Electrochemical Fabrication of Pd–Au Heterogeneous Nanocontact Showing Stable Conductance Quantization under Applying High Bias Voltage

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(Received December 9, 2004; CL-041507)

A novel nanostructure, heterogeneous Pd–Au nanocontact showing conductance quantization, was fabricated via selective electrochemical deposition of Pd at a gap of two sustainable thin Au wires in solution. The stability of Pd monatomic contact increased when the potential of the electrode was kept at negative potential. Contribution of the adsorbed hydrogen on Pd–Au contact was considered as the origin of the improved stability.

Fabrication and characterization of metallic nanocontact have attracted much attention because of its potential application in nanoelectronics.[1] Recently, electrochemical deposition has been applied in fabricating nanocontacts.[2,3] We have also succeeded in preparing several types of nanocontacts, such as, Au, Cu, Ag, Pd, Ni, and Pb by the electrochemical method,[4–6] where metal-dependent quantized conductance was exhibited.[4,5] Generally, the transition metals do not show clear conductance quantization due to the influence of the d orbital.[7] But our previous report proved that the first peak in conductance histogram of Pd was located at 1 G_0 (G_0 is the unit value $2e^2/h$ of conductance quantization[1–3]) under applying a small bias 20 mV.[5] Successful observation of 1 G_0, which was not realized by using the technique of the mechanical break junction,[8] could be attributable to the formation of well-controlled nanocontacts in solution.[5] In this report, a modified electrochemical method was utilized to investigate the performance of Pd contact under high bias.

Heterogeneous Pd–Au nanocontact was prepared by selective electrochemical deposition of Pd onto one of the Au electrodes at a gap in solution. Working electrode, a Au thin wire, was covered by insulating tape with an exposed length less than 100 µm. Optical microscope was adopted to monitor the structure evolution of the exposed part. Bipotentionstat (Fuso Industry Co., HECS990C) was used to control electrochemical process and to measure current in the wire. Electrochemical dissolution of Au wire in 0.5 M KCl electrolytic solution resulted in the formation of a gap with separation less than few µm. Following the preparation of the gap, a aqueous electrolyte, containing 1 mM of $PdCl_2$ and 50 mM of H_2SO_4, was introduced into electrochemical cell to deposit Pd. Conductance of the contact was determined by the potential difference between both ends of the Au wire and the observed current in the wire. Electrochemical potential of the wire was referred to Ag/AgCl reference electrode.

For the fabrication of Pd nanocontacts, generally, both ends of the Au wires were kept at Pd bulk deposition potential ($\phi_{Pd} < 0.42$ V for Pd), wherein the bias was small (20 mV).[4,5] On the other hand, when only one of the Au electrodes was kept at the Pd deposition potential, selective metal deposition onto this electrode proceeded, which was confirmed by observation using optical microscope. Figure 1 clearly exhibits that the electrodeposition only occurred on one electrode till the deposited Pd atoms contacted to the other bare Au electrode. In this case, Pd–Au 'heterogeneous' nanocontact was formed.

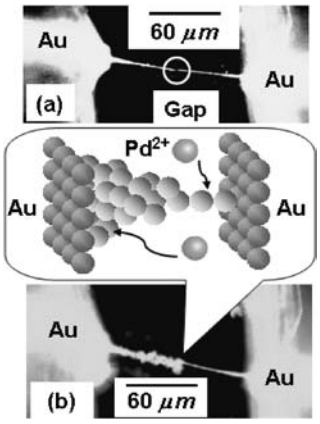

Figure 1. Images of (a) the Au gap with a separation distance around 2 µm and (b) the Pd–Au contact prepared by the Pd deposition onto one of the Au electrodes in solution. Inset shows the schematic presentation of the expected structure of Pd–Au heterogeneous nanocontact.

Figure 2 shows time-dependent conductance change of Pd–Au heterogeneous contact under applying relatively high bias. When two electrodes were kept at the Pd deposition potential ($\phi_{Pd} = 0.3$ V) and the bare-Au potential ($\phi_{Au} = 0.9$ V), respectively, conductance fluctuation was observed as shown in Figures 2a and 2b. The conductance quickly jumps up to around 1 G_0, and then abruptly jumps down to zero without a noticeable time-dependent decay. Observed oscillation of the conductance should be attributable to the formation and breaking process of the Pd–Au heterogeneous contact, in which the transiently formed Pd–Au contact may be immediately dissolved due to the relatively positive potential of the opposite Au electrode. Occurrence of 1 G_0 implies that this Pd–Au heterogeneous contact formed under this condition has the size in monatomic scale. Moreover, clear observation of 1 G_0 in both Pd–Au heterogeneous and Pd–Pd homogeneous contacts[5] suggests the measured conductance in this experiment reflects the intrinsic electrical property of Pd monatomic contact.

When ϕ_{Pd} became more negative, time-dependent profile of the conductance was changed. Figures 2c and 2d shows typical change of conductance observed at the condition of $\phi_{Pd} = 0.1$ V and $\phi_{Au} = 1.0$ V. Although the applied bias was much higher (0.9 V) than that in the case of Figures 2a and 2b (0.6 V), much more stable conductance quantization behavior was observed clearly, showing several plateaus staying for several tens ms at the contact formation. At a certain point, the conductance spon-

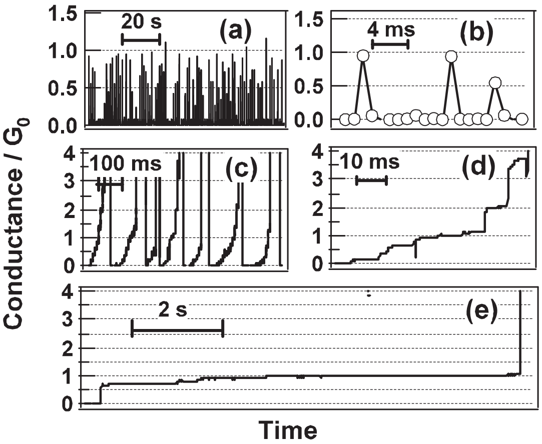

Figure 2. Time-course of the conductance evolution in 1 mM $PdCl_2$ + 50 mM H_2SO_4: (a) the potentials of two Au electrodes kept at 0.3 and 0.9 V, separately; (b) the extended plot; (c) the potentials of two Au electrodes kept at 0.1 and 1.0 V, separately; (d) the extended plot; (e) the potentials of two Au electrodes kept at −0.3 and 1.2 V.

taneously dropped to zero. Soon after the contact was broken, the contact recovered again because of the deposition of Pd. The above experimental result has apparently demonstrated that the conductance quantization under high bias condition becomes stable when ϕ_{Pd} was kept at more negative potential.

When ϕ_{Pd} was kept at negative than −0.2 V, more stable plateaus were observed during the evolution of quantized conductance. As shown in Figure 2e for the Pd–Au heterogeneous nanocontact under applying high bias (1.5 V, $\phi_{Pd} = -0.3$ V, $\phi_{Au} = 1.2$ V), consecutive breaking/formation behavior disappeared. A clear plateau at 1 G_0 was observed showing lifetime in a range of several seconds.

Present result proves that the stability of the Pd–Au nanocontact under high bias of 1.5 V was comparable to that of Pd–Pd homogeneous contact at the low bias of 20 mV.[5] Generally, the lifetime of the conductance quantization plateau decreases as applying bias voltage increases. This tendency was often observed at Au nanocontact prepared by mechanical method.[8,9] Increment in the stability under applying high bias is a characteristic of the Pd nanocontact.

Figure 3 illustrates conductance histogram under a variety of bias voltages. Each histogram was constructed from at least ten individual experiments composed of several tens to hundreds of traces. In the histogram obtained at the bias of 20 mV (Figure 3a), it is clearly shown 1 G_0 peak is dominant. This characteristic of 1 G_0 peak strongly suggests this peak corresponds to relatively high stable contact geometry, such as Pd monatomic contact in solution.[5] As the bias was increased to 0.9 V, occurrence of the conductance at 1 G_0 became small (Figure 3b). A narrowly distributed 1 G_0 peak was observed as a prominent component at the bias of 1.5 V (Figure 3c).

It should be noteworthy that the improved stability of the conductance plateau for Pd–Au contact in present system was observed when ϕ_{Pd} became negative than the potential of the hydrogen adsorption/evolution at Pd deposited electrode ($\phi_{Pd} <$ −0.2 V).[10] It is well known that hydrogen adsorption to Pd modifies its electronic structure significantly.[11] Ruitenbeek et al.[12,13] have shown that a single hydrogen molecule between Pt electrodes has a conductance of 1 G_0. Similarly, recent study also showed that Pd contacts in hydrogen gas environment had conductance of ≈0.5 and/or 1 G_0.[14] It is important to remind that the influence of hydrogen disappears at high bias in gas environment because adsorbed hydrogen removed by local heating at the contact.[12,14] In the present system, however, the quantization was maintained under applying high bias. Interaction between H and Pd atoms under electrochemical potential control should be responsible for the enhanced stability of the Pd–Au nanocontact in solution.

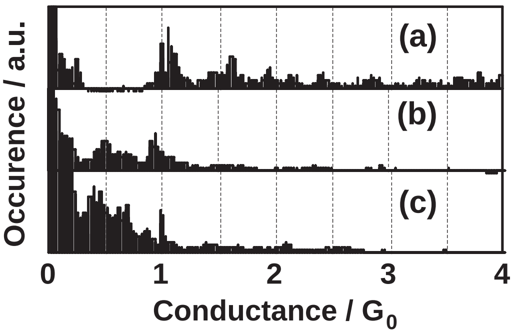

Figure 3. Conductance histograms of Pd nanocontacts in 1 mM $PdCl_2$ + 50 mM H_2SO_4 obtained at different bias voltages: (a) $V_{bias} = 20$ mV, $\phi_{WE1} = 400$ mV, $\phi_{WE2} = 380$ mV; (b) $V_{bias} = 0.9$ V, $\phi_{WE1} = 1.0$ V, $\phi_{WE2} = 0.1$ V; (C) $V_{bias} = 1.5$ V, $\phi_{WE1} = 1.2$ V, $\phi_{WE2} = -0.3$ V.

In summary, the Pd–Au heterogeneous nanocontact was fabricated with the narrowest portion consisting of single or several Pd atoms under applying relatively high bias via selective electrochemical deposition/dissolution. Stable 1 G_0 plateau was recorded for Pd–Au monatomic contact with bias up to 1.5 V, especially when ϕ_{Pd} was set to more negative potential than the hydrogen adsorption/evolution potential.

References and Notes

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Published on the web (Advance View) February 12, 2005; DOI 10.1246/cl.2005.374