Development of nanoscale electrical measurement for molecular electronics

Understanding the electrical properties of molecules in nanoscale is needed for the research of molecular electronics. We have been working on the developments of measurement techniques. Here, we introduce two representative techniques.

One is the electrical measurement technique by atomic force microscope (AFM). Point-contact current imaging atomic force microscope (PCI-AFM) enables us to obtain the relationship between the nanostructure and the electrical conductivity.

The other is the fabrication technique of nanogap electrodes for the top-contacted geometry without wet processes. It is possible to make nanogap electrodes onto the molecules which are immobilized on a flat substrate beforehand.

Development of PCI-AFM

AFM enables us to measure the surface structure and the local characteristics by a scanning probe. We have upgraded the commercial AFM system to realize the simultaneous measurement of nanostructure and electrical conductivity of materials.

Realization of simultaneous measurement of the structure and the electrical property in nanoscale

As shown in Fig.1, fast switching from tapping mode to point-contact mode at a specific measurement position enables us to obtain the height information and the current-voltage characteristics, in a single measurement. Because the alternative measurements are executed, the thermal drift of sample stage, which is problematic for the conventional point-contact method, is suppressed.

The development of PCI-AFM was realized by upgrading the commercial AFM with the two function generators. The control signals of the probe oscillation and the tip-sample distance are synchronized with the reference clock that is generated by the CITS (current imaging tunneling spectroscopy) mode operation. The measurement for 128 by 128 points (16,384 points) is completed within 15 min.

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Example: Bundled single walled carbon nanotubes

For the demonstration of PCI-AFM, bundled single walled carbon nanotubes (SWCNT) on the substrate is measured. The sample is prepared by depositing the solution of SWCNT and the gold electrode, successively.

Fig.2 (a) and (b) shows the topography and the current image by PCI-AFM. It is confirmed that the bundled SWCNT on the substrate is connected to the gold electrodes as shown in the upper part of (a). Moreover, the height profile along the sample indicate that the additional SWCNT is attached to the bundle at the region B.

The contrast of the current image (Fig.2 (b)) is correspond to the current value of at the bias voltages of 1V. The contrast of current image at the region B is weaker than that at the region A. This results indicate that the contact resistance (R3) between SWCNTs at the region B, as shown in Fig.2 (c).

PCI-AFM enables us to study the relationship between the nanostructure and its electrical conductivity. This method has been used by other research groups.

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Fabrication of nanogap electrode

Bottom contact geometry for electrical measurement of molecules.

For the stable electrical measurement, the preservation of molecular structure is important. The deformation of structure might cause local electric state that is a potential resistance.

If molecules are immobilized on the electrodes, (top contact geometry) the molecules would be bent at the edge of electrodes. On the other hand, if the electrodes are fabricated on the molecules (bottom contact geometry), the problem in top contact geometry is expected to be solved.

It is possible to fabricate nanogap electrodes by photolithography, but the use of organic solvent and/or polymer resist have a potential damage to molecular structure. Therefore, the fabrication method of nanogap electrodes without wet processes.

Nanogap fabrication without wet processes

We have developed the fabrication technique of nanogap electrode without wet processes. The nano gaps over 50 nm is confirmed to be fabricated.

Fig.4 (a) shows the fabrication process. The molecules are immobilized on the substrate beforehand. The cleaved silicon substrate, which is used as the mask, is mounted on the sample surface. The 1st electrodes are fabricated by thermal deposition. After removing the silicon mask, the 2nd electrodes are fabricated by angle-controlled thermal deposition. The oblique angle resulted in the formation of shadow of 1st electrodes, and hence the nanogap is formed between 1st and 2nd electrodes (Fig.4 (b)).

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The electrical property of blank nanogap electrodes shows the higher resistance enough for the electrical measurement of molecules (Fig. 4 (c)).

**Example: Porphyrin nano rod**

Porphyrin derivative, TPPS ($5,10,15,20$ - tetraphenyl - $21H, 23H$ - porphyrine tetrasulfonic acid) molecule is known to form nanorod on a substrate. Sample was prepared by casting the solution and drying at 55 degree C (Fig. 5 (a)). UV-Vis absorbance spectra indicates the formation of J-aggregates inside nano rods (Fig. 5 (b)).

We have fabricated the nanogap electrodes on the TPPS nanorods and measured the electrical conductivity under different condition (vacuum, nitrogen, oxygen). Gap size was about 225 nm.

Fig. 6 (a) shows the current-voltage characteristic of TPPS nanorod under vacuum condition. Linear characteristics are measured. The conductivity of TPPS nanorod was drastically decreased under nitrogen and oxygen gas condition as shown in Fig. 6 (b). Compared to the vacuum state, single and triple digit decreases in current level were measured under nitrogen and oxygen gas condition, respectively.

The dynamic recovery in current was also measured. As shown in Fig. 6 (c), the current decreased immediately after the introduction of oxygen gas and it recovered slowly after the evacuation of oxygen gas. The speed of decrease in current under nitrogen gas was found to be slower than that of oxygen (Fig. 6 (d)).

The CD spectra of TPPS nanorods also indicated the charity change of J-aggregates under gas environment. Our results would indicate the absorption of gas molecules to TPPS nanorods cause the structural change and suppression of conductivity.