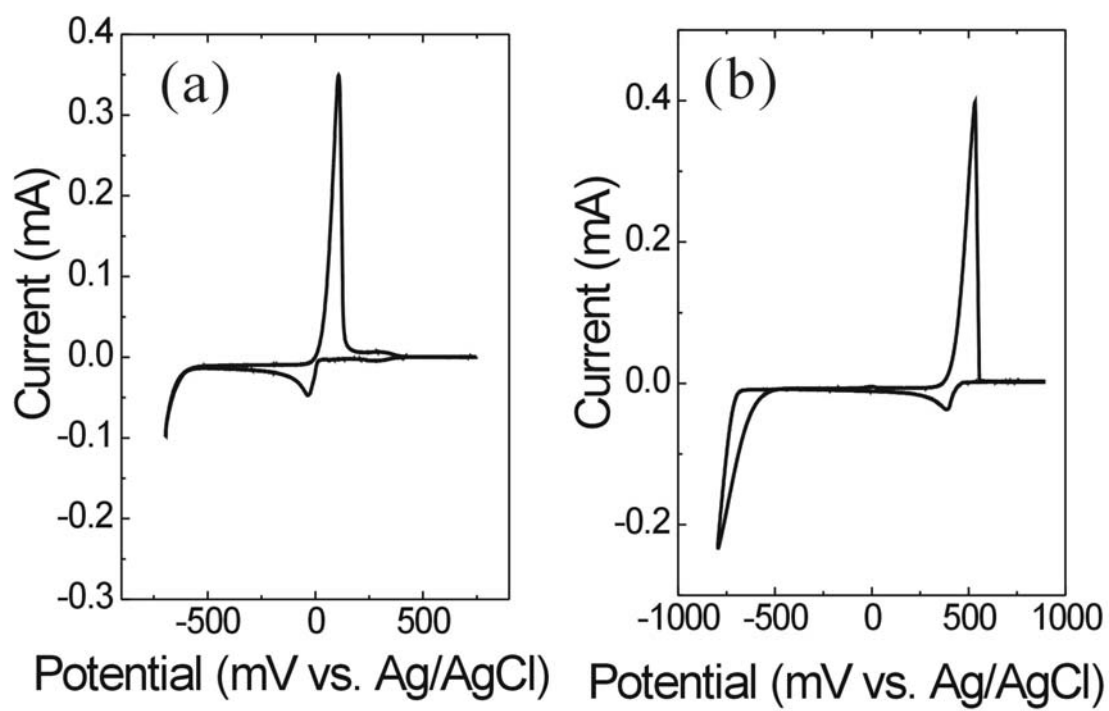


Fig. 3: Cyclic voltammogram of a polycrystalline Au electrode in (a) 1 mM CuSO_4 and 50mM H_2SO_4 , (b) 1 mM Ag_2SO_4 + 50 mM H_2SO_4 .

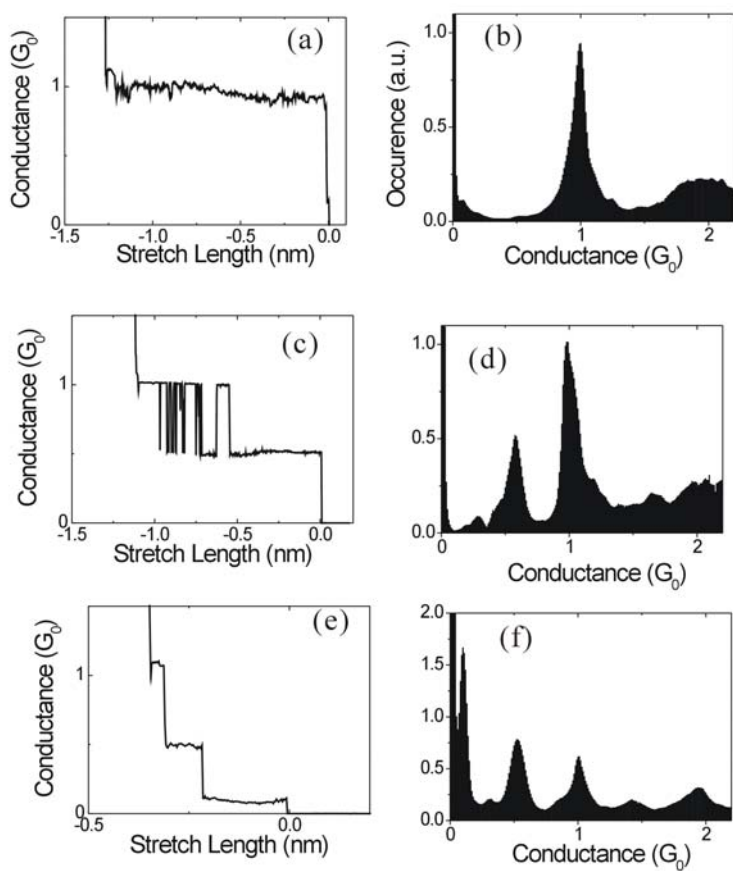


Fig. 4: Typical conductance traces (a,c,e) and conductance histograms (b,d,f) of the Au nano contacts in (a-d) 0.1 M Na_2SO_4 , (e,f) 0.05 M H_2SO_4 . The electrochemical potential of the Au nano contacts was kept at $\Phi_0 = 500$ mV (a,b), $\Phi_0 = -1000$ mV (c,d) and $\Phi_0 = -300$ mV (e,f).

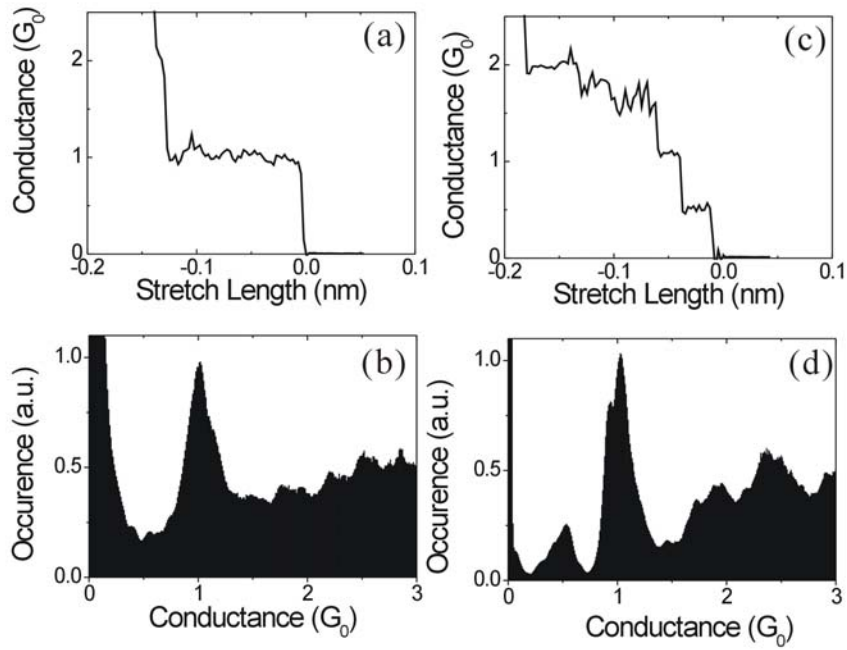


Fig. 5: Typical conductance traces (a,c) and conductance histograms (b,d) of the Cu nano contacts at $\Phi_0 = -100$ mV (a,b), $\Phi_0 = -550$ mV (c,d).

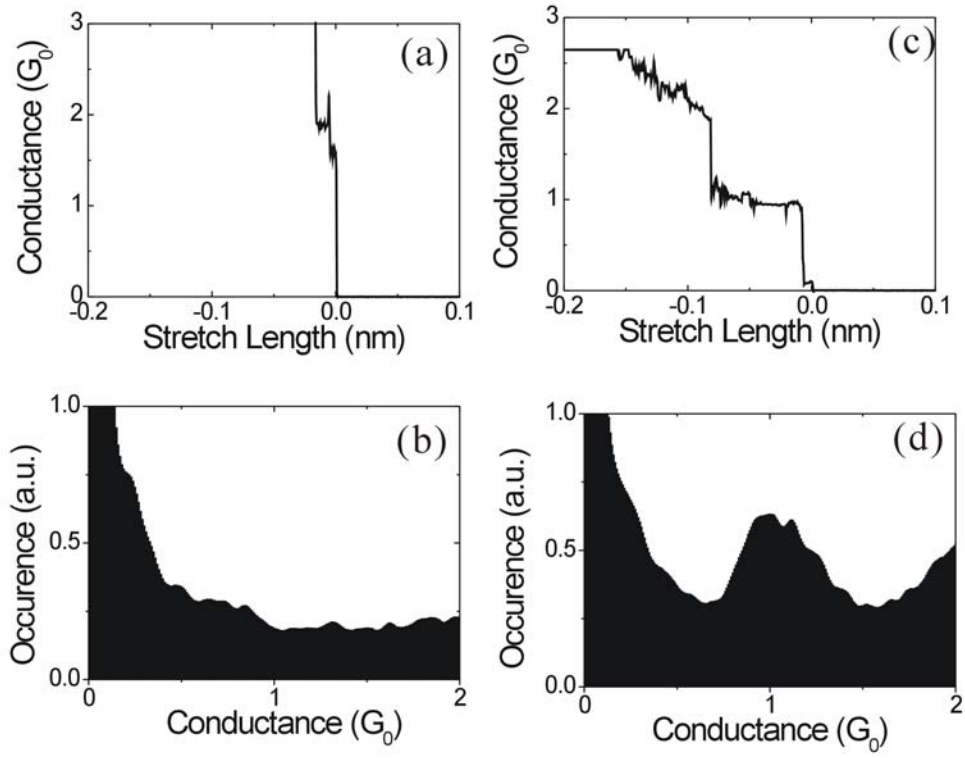


Fig. 6: Typical conductance traces (a,c) and conductance histograms (b,d) of the Ag nano contacts at $\Phi_0=0$ mV (a,b), $\Phi_0= - 550$ mV (c,d).