Electrical Conductance Measurement of Oligothiophene Molecular Wires Using Nanogap Electrodes Prepared by Electrochemical Plating

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Nanogap electrodes were prepared by electroplating. The starting electrodes of gold were patterned by conventional photolithography and lift-off techniques, and the gap separation was reduced by depositing gold in electroplating solution. Careful control of deposition conditions by monitoring the current through the electrodes enabled us to obtain the electrodes with the separation of less than 10 nm. Electrical conductunce of newly designed oligothiophene wires was measuerd with the nanogap electrodes prepared.

Preparation of a single molecular device is one of the most challenging subjects in nanoscience. Since the construction of electrodes with a gap separation of a few nm, i.e., nanogap, is difficult by conventional lithographic techniques, various methods such as mechanical break junction[1,2] and electromigration[3] have been developed.[4] Using these electrodes, electrical conductance of small molecules such as thiol derivatives and oligomers of small molecular weight was measured.[4]

These methods have some difficulties in the control of the gap separation for larger molecules. Electrochemical formation of the nanogap electrodes is one of the most promising methods to overcome these difficulties since the gap separation can be monitored and tuned during the process.[5–10] Gap electrodes are initially fabricated by conventional lithography techniques. Metals are, then, deposited electrochemically on the gap electrodes. As metal layers grow, the gap between the electrodes becomes narrower. The nanogap electrodes can be formed when the electrodeposition is finished just before the formation of an atomic contact, which can be detected from appearance of the quantum resistance.[5,11]

In this work, we fabricated gold nanogap electrodes by the electrochemical method. The starting electrodes with the gap separation of 2 µm were prepared by conventional photolithography and lift-off techniques on thermally grown SiO_2 layers (600 nm). Gold electrodes (10 nm in thickness) were prepared on the substrate with adhesion layers of Ti (5 nm in thickness). Part of electrodes was covered with SiO in order to reduce the contribution of ionic conduction during electrodeposition.

Figure 1 shows a schematic diagram of the electrochemical system. The electrochemical potential of the electrodes were independently controlled with respect to the reference electrode of Au wire by a multichannel potentiostat (PS08, Toho Technical Research). Electrodeposition of gold was carried out on both of the electrodes at ca. −0.6 V with respect to the gold reference electrode in a commercially available gold-electroplating solution (TEMPEREX 8400, 0.045 M $KAu(CN)_2$ solution at pH 6.0, Electroplating Engineers of Japan Ltd.) at room temperature. The deposition current was typically ca. 1.0 µA. Potential difference of 10 mV was added in case to monitor the DC current between electrodes. A small AC modulation (ca. 3 mV at 3 Hz) was added to the potential of one of the electrodes (E1), and the current synchronizing to the potential modulation was detected at another electrode (E2) by a lock-in amplifier (LI5640, NF Corporation).

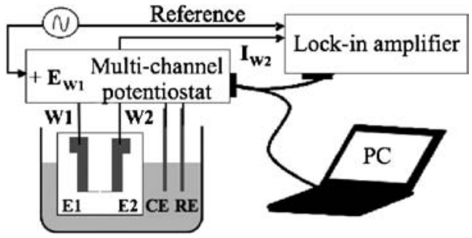

Figure 1. Schematic diagram of the electrochemical system. CE and RE represent counter and reference electrode, respectively. See text for details.

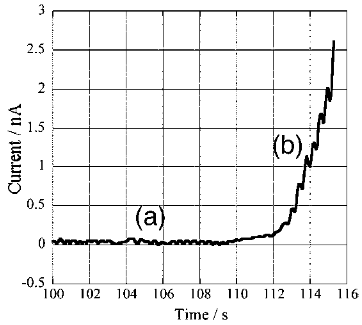

Figure 2. Time evolution of the current between electrodes during the electrodeposition. Initially, the current was in the order of 100 pA (a). The current suddenly increased at a certain period (b).

Figure 2 shows a typical time evolution of the current through the gap measured by a lock-in detection. Initially (Figure 2a), the observed current was less than 100 pA, which is attributed to the ionic conduction between E1 and E2. As deposition of gold proceeded, the current suddenly increased (Figure 2b). The electrodeposition was finished when the current was larger than 2.5 nA which was smaller than the current expected for the quantum resistance. Tunneling current is supposed to be a major component of the current at this stage.[5–10] Ionic and capacitive currents, however, seemed to have some contribution

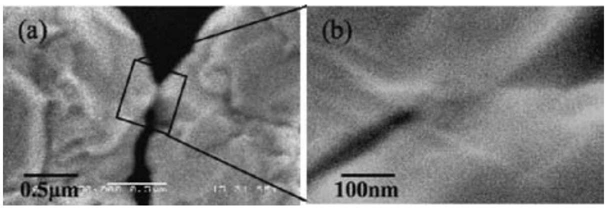

Figure 3. SEM images of the nanogap electrodes. The square region in (a) was magnified (b).

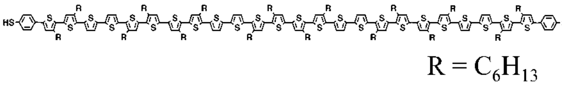

Figure 4. Molecular structure of HSPh24TPhSH. Thiol groups are attached to the both ends of 24-thiophene units.

to the observed current since phase shifts of the current with respect to the potential modulation were sometimes observed. Details would be subjects for further studies. Figure 3 shows typical SEM images of the gap electrodes after the electrodeposition was finished. The gap separation was roughly estimated to be 10 nm. We succeeded in fabricating 19 pieces of similar nanogap electrodes out of 51 trials. The most of the unsuccessful cases resulted in the connection of the gap probably because of the formation of the very unstable gap. The nanogap electrodes were sometimes connected after the SEM observations and storage.

The nanogap electrodes were rinsed with pure water and subjected to UV/O_3 treatment to remove surface contaminations before modification of molecules. Oligothiophene molecules of 10 nm long, HSPh24TPhSH (Figure 4),[12–14] were modified to the nanogap electrodes by self-assembly in a droplet of a dilute solution (ca. 10 µM) in dichlorobenzene for 30 s. The substrate was then rinsed with pure solvent and ethanol. Current–voltage (*I–V*) characteristics were measured in vacuum conditions (10^{-4} Pa) at room temperature by a source meter (Keithley 6487).

Figure 5a shows the *I–V* characteristics measured before the modification of the nanogap electrodes. The current was below the detection limit, indicating that the tunneling current through the vacuum gap was negligible. Two samples out of 19 trials showed the increment of the current after the modification of the molecules. Nonlinear *I–V* curve was observed as shown in Figure 5b. The magnitude of the observed current was comparable to that observed for single polymer chain of poly(*p*-phenyleneethynyl) with a length of 18 nm.[15] Asymmetric *I–V* curves were sometimes observed, indicating that the asymmetric contacts between the molecule and the electrodes were possibly formed. The current sometimes increased during the measurement. Since the nonlinear behavior was still observed, we attributed the increment of the current to that of the number of the molecules bridging over the gap.

In summary, we prepared electrodes with ca. 10 nm gap separation by electrodeposition of gold starting from electrodes with a gap separation of 2 µm. The oligothiophene molecular wire, HSPh24TPhSH, was modified to the electrode by self-assembly. It was shown that the electrical conductance of the molecule was measured by the nanogap electrodes.

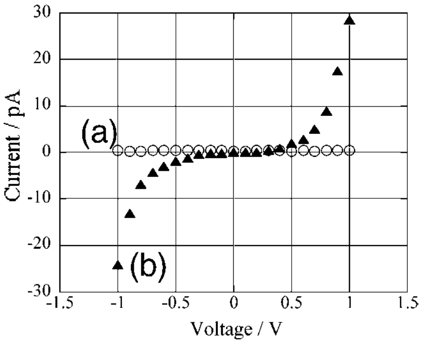

Figure 5. *I–V* characteristics of the junction before (a) and after (b) modification with molecules.

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