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Quantized conductance behavior of Pt metal nano constrictions under electrochemical potential control

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We studied the quantized conductance behavior of mechanically fabricated Pt nanoconstrictions under electrochemical potential control in H₂SO₄, Na₂SO₄ and NaOH solutions. There was no clear feature in the conductance histogram, when the electrochemical potential of the nanoconstrictions was kept at the double layer or the under potential deposited hydrogen potential. At the hydrogen evolution potential, the conductance histograms showed clear features around 0.5 and 1 G_0 in the H₂SO₄ solution. In Na₂SO₄ and NaOH solutions, a 1 G_0 feature with a shoulder appeared in the histogram. The quantized conductance behavior of Pt nanoconstrictions could be controlled by the electrochemical potential and solution pH.

Keywords: Scanning tunneling microscopy, Electrochemical potential, Conductance quantization, Point contact, Hydrogen, Platinum

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1. Introduction

In recent years, metal nanoconstrictions have attracted attention for interest of fundamental science as well as expectation of applications for nano devices [1,2]. The electrical conductance through an atomic scale metal nanoconstriction is expressed by $G = (2e^2 / h)\Sigma T_i$, where T_i is the transmission probability of the i -th conductance channel, e is the electron charge, h is **Planck's** constant, and $G_0 = 2e^2/h$ is a unit of quantum conductance [1]. Various quantized conductance behavior has been observed for metal nanoconstrictions fabricated using a scanning tunneling microscope (STM) and mechanically controllable break junctions (MCBJ) technique. While detailed studies have been done for the conductance properties of the atom-size nanoconstrictions, the single molecular junction has not been studied **satisfactorily**. Several pioneering attempts, however, provided important information on the nature of the single molecular junction [3,4]. Smit *et al.* could determine the conductance of a single hydrogen molecule bridging between Pt electrodes at ultra low temperature in ultra high vacuum (UHV) [3]. They observed a clear $0.9 G_0$ feature in the conductance histogram by dosing hydrogen gas to the Pt nanogap. The conductance fluctuation, point contact spectroscopy [5] shot noise measurements [6], and theoretical calculation result [7-9] show that the $0.9 G_0$ feature is the conductance of a single hydrogen molecule bridging between Pt electrodes.

Adsorbed hydrogen on Pt is an attractive system for the conductance measurement of single molecules. It should be noteworthy that the hydrogen/Pt system can be controlled by the electrochemical potential of substrates. Hydrogen evolution reaction is catalyzed most effectively by Pt-group metals electrode [10]. When the electrochemical potential of the Pt electrode is kept at the hydrogen evolution potential, the Pt electrode surface is covered by hydrogen molecules and dissociated atomic hydrogen. Dissociated atomic hydrogen, which is the intermediate of hydrogen evolution reaction, adsorbs on the on-top site of the Pt surface. At the under potential deposited hydrogen (UPD) potential, hydrogen atoms adsorb on the hollow site. The adsorbed hydrogen atoms and molecules would affect the conductance behavior of Pt nanoconstrictions. In the present

study, we studied the quantized conductance behavior of mechanically fabricated Pt nanoconstrictions under electrochemical potential control in H_2SO_4 (acid), Na_2SO_4 (neutral) and NaOH (alkaline) solutions. The effect of the hydrogen on the quantized conductance behavior of Pt nanoconstrictions was discussed to consider the structure of the nanoconstriction.

2. Experimental

An electrochemical scanning tunneling microscope (EC-STM) was used to fabricate metal nanoconstrictions. A STM tip was made of a Pt wire (diameter ~ 0.25 mm, $> 99.9\%$) coated with wax to reduce a Faradic current in an electrolyte solution. The Pt polycrystalline electrode was prepared by a flame annealing and quenching method. The experiments were performed in an electrochemical cell in a chamber filled with high purity N_2 gas ($> 99.999\%$) to reduce the effect of oxygen in air. The electrochemical potential of the substrate and tip was controlled using a potentiostat (Pico-Stat, Molecular Imaging Co.) with respect to a Ag / AgCl reference electrode. A Pt wire was used as a counter electrode. The electrolyte solutions were 0.05 M H_2SO_4 , 0.1 M Na_2SO_4 , and 0.1 M NaOH .

Atomic scale Pt nanoconstrictions were created **in** the following manner. The tip was pressed into the substrate and then pulled out from the substrate at a typical rate of 50 nm/s in the electrochemical cell. During the contact breaking, the Pt nanoconstriction was formed between the tip and substrate. Conductance measurements were carried out at the breaking process under an applied bias voltage of 20 mV between the tip and substrate. The conductance histograms were obtained from 1000 individual conductance traces.

3. Results

Figure 1(a) shows the cyclic voltammograms (CV) of a polycrystalline Pt electrode in the 0.05 M H_2SO_4 solution. The double layer regime extended from 0.1 V to 0.6 V. When the electrochemical potential of the Pt electrode was kept at potential more positive than 0.6 V, the

oxygen evolution reaction occurred via the formation of an oxide layer on the Pt electrode. A reduction current due to the under potential deposited hydrogen was observed at a potential regime from -0.2 V to 0.1 V. The hydrogen evolution reaction occurred at a potential more negative **than** -0.2 V. The potentials of boundary of the **hydrogen evolution, UPD, double layer, and oxygen evolution** regimes were defined as Φ_1 , Φ_2 , and Φ_3 to be **-0.2, 0.1 and 0.6 V** respectively. Figure 1(b) and (c) show the CV obtained in the 0.1 M Na₂SO₄ and 0.1 M NaOH solutions. Φ_1 , Φ_2 , and Φ_3 were **-0.8, -0.4, and 0.3 V** for 0.1 M Na₂SO₄, and were **-0.8, -0.5, and -0.3 V** for 0.1 M NaOH, respectively. Conductance of Pt nanoconstrictions was measured considering these boundary potentials of the double layer, UPD, and the hydrogen evolution potentials.

Figures 2 and 3 (a-c) show conductance traces and histograms of Pt nanoconstrictions when the electrochemical potential of the Pt nanoconstrictions was kept at the double layer potential. The conductance changed without showing any clear plateaus, which **leads** to the featureless conductance histograms. The conductance behavior did not change at UPD potential (see Fig. 2, 3(d-f)). When the electrochemical potential of the Pt nanoconstrictions was kept at the hydrogen evolution potential, the conductance behavior drastically changed from **those** at the double layer and UPD potentials. The conductance of the Pt nanoconstrictions changed in a stepwise fashion as shown in the trace (see Fig. 2(g-i)). Furthermore, the 0.5 G_0 and 1 G_0 plateau were frequently observed at these steps. As **a** result, the conductance histogram shows clear features around 0.5 and 1 G_0 in the 0.05 M H₂SO₄ solution. In the 0.1 M Na₂SO₄ and the 0.1 M NaOH **solutions**, there are clear **features** around 1 G_0 with a shoulder around 0.5 G_0 .

4. Discussion

These experimental results clearly showed that the quantized conductance behavior of the Pt nanoconstrictions depended on the electrochemical potential and solution pH. The origin of the quantized conductance behavior of the Pt nanoconstrictions is discussed in the following.

At the double layer potential, the conductance traces did not show any clear plateaus and, thus,

the conductance histograms were featureless. This conductance behavior is discussed considering the effect of molecular adsorption on the conductance of metal nanoconstrictions. While the conductance histogram of clean Pt nanoconstrictions shows a clear feature around $1.5\sim 2 G_0$ [7,11,12], a broad feature around $1 G_0$ is observed in the histogram with a bias voltage of 200 mV in $N_2 + 5 \% H_2$ at room temperature [12]. The decrease in the conductance is attributed to the adsorption of gas molecules (O_2 , CO, H_2 , etc). A similar conductance change is observed for Cu and Au nanoconstrictions in solution [13,14]. Adsorbed molecules change the electronic structure and/or **scatter** the conduction electrons of the metal nanoconstrictions, leading to the decrease in the conductance. At the double layer potential, a Pt electrode surface is covered by sulfate anions and water molecules in the H_2SO_4 solution [15,16]. Since sulfate anions and water molecules would adsorb on various sites of the Pt nanoconstriction, the variation of the adsorption states may lead to **the loss** of a fixed conductance value, **which gives** the featureless conductance histogram. At the UPD potential, the polycrystalline Pt electrode surface is covered by the UPD hydrogen and sulfate anions [10]. The adsorption of the UPD hydrogen and sulfate anions would make the conductance histogram featureless.

At the hydrogen evolution potential, the conductance histogram showed clear features around 0.5 and $1 G_0$ in the H_2SO_4 solution, while the histograms showed a $1 G_0$ feature with a shoulder around $0.5 G_0$ in the $0.1 M Na_2SO_4$ and $0.1 M NaOH$ solutions. At the hydrogen evolution potential, the Pt electrode surface is covered by the UPD hydrogen, the over potential deposition (OPD) atomic hydrogen, and evolved hydrogen molecules. There are no sulfate anions and water molecules on the Pt electrode surface [10,16]. Under the condition that only hydrogen species adsorb on the Pt nanoconstriction, a certain atomic configuration with the conductance of $1 G_0$ was stabilized. Similar $0.9 G_0$ feature was also observed for the Pt nanoconstrictions under hydrogen dosing in UHV. The feature is attributed to the hydrogen molecule bridging between two Pt electrodes [3,5,6]. Therefore, the observed $1 G_0$ feature would originate from a hydrogen molecule bridging two Pt electrodes in solutions. Figure 4 (a) shows proposed model of the structure showing

conductance of $1 G_0$.

The $0.5 G_0$ feature observed in the present system has never been reported. It is noteworthy that the $0.5 G_0$ feature was clearly observed in the 0.05 M H_2SO_4 solution, while only a shoulder around $0.5 G_0$ was observed in the 0.1 M Na_2SO_4 and 0.1 M NaOH solutions. The origin of the $0.5 G_0$ feature is discussed based on the difference of the $0.5 G_0$ feature among the solutions. The coverage of the OPD hydrogen on the Pt electrode is evaluated in acid, neutral and alkaline solutions by current-potential curves and infrared spectroscopy [17,18]. The coverage is more than 1 monolayer (ML) and below 0.1 ML in the H_2SO_4 and NaOH solutions, respectively [17]. Therefore, the coverage of the OPD hydrogen would play a decisive role in appearance of the $0.5 G_0$ feature. The conductance of nanoconstrictions depends not only **on** the electronic structure of the point contact of atoms or molecules bridging the two electrodes, but also **on** that of the stem part of the contact. At higher coverage of the OPD hydrogen, the stem part of the Pt electrode would be also covered by the OPD hydrogen. The adsorbed OPD hydrogen is expected to change the electronic structure of the stem part of the Pt electrodes, leading to the change in the conductance of the metal or molecule bridging Pt electrodes. **In addition to** the possibility of the contribution of the OPD hydrogen, a hydrogen molecule bridging Pt electrodes could be also considered as the origin of the $0.5 G_0$ feature (see Fig. 4 (b)). One or two hydrogen molecules could bridge between Pt electrodes at higher coverage of the OPD hydrogen. Additional adsorption of hydrogen would decrease the conductance of the hydrogen molecule bridge with the conductance of $1 G_0$ (Fig. 4 (a)). Figure 4(c) shows another structure model showing the conductance of $0.5 G_0$, in which two hydrogen molecules bridge between Pt electrodes. At this moment, the origin of the $0.5 G_0$ and $1 G_0$ features is not clear, since we have not directly observed hydrogen atom or molecule at the nano constriction. Systematic investigation, such as electrochemical potential, solution pH, metal dependence, would clarify the origin of the feature, and is in progress in our laboratory.

5. Conclusion

We studied the quantized conductance behavior of Pt nanoconstrictions under electrochemical potential control in 0.05 M H₂SO₄, 0.1 M Na₂SO₄ and 0.1 M NaOH solutions. The conductance of Pt nanoconstrictions was measured at the double layer, the UPD, and the hydrogen evolution potential. Conductance histograms were featureless at the double layer or the UPD potential. At the hydrogen evolution potential, there were clear features in the histograms around 0.5 and 1 G_0 in the 0.05 M H₂SO₄ solution, while 1 G_0 with a shoulder around 0.5 G_0 in 0.1 M Na₂SO₄ and 0.1 M NaOH solutions. Contribution of a hydrogen molecule bridging Pt electrodes was considered as the origin of the 0.5 G_0 and 1 G_0 features in the histogram.

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Figure captions

Figure 1 : Cyclic voltammogram of a polycrystalline Pt electrode in (a) 0.05 M H₂SO₄, (b) 0.1 M Na₂SO₄, (c) 0.1 M NaOH. Φ_1 , Φ_2 , Φ_3 are the potential of boundary between the **hydrogen evolution and UPD** , double layer, **oxygen evolution**.

Figure 2 : Typical conductance traces of Pt nanoconstrictions at the double layer (DL: a-c), the UPD (UPD: d-f) and the hydrogen evolution potential (OPD:g-i). These traces were measured in 0.05 M H₂SO₄ (a,d,g), 0.1 M Na₂SO₄ (b,e,h), and 0.1 M NaOH (c,f,h).

Figure 3 : Conductance histograms of Pt nanoconstrictions at the double layer (DL: a-c), the UPD (UPD: d-f) and the hydrogen evolution potential (OPD:g-i). These histograms were obtained in 0.05 M H₂SO₄ (a,d,g), 0.1 M Na₂SO₄ (b,e,h), and 0.1 M NaOH (c,f,h).

Figure 4: Schematic models of the structure showing conductance of $1 G_0$ (a) and $0.5 G_0$ (b,c). (a) a hydrogen molecule bridging between Pt electrodes, (b) a hydrogen molecule bridging between Pt electrodes covered by the hydrogen. (c) two hydrogen molecules bridging between Pt electrodes.

Figure1

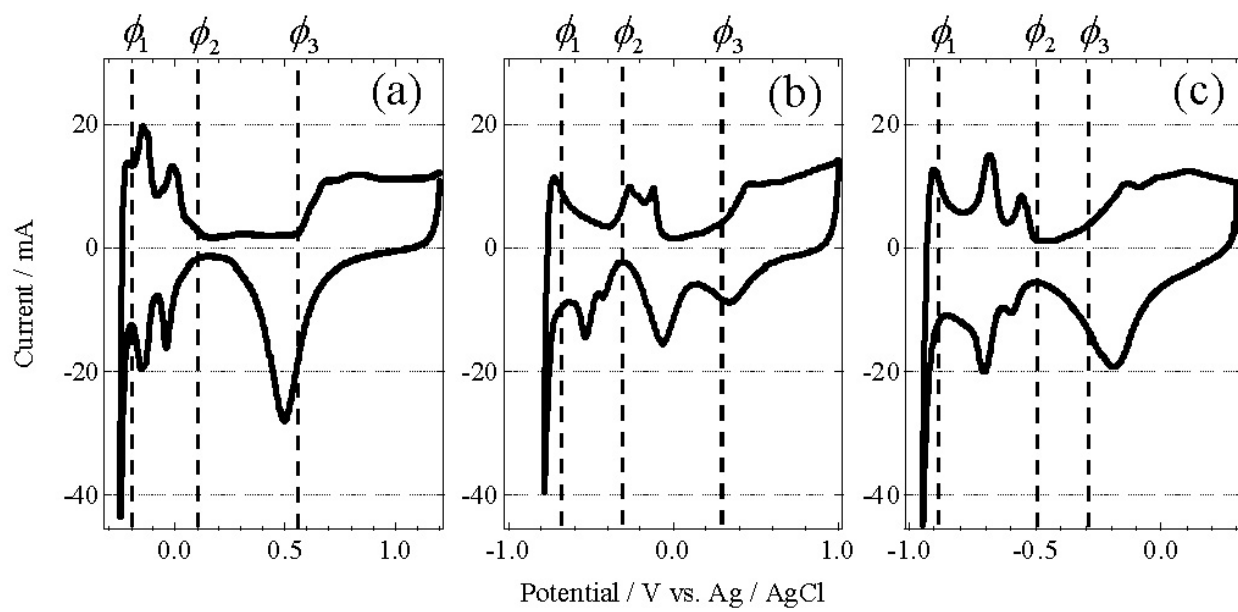


Figure2

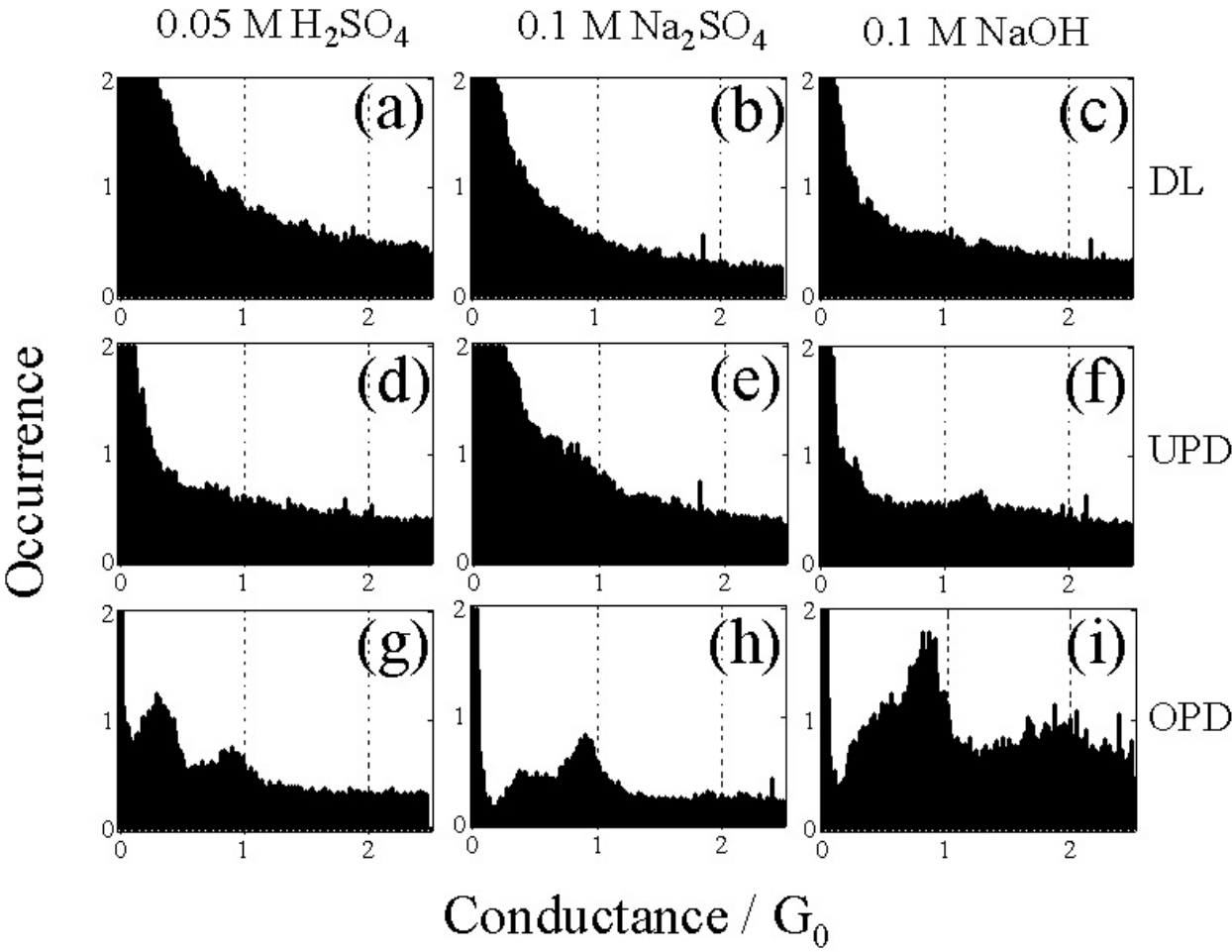


Figure3

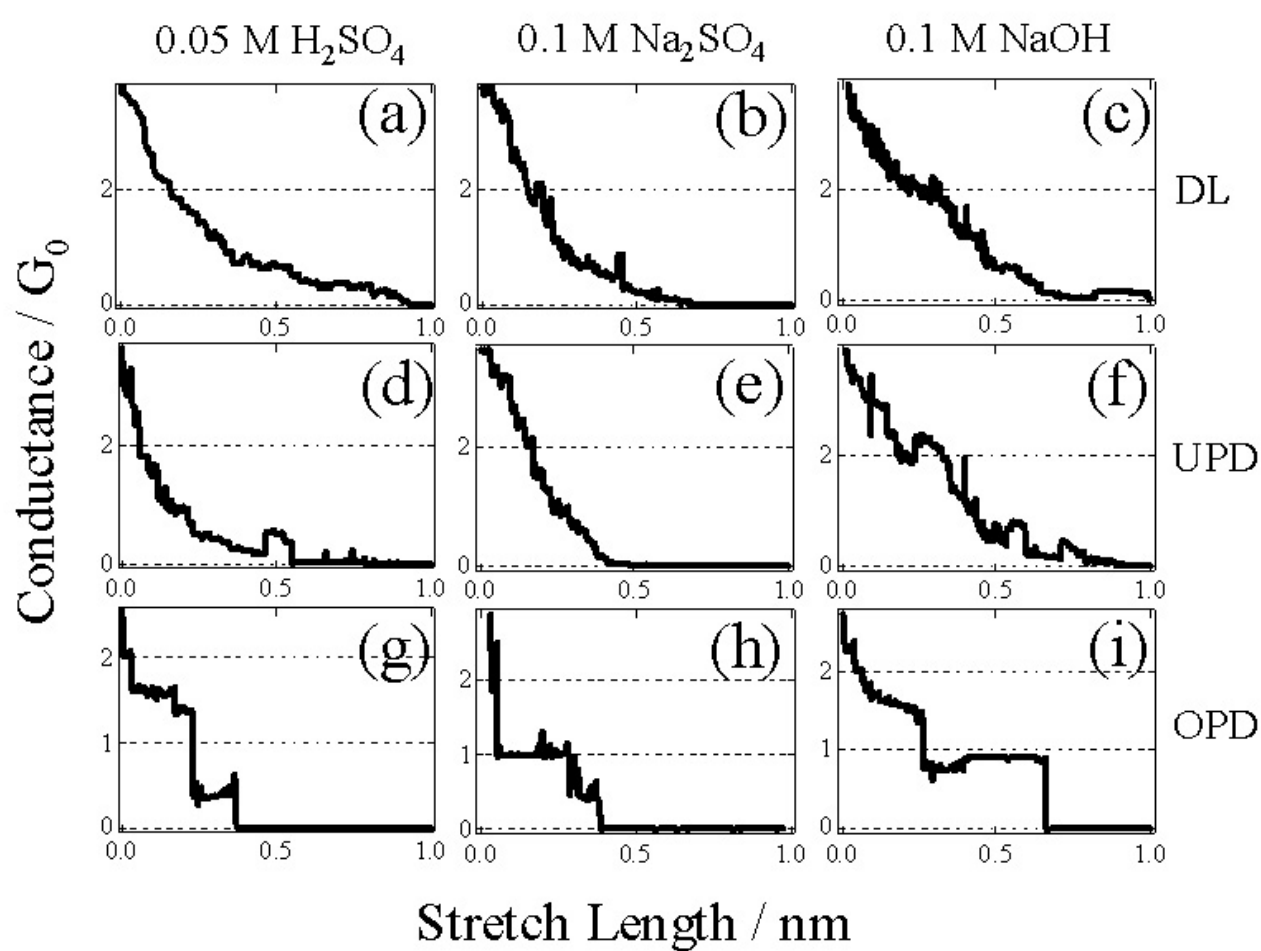


Figure4

