

Effect of UV/ozone Treatment on Nanogap Electrodes for Molecular Devices

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1. Introduction

Molecular devices are receiving a lot of attention as future high-density devices because molecules can be tailor-made by chemical synthesis, and their physical properties can be tuned by their structures [1]. However, the stability of nanogap electrodes for molecular devices on repeat measurements is not clearly understood. It is important to study the stability of nanogap electrodes with respect to cleaning, thermal cycling and elapsed time as part of further research on molecular devices. Here, we report the effect of cleaning by using a UV/ozone treatment and its relation to the stability of nanogap electrodes.

2. Experimental

Au/Ti nanogap electrodes on a 20-nm-thick SiO₂ layer were fabricated by double oblique deposition [2]. The gap distances of the electrodes were estimated to be 1-2 nm (natural nanogaps). Some shorted contacts were converted to nanogap electrodes by the break-junction technique (break-junction nanogaps) [3]. Nanogap electrodes were then immersed in solutions of 4,4'-*p*-terphenyldithiol (TPDT), and self-assembled monolayers (SAMs) were formed on the surfaces of the nanogap electrodes [Fig. 1].

The electrical properties of the nanogap electrodes were observed in a vacuum at temperatures ranging from 25 to 300 K. Once the first set of electrical measurements had been completed, the nanogap electrodes were placed in a UV/ozone cleaner (UV-1, Samco) to remove the SAMs. Then the samples were exposed for 6 min to UV irradiation in a 2-g/m³ ozone atmosphere. During the UV/ozone treatment, the organic molecules on the surface of nanogap electrodes were removed, and the Au surface was oxidized. After the UV/ozone treatment, the nanogap electrodes were immersed in ethanol for 20 min to reduce the gold oxide to metallic Au [4]. As a final step, the nanogap electrodes were washed in pure water for 10 min. After the UV/ozone treatment had finished, the SAMs were re-formed and the electrical properties measured [Fig. 2].

3. Results and Discussions

The spectroscopic ellipsometry spectra [Fig. 3] clearly show that the UV/ozone treatment removed the organic molecules from the Au surface and reproduced the surface condition before SAM formation. From these spectra, while the fixed optical index of the SAMs is 1.5, we calculated the thickness of the SAM layer to be about 1.6 nm, which is in good agreement with the length of the TPDT.

Figure 4 is a plot of the resistances of the nanogap electrodes after SAM formation. The nanogap electrode temperature was changed from room temperature to 25 K and then back to room temperature again. In this thermal cycle, most of the resistances of the natural and break-junction nanogap electrodes returned almost to their initial values. These results indicate that the thermal cycle does not seriously affect the nanogap electrodes.

Figure 5 shows the relationship between the resistances of the nanogap electrodes after SAM formation at a drain voltage (V_d) of 500 mV and the number of UV/ozone treatments. Although the resistances of the natural and break-junction nanogaps increase with increases in the number of UV/ozone treatments, the resistances of the break-junction nanogaps increase more than those of the natural nanogaps. These results indicate that the gaps of the break-junction nanogap electrodes tend to be slightly wider by the UV/ozone treatment.

We also observed Coulomb-diamond (CD) characteristics at 25 K. Figure 6 shows examples of the CD structures before and after the UV/ozone treatment in the drain voltage-gate voltage (V_d - V_g) plane. It is significant that identical nanogap electrodes exhibit CDs again after the UV/ozone treatment and SAM re-formation. The CD in Fig. 6(a) might be explained by assuming the presence of metallic dots [5]. On the other hand, after the UV/ozone treatment and SAM re-formation, CDs with non-uniform shapes and sizes are observed [Fig. 6(b)]. These CD structures seem to reflect the discrete energy level of TPDT.

4. Conclusions

We evaluated the UV/ozone effect on nanogap electrodes. Removal of SAMs from the Au surface by a UV/ozone treatment was confirmed with a spectroscopic ellipsometer. The resistances of the nanogap electrodes increased after this UV/ozone treatment presumably due to the widening of nanogaps. Some devices repeatedly showed CDs after the UV/ozone treatment. After the treatment, the shapes and sizes of CDs had changed and these characteristics seem to reflect the electronic structure of the molecules more than that of the CDs before the UV/ozone treatment. Although the resistances increased, these results indicate that the Au nanogap electrodes endure after UV/ozone treatment and can be used for molecular attachment several times.

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References

- [1] C. Joachim et al. Nature **408** (2000) 541.
- [2] G. J. Dolan, Appl. Phys. Lett. **31** (1977) 337.
- [3] H. park, et al., Appl. Phys. Lett. **75** (1999) 301.
- [4] H. Ron, et al., Langmuir **14** (1998) 1116.
- [5] T. Goto et al. Jpn. J. Appl. Phys **45** (2006) 4285.

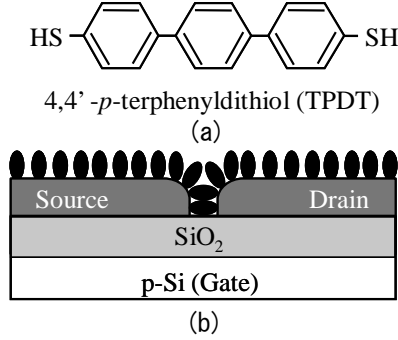


Figure 1. (a) Structure of TPDT. (b) Illustration of ideal nanogap electrodes after SAM formation.

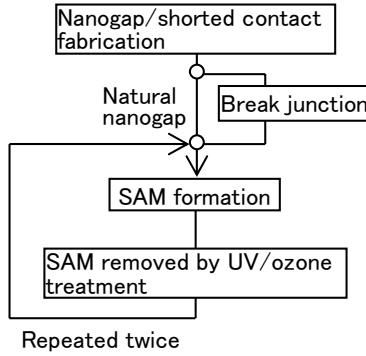


Figure 2. Experiment flowchart.

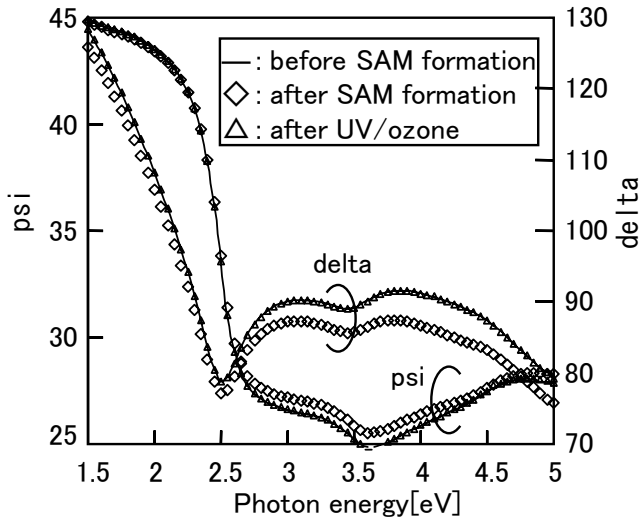


Figure 3. Spectra of spectroscopic ellipsometry. SAMs were formed on Au surface.

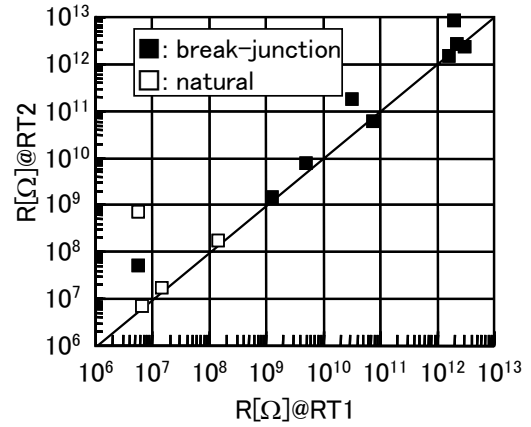


Figure 4. Plot of the resistances of nanogap electrodes after SAM formation at $V_d=500$ mV. Temperatures were changed from room temperature (RT1) to 25 K and then back to room temperature again (RT2).

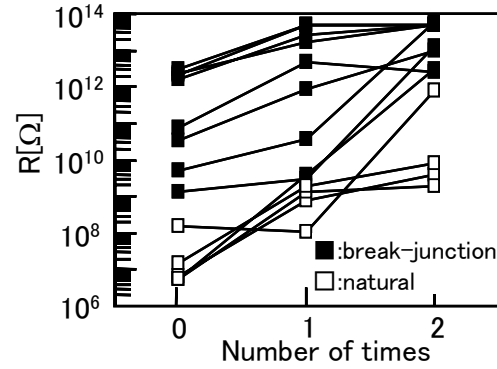


Figure 5. Plot of number of UV/ozone treatments and resistances of nanogap electrodes at $V_d=500$ mV after SAM formation.

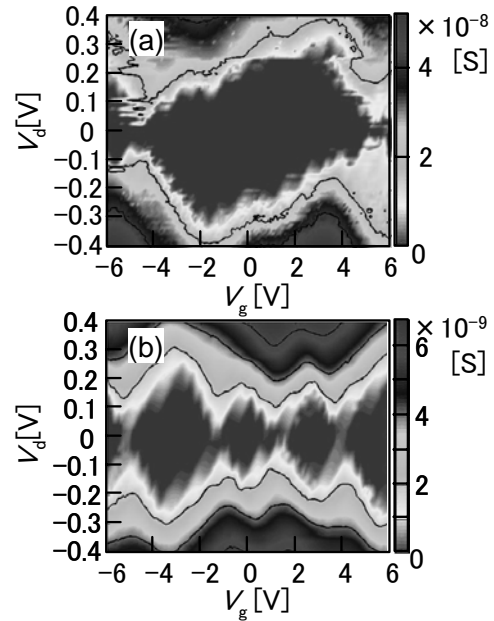


Figure 6. Conductance contour (Coulomb diamond) plot in V_g and V_d plane at 25 K. (a) before and (b) after UV/ozone treatment. Measurements are performed after SAM formation on natural nanogaps.