Conduction-channel analysis of hydrogen-molecule bridge between superconducting electrodes

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Abstract. Using the mechanically-controllable break-junction technique, we have measured the current-voltage characteristics of hydrogen molecular bridges between superconducting niobium electrodes, and analyzed them by the theory of multiple Andreev reflection. From the fitting to the theory, we have determined a set of transmission coefficients for each curve. Deposition of hydrogen caused a change in the conductance histogram of niobium junction and a small peak appeared at around $2e^2/h$. Though perfect transmission events have not been observed in the data, in the composition of transmission coefficients the contribution of the main channel is larger in Nb-H$_2$ system.

1. Introduction
Growing interest of molecular electronics leads to intensive study of single-molecular conduction in recent years. The electron transport through a nano-structured system such like a single molecular bridge is understood based on Landauer’s picture, where the conduction channel and the transmission coefficient are the central ideas. In ohmic region, the conductance of the system is given by the Landauer formula, $G = G_0 \sum \tau_i$, where $G_0 = 2e^2/h$ and $\tau_i$ being the quantum conductance and the transmission coefficient of $i$-th channel, respectively. Thus, the total sum of the transmission coefficient determines the linear conductance.

In several mono-valent atomic point contacts, e.g., Au, a sharp peak is observed at $G = 1G_0$ in so-called conductance histogram[1], which suggests that the current is carried through a single ballistic channel in a single Au atom contact. In order to proof this expectation, one has to determine not only the sum of $\tau_i$ but also their composition $\{\tau_i\}$. Three methods have been reported to determine the composition[2]: both the shot noise[3] and the conductance fluctuation[4] are strongly suppressed at $G = G_0$ which means existence of fully open channel. The third method uses the superconducting electrodes. The problem of superconducting nano-link is now well understood within Landauer’s picture by taking into account the Andreev reflection peculiar to superconductors. According to the theory[5], the I-V curve has characteristic structure due to the multiple Andreev reflection (MAR) in the sub-gap region, and it varies strongly as a function of $\tau$. Thus, using the relation one can decompose the I-V curve into a sum of single-channel curves. Obviously it is superior to the shot noise method and the fluctuation method in determining $\tau$ of plural channels. This method was adopted by Scheer et al.[6] for the first time, and they successfully determined the channel transmission of aluminum...
up to six channels. Although the method is applicable only for superconducting junction, Scheer et al. succeeded in determining the transmission coefficient of gold atomic point contact using the superconducting proximity effect[7].

Determination of transmission coefficients should also be important for molecular junction. In this paper we apply this method to bridges of the simplest molecule, hydrogen molecule. So far we did the experiment using niobium (Nb) and lead (Pb) electrodes, and we report the result of Nb in this paper. The hydrogen molecule bridging platinum electrodes are known to show a peak at about $1G_0$ in the conductance histogram[8]. Like the similar peak in Au atomic point contact mentioned above, it may mean the existence of ballistic channel in the hydrogen single-molecule bridge. According to Halbritter et al.[9], niobium - hydrogen system also shows a small peak at about $1G_0$. By the channel analisys of lots of bridge we expect to know the formation of conduction channel in the system.

2. Experiments
We realized the molecular bridge by means of a mechanical break junction. The experiment was done as follows: Firstly, we prepared an Nb or Pb wire 0.1 mm in diameter, 10~15 mm long and notched at the center. Then we attached it upon a polymid-coated phosphor bronze plate, 4 mm wide, 22 mm long and 0.3 mm thick using two drops of epoxy adhesive (Stycast 2850GT) at the both sides of the notch. The gap distance between the drops was 0.1~0.3 mm. The sample was set on a bending stage in an insert chamber. The bending mechanism consists of a motor-driven differential screw and a piezo actuator. The insert chamber was set in a variable-temperature liquid-helium cryostat equipped with superconducting magnet. A small amount of helium gas was introduced in the insert chamber for the sake of heat exchange. Hydrogen was deposited at about 10 K onto the substrate through a double-wall vacuum-insulated thin tube. The inside of the tube was warmed by a manganin heater to prevent freezing.

3. Results and Discussions
Figure 1 shows the conductance histograms of Nb and Nb-H$_2$ junction. They are composed from 693 and 794 conductance traces that were obtained at 9.5K to kill the superconductivity. The conductance trace of Nb junction consisted of plateaus and discontinuous jumps, and the size of the jump was of the order of $G_0$. The last jump, i.e. the fracture occurred at around 2 $G_0$. The curve changed rather drastically after deposition of hydrogen: it became noisy and
small irregular fluctuation appeared besides plateau and jump structure. The fracture occurred at smaller conductance. The histogram of Nb junction shows a broad peak at about 2.7$G_0$ that corresponds the last plateau before fracture. This peak disappears in Nb-H$_2$ junction and a small peak appears at about 1$G_0$ instead. They are essentially the same as the results in ref.[9].

In the tunnel region after fracture, the conductance of Nb junction decreased exponentially as a function of the piezo voltage $V_P$. By fitting to the equation $\log G = -aV_P + b$, we calculate the coefficient $\gamma$ between the elongation $\Delta u$ and the piezo voltage, $\Delta u = \gamma \Delta V_P$, assuming the work function of bulk Nb. In Nb-H$_2$ junction, the fluctuation of current persisted even in the tunnel region. Althogh it leads to larger residual, the conductance globally obeyed exponential dependence, whose attenuation rate is about a half of that for Nb junction. The temperature 9.5 K is not far from the melting point of hydrogen, 14 K. Therefore, the small fluctuation in the conductance curve of Nb-H$_2$ junction is reasonably attributed to the random motion of adsorbed hydrogen molecules. Occasional movement of hydrogen molecules adsorbed around the contact area will change the potential for conduction electrons. Change of the attenuation rate in the tunnel region implies that the thickness of the absorbed hydrogen is at least larger than 1 nm, and that the electrons tunnel through the hydrogen medium instead of vacuum. From the change of the attenuation rate, the barrier height of hydrogen medium for electron tunneling is estimated at a quarter of that of the vacuum.

In order to determine the transmission coefficients, we measured the current-voltage ($I-V$) curves at 4.2K with keeping the piezo voltage unchanged. Figure 2 shows an example of results for the Nb-H$_2$ junction. The direct quasi-particle tunneling occurs above $V = 2\Delta/e = 2.6$ meV. The wavy structure in the subgap region is due to the MAR process, and zero-voltage supercurrent is not observed. After Scheer et al.[6], we analyze the result by fitting to the theory of MAR[5] assuming the current is a sum of the single-channel MAR current. In the fitting, we used the theoretical value at $T=0K$ and took the gap parameter $\Delta$ as well as the transmission coefficients as fitting parameters. The solid curve in Fig. 2 is a result of the fitting. In this case, the junction consists of two channels with $\tau$ being 0.40 and 0.06.

Just as the conductance histogram, $\{\tau_i\}$ of a specific junction would have little meaning and we need to discuss their statistical feature. So, we have analyzed hundreds of $I-V$ curves to obtain the composition of channels, and show the results in Fig.3. In the figure, we plot the averaged composition of channel transmission coefficient for each bin as composite bar charts. The figures on each bar are the number of $I-V$ curves used to average. According to Scheer et al.[7], the number of conduction channel of single-atom point contact is determined by the valence of the atom. namely, they found one channel for monovalent metal Au, and three
channels for trivalent metal Al. In the case of Pb and Nb, four and six channels were found, respectively, but one channel of them were vanishingly small in accordance with the symmetry considerations. As Fig.3(a) shows the channel number at $G = 2G_0$ which is the typical value of the conductance at the fracture is five or six, which agrees with ref.[7]. Figure 3(a) also shows that the junction with $G < 0.2G_0$ is described well by one channel formula, and that the second and the third channel join at about $G = 0.3G_0$ and $0.5G_0$, respectively.

We did the same channel-analysis for Nb-H junction, and the result is shown in Fig.3(b). As Fig.2 shows, the conductance histogram of Nb-H junction also shows a peak, even though small, at about $1 \cdot G_0$. In the $I-V$ measurement we have 17 data in a bin at $G = (1 \pm 0.05)G_0$, but no data shows ballistic dependence. However, examining Fig.3(a) and Fig.3(b) carefully, we notice the tendency that the relative contribution of $\tau_1$ is larger in Nb-H than in Nb within the region $G = 0.3G_0 \sim 0.9G_0$, suggesting the dominant channel of hydrogen origin.

Finally, we will discuss two peculiar behaviors found in Nb-H junction. The first one is the $I-V$ curve. The Nb-H junction sometimes shows a peaklike structure just above the gap edge, which cannot be reproduced by the MAR theory. (In Fig.3(b), we have omitted this kind of data that have large residual after fitting.) This kind of behavior was never seen in Nb junctions. We also found the gap energy $\Delta$ obtained by the fitting reduced much in Nb-H junctions from that of Nb junctions. Similar $I-V$ curves in MBJ experiment are reported in Nb-Au-Nb system by Scheer et al.[10]. In this system, the cooper-pairs penetrate into the normal conducting Au region by the diffusive proximity effect, and the peak in the curve is attributed to to the peak structure of the density of state in the normal conducting region. So our experiment seems to indicate that the deposited hydrogen affects strongly the superconductivity of Nb, and the surface layer becomes rather proximity-induced superconducting state. At the top of the break junction, its shape might be needlelike, and be easily influenced by the adsorbed hydrogen. Or, in the elongate-retract cycle, the top of the break junction undergoes heavy plastic deformation, which may result in the alloying the hydrogen into the niobium metal. We need search these possibilities in future.

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