Low-temperature hydrogen absorption in metallic nanocontacts studied by point-contact spectroscopy measurements

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Abstract. We report on hydrogen (H) and deuterium (D) atoms absorption below $T = 20$ K in metallic palladium (Pd) via quantum tunnelling (QT). When a small bias voltage is applied between Pd nanocontacts that are immersed in liquid H\textsubscript{2} (D\textsubscript{2}), the differential conductance spectra measured by point-contact spectroscopy change enormously. The results indicate H (D) absorption in Pd nanocontacts at the temperature where H (D) absorption due to thermal hopping process is not expected, and can be explained by QT. The QT occurs when the energy level of the potential well trapping the H (D) atom coincides with those not trapping the H (D) atom, and is assisted by phonons induced by ballistic electrons.

1. Introduction
The use of fossil fuels causes devastating environmental impacts such as global warming due to carbon dioxide emissions. In addition, their supplies will deplete in near future. These situations accelerate the research on the engineering application of hydrogen (H), which is expected to be an ideal replacement for fossil fuels, because H\textsubscript{2} has high energy density by weight and its combustion products, H\textsubscript{2}O, is environmentally clean. A large amount of H atoms are absorbed in metal hydride, therefore which is studied as carrier and storage for H. Although intensive efforts have been devoted to understand the absorption and diffusion process of H atom in hydride, it is unclear because of its strong quantum character arising from the lightest mass.

Quantum tunnelling (QT), which is one of the most fundamental concepts in quantum mechanics, is essential for H absorption and diffusion process in metal [1]. QT of neutral atoms, including H atom in metal, has been studied with a variety of experiments such as quasi-elastic neutron scattering and nuclear magnetic resonance [2,3]. However, QT is experimentally difficult to detect, in contrast to QT of electronic systems which can be detected directly via transport measurements. Hence, most studies on QT of H are discussed in terms of the temperature dependence of the reaction rate or the relaxation time [1,4,5]. In the thermal region, the temperature dependences of these processes obey the Arrhenius equation; while in the quantum region, there is no temperature dependence. These indicate that QT of H is ambiguous when the temperature dependences are complex.

We focus on point-contact spectroscopy (PCS) to investigate low-temperature properties of hydrides [6]. For the contact smaller than the mean free path of conduction electrons, the electrons accelerated by the bias voltage are moved in the contact without energy dissipation (ballistic electron). Hence, we can explore the properties of hydride through the inelastic scattering process between the electrons and H atoms using PCS [7-10]. Moreover, we found that the inelastic scattering induces low-temperature H absorption in Pd nanocontacts.
absorption in palladium (Pd) nanocontacts from liquid H₂ [6].

In this paper, we report the effect of high bias voltage for H absorption in Pd nanocontacts. The results indicate that the maximum concentration of H is almost ~ 0.6, which is attained by applying the bias voltage larger than 60 mV. Additionally, we perform deuterium (D) absorption experiments to study the generality of the low temperature absorption. Although the H and D spectra show a difference because of the mass difference, the absorption process can be explained by the same scheme.

2. Experimental

The present experiments are carried out with a homemade cryostat attaching a mechanically controllable break junction (MCBJ) apparatus in vacuum and low-temperature environment, which prevents surface contamination and oxidation. Pd polycrystalline wire (99.998%, 0.2 mm diameter) on a phosphor-bronze substrate is stretched by bending the substrate with mechanical force, which is generated by a screw and a piezo element as shown in figure 1. The size of nanocontact is changed continuously from atomic scale to micrometres and is kept constant over several hours by avoiding thermal input to the sample space [11, 12]. In order to immerse the nanocontacts in liquid H₂, the MCBJ apparatus is mounted in an inner cell with flexible bellows inside the vacuum chamber [13]. Note that the differential conductance measurements to detect H absorption and diffusion are performed in liquid H₂, preventing the temperature increase due to Joule heating in the nanocontacts during the measurements.

![Schematic illustration of MCBJ experimental cell.](image)

Figure 1. (Color online) Schematic illustration of MCBJ experimental cell. H absorption and diffusion experiments can be carried out in liquid H₂, avoiding the temperature increase due to Joule heating in the nanocontacts during the measurements.

The differential conductance dI/dV spectra are measured as a function of bias voltage using a lock-in technique (1 kHz modulation). d²I/dV² spectra are obtained from the numerical derivative of dI/dV.

3. Results

Figures 2(a) and 2(b) show dI/dV spectra, and its numerical derivative of d²I/dV² for pure Pd and PdH₀.₆ nanocontacts, respectively. The spectra are measured in vacuum at T = 18 K, where the vertical axis is plotted in the universal conductance unit G₀=2e²/h. Note that H atoms in PdH₀.₆ are loaded at room temperature by the following procedure. Pd wire is exposed to 1 atm of H₂ gas in the inner cell at 300 K for several hours, making the H concentration to be x ~ 0.6. Then, the H₂ gas is evacuated from the inner cell at 80K to avoid H desorption from PdH₀.₆ wire. Finally, we prepare the nanocontact by stretching PdH₀.₆ wire at 18 K.

In pure Pd, a peak is observed at around the zero bias in dI/dV spectra, while a sharp peak due to electron-phonon scattering is observed at |V| ~ 20 mV in d²I/dV² spectra. These features are consistent with other pure metals, indicating formation of clean nanocontacts without impurities on the surface. As shown in figures 2(a) and 2(b), the spectra are changed significantly from those of pure Pd by hydrogenation. The zero bias peak in dI/dV spectrum broadens. Moreover, in d²I/dV² spectrum a new broad peak emerges at around |V| ~ 60 mV, while the peak at |V| ~ 20 mV is suppressed. From the neutron experiments, the first excited level of H atom trapped in fcc Pd octahedral site is estimated to be at E ~ 60 meV from the ground state [14], which is consistent with the bias voltage of the new broad peak. This indicates that the excited energy level of H atom trapped in Pd can be measured with PCS.
Simultaneously, the vibrational mode of H atom is induced by scattering with ballistic electrons accelerated by bias voltage. These results strongly suggest that H absorption and diffusion phenomena can be detected through PCS measurements.

Using PCS, we have performed H absorption and diffusion experiments into Pd nanocontacts from liquid H\textsubscript{2}. After the pure Pd nanocontact is prepared at \(T \approx 18\) K in vacuum, liquid H\textsubscript{2} is introduced in the inner cell. Then we start the differential conductance measurements with increasing the amplitude of the bias voltage from \(|V| = 20\) mV to 100 mV with 20 mV step. After starting the measurements, the spectra shape changes gradually and finally becomes almost constant several hours later for all the bias amplitudes. Figures 3(a) and 3(b) show the bias voltage dependence of the \(dI/dV\) and \(d^2I/dV^2\) spectra after finishing their changes. It is seen that the width of \(dI/dV\) curve broadens as the bias amplitude is increased. In addition, the peak value at \(|V| \approx 20\) mV in \(d^2I/dV^2\) curve is rapidly decreased. Significantly, the shapes of the \(dI/dV\) and \(d^2I/dV^2\) spectra for the bias voltage larger than 60 mV are nearly the same with those of the spectra plotted in figures 2(a) and 2(b). These results demonstrate that H absorption into the nanocontacts is gradually progressed by applying the bias voltage although the thermal hopping of H atom is not expected. Furthermore, H concentration in the contact is almost saturated for the bias voltage larger than 60 mV. From comparison with figures 2(a) and 2(b), the final H concentration is considered to be \(x \approx 0.6\).

**Figure 2.** (Color online) (a) \(dI/dV\) spectra for pure Pd and Pd\textsubscript{H0.6} nanocontacts in vacuum at 18 K, where the vertical axis is the universal conductance unit \(G_0=2e^2/h\). (b) \(d^2I/dV^2\) spectra, which are the numerical derivative of (a). The spectrum for pure nanocontact is scaled down one-half.

**Figure 3.** (Color online) The bias voltage dependence of \(dI/dV\) (a) and \(d^2I/dV^2\) (b) spectra of Pd immersed in liquid H\textsubscript{2}. The spectra in (a) and (b) are measured for the bias amplitude at \(|V| = 20, 40, 60, 80\) and 100 mV, after finishing the spectra changes by H absorption into the nanocontacts. For comparison, the spectra for pure nanocontact (dashed line) are plotted in the figures. The \(d^2I/dV^2\) curve is scaled down one-fifth.
Next, we perform D absorption experiments into Pd nanocontacts from liquid D$_2$ at $T \approx 20$ K to confirm the generality of H absorption observed in figures 3(a) and 3(b). The experimental procedure is the same with that of H absorption experiments. Figures 4(a) and 4(b) show the spectra change by D absorption, where the differential conductance is measured in liquid D$_2$ with the bias amplitude for $|V| \leq 80$ mV. As in the case of H absorption measurements, the spectra shape changes gradually after starting the measurements and finally becomes almost constant several hours later, indicating that D absorption process is the same as H one. In figure 4(b), the new peak appears at $|V| \approx 40$ mV, which is smaller than that at $|V| \approx 60$ mV due to the H excitation. This shift is explained by the mass difference between H and D. Indeed, the value of $V \approx 40$ mV is in an excellent agreement with the first excited level of D trapped in fcc Pd octahedral site detected by the neutron experiments [14].

![Figure 4](image1.png)

**Figure 4.** (Color online) (a) $dI/dV$ spectrum for pure Pd nanocontact (black line), Pd nanocontacts immersed in liquid H$_2$ (red line) and liquid D$_2$ (blue line), where the bias voltage of $\approx 80$ mV is applied in liquid H$_2$ and D$_2$. (b) $d^2I/dV^2$ spectra for pure Pd nanocontact, Pd nanocontacts immersed in liquid H$_2$ and liquid D$_2$. The spectrum for pure nanocontact is scaled down one-half.

Finally, let us discuss the origin of H/D absorption and diffusion below $T = 20$ K. Thermal hopping and QT are the two possible modes for the absorption and diffusion process. In thermal hopping mode, H atom trapped in an octahedral site of fcc Pd moves to a vacant site by jumping over the activation barrier $E_{\text{diff}} \approx 230$ meV for the absorption and diffusion process [15]. The diffusion coefficient is expressed by $D = D_0 \exp(-E_{\text{diff}}/k_B T)$ so that the thermal hopping is rapidly suppressed with decreasing temperature. Here, $k_B$ is Boltzmann’s constant. When $D_0 = 2.9 \times 10^{-7}$ m$^2$s for Pd [1], $D$ is estimated to be $\approx 10^{-70}$ m$^2$s at $T = 18$ K, implying that the thermal hopping process is prohibited in the present experiments. From these facts, it is reasonable to consider that QT is responsible for H/D absorption and diffusion below $T = 20$ K. We propose the following scenario to understand the results. When H/D atoms

![Figure 5](image2.png)

**Figure 5.** (Color online) (a) The self-trapped state of an H atom, where the energy level of the atom is $\approx 50$ meV lower than that of the vacant site. The first excited state is at $\approx 60$ mV from the ground state. (b) The diffusion process from the self-trapped state, where the H atom is excited by phonon vibrations generated by scattered inelastic electrons, and can tunnel to the neighbouring site.
are absorbed in metals, the lattice structure should be distorted, forming a “self-trap state” in Pd. In the case of H atoms, the energy level of the H trapped site is ~ 50 meV lower than the corresponding level in the H vacant one as shown in figure 5(a) [16]. Diffusion due to QT occurs when the energy level of H atom in the self-trapped state is equal to that of the vacant one as shown in figure 5(b). This process is induced by phonon vibrations, which are excited by the scattering with the ballistic electrons.

The present results indicate that when a small bias voltage is applied between the metallic surface and liquid H₂, H atoms are absorbed and diffused in metal due to QT. This would result in progress of H embrittlement even below 20 K, hindering safe utilization of liquid H₂. Obviously, further investigations on QT, e.g., material dependence, time dependence, are necessary to advance the industrial applications of liquid H₂.

4. Conclusion
We report on H and D atoms absorption in metallic Pd via QT. The differential conductance dI/dV and d²I/dV² spectra show significant change when H or D atoms exist in Pd nanocontacts. Using the phenomena, we demonstrate that H and D atoms are absorbed in Pd nanocontacts from liquid H₂ (D₂) even below T = 20 K, when a small bias voltage is applied between Pd nanocontacts. The thermal hopping process is prohibited at this temperature, indicating that QT plays a crucial role for the absorption and diffusion of H and D. We explain that the QT occurs when the energy level of the potential well trapping the H atom coincides with those not trapping the H atom, and is assisted by phonons induced by ballistic electrons.

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