Fabrication of various metallic nanogap electrodes using molecular ruler technique

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1. Introduction

A pair of two metal electrodes, which is separated by below ten nano-meters, is generally called a nanogap electrode, and is an attractive tool which makes it possible to measure electrical transport of low dimensional nanostructures such as nano-particles or single molecules. Recently, some fabrication methods of the nanogap electrode have been suggested, such as a shadow evaporation technique, a break junction technique and a mechanical break junction technique. In particular, the molecular ruler technique takes advantage of preciseness of the fabrication of the nanogap electrodes [1],[2],[3]. However, the materials of the nanogap electrodes have been restricted to Au or Pt metals with this method. This is because the molecular resist was not sufficiently formed on the surface of metal electrodes on other metals. We assumed that existence of natural oxide on the surface of the metals prevent bonding with thiol termini molecule of the molecular resist, or the termini molecule of thiol is difficult to bond to those metals. Therefore, fabrication processes have to be improved to apply the technique to those metals. In this work, we demonstrate a technique to fabricate nanogap electrodes with Al, Ni, Co, and Nb metals. We fabricated monodispersed bridging structure which consists of the Nb nanogap, Au nano-particles and linker molecules. This structure exhibited the property of single electron tunneling.

2. Experimental procedure

Nanogap electrodes of some metals were prepared using the combination of the molecular ruler technique and electron beam lithography. First, the 1st electrode was fabricated by electron beam lithography^{[2], [3]}, electron beam evaporation and metal lift off. Then, self assemble moleculars (SAMs) were deposited on the 1st electrode. This is the molecular ruler treatment. Before the molecular ruler treatment, the sample was dipped into the solution of the ACT935J to remove the organic materials and the surface natural oxide. After that, the 2nd electrodes were fabricated in the same way as was used for the fabrication of the 1st electrode. Finally, the nanogap electrodes were fabricated by the metal lift off with the SAMs. Figure 1 shows scanning electron microscope images of various metal nanogap electrodes. Especially, the Co-Nb asymmetric nanogap electrode can be fabricated only by this technique. In this work, we found that some metals except Au and Pt must be treated in the nitrogen ambient, to avoid oxidization on the metal electrode surface. Consequently, the nanogap electrodes were fabricated with high yields. In Table 1, fabrication conditions of various metallic nanogap electrodes are summarized. The ACT935J was used for metal lift off with the SAMs too. The sonications easily gave the damage to the 1st electrode to remove SAMs. As for the fabrication process of the Nb electrode, the Co/Al sacrificed layer was deposited on the 1st Nb electrode, because, the formation of SAMs on the surface of Nb was difficult. Finally, Co/Al sacrificed layer was removed by HCl after removing the molecular resist.

In order to test the feasibility of the nanogap electrode, the bridging structure was fabricated by placing Au nano particles between nanogap electrodes. Au nano-particles were linked by 1,8-octanedithiol between the 1st Nb electrode and the 2nd electrode (figure 2(c)), where we confirmed connections between termini molecule and metal electrodes by X-ray photoelectron spectroscopy (XPS). This structure, with a single Au-nanoparticle as shown in Fig. 2(c), was realized with monodispersity. Figure 2(a) and (b) show the I-V and dI/dV-V curves in the applied magnetic fields. It was found that the Coulomb blockade region without current flow (Coulomb gap) depended on the applied magnetic field. The Coulomb gap at 0T is wider than that at 4.0T, as seen in Fig.2(c). This result originates from the existence of the superconductive gap. We have demonstrated behaviors of single electron transistor with a clear gate voltage modulation in polydispersed system^[4].

3. Summary

In summary, we have developed techniques to fabricate Al-Al, Ni-Ni, Co-Co, Nb-Nb and Co-Nb nanogap electrodes by combining molecular ruler technique and electron beam lithography. The monodispersed bridging structure was fabricated, which consists of the Nb-Nb nanogap electrodes with a single Au nano-particle and 1,8-octanedhithiol in between.



Fig. 1 SEM images of various metallic nanogap electrode. (a) Al-Al nanogap. (b) Ni-Ni nanogap. (c) Co-Co nanogap. (d) Nb-Nb nanogap. (e) Nb-Co nanogap.

	Al-Al nanogap	Co-Co (Co-Nb) nanogap	Ni-Ni nanogap	Nb-Nb nanogap
Atmosphere	N_2	N_2	N_2	N_2
ACT time pre-etching	10min. (65°C)	10min. (65°C)	1min. (65°C)	10min. (65°C)
Molecular ruler	2-3 days	2-3 days	2-3 days	2-3 days
Sonication	1-5 min.	1 min.	1-1.5 min.	30 sec.
ACT time molecular ruler	60-90 min. (65°C)	10 min. (65°C)	1min. (65°C)	20 min. (65°C)
Sonication	1-3 min.	5 sec.	15 sec	10 sec.
Yield	63/67 (94%)	88/96 (91%)	15/16 (94%)	86/89 (96%)

Table 1 Fabricating conditions of various metallic nanogap electrodes

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Fig. 2 (a) I-V property, (b) dI/dV-V property of bridging structure which consists of Nb nanogap, Au nano-particles and linker molecules. (a) The curve of 4.0T offset 4.0nA. (b) The curve of 4.0T offset 4.0nS. (c) SEM image around Nb nanogap

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