Scanning Conductive Probe Microscopy of Thiophen
Molecules incorporated into Chemically Adsorbed Monolayer

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Abstract We will describe a technique for acquiring the current-voltage characteristics of a metal-molecule-metal probe junction in the lateral direction using a conducting probe atomic force microscopy (CP-AFM) technique. To conduct a repetitive experiment efficiently, we have utilized the current imaging mode of the CP-AFM system. We have prepared a chemically adsorbed monolayer (CAM) of 3-{6-[11-(Trichlorosilyl)undecanoyl]hexyl} thiophene (TEN) on a glass substrate. The sample s with the electric path were prepared by a chemical adsorption technique with TEN on a glass substrate, followed by an electro-oxidative polymerization with pure water. The conductivity of a polythiophene derivative monolayer was investigated for its application as a wire. The corresponding I–V curves have exhibited stability and are steep in current.

1. Introduction

Conducting molecules such as oligothiophenes [1] and oligo(p-phenylenevinylene)s [2] have attracted considerable attention because of their potential use in molecular-based devices, for example, biosensors with high sensitivity [3] and low-power electronic devices. Conducting probe atomic force microscopy (CP-AFM) also seems to be a powerful method for investigating the current-voltage (I–V) characteristics of a metal–molecule–metal junction [4]. In these methods, the preparation of a sample where molecules of interest are fixed in a controlled manner is very important. For example, Leatherman et al. prepared such SAMs where thioldervatized carotene molecules are sparsely dispersed in SAMs of 1-docosanethiol [4]. Cui et al. inserted 1,8-octanethiol in a matrix SAM of 1-octanethiol [5]. In the present paper, we investigated direct conductivity measurements of an electric path in the lateral direction between a Pt electrode and a conductive metal probe of a CP-AFM, which may contain super long polythiophene -conjugated bonds.
2. Experiments

2.1 Sample Procedure

For the ‘top-contact process’ we chose to measure the conductivity of a monolayer in the lateral direction so as not to cause any damage to the chemically absorbing monolayer (CAM) on the glass substrate with the Pt patterned electrodes as shown in Fig. 1. To remove contamination, the glass substrate was exposed to Ultra Violet irradiation for 30 min followed by blow-drying with N₂. Freshly prepared glass substrates were immersed in a CAM solution of 3-{6-{11-(Trichlorosilyl) undecanoyl} hexyl} thiophene (TEN) for 3 h to form a monolayer. After rinsing with chloroform, they were then dried by a gentle flow of N₂ in weighing bottles before measurements.

![Diagram of monolayer deposition and polymerization](image)

Fig. 1. Schematic drawing of the deposition process and polymerization by electro-oxidation

The electrical resistivity of pure water used for electro oxidation was about $10^7 \, \Omega \cdot \text{cm}$. After the monomolecular layer attachment and the alignment procedure, an electro oxidative polymerization was carried out in pure water by applying a DC voltage of 10V between the two Pt electrodes at room temperature for about 3 h. Although the polythiophen conjugated bonds contributing to the electric conduction were formed by the self-assembly perpendicular wire to the edge of the two electrodes by applying the electric field. It is unlikely that all the conjugated molecules between the two electrodes were polymerized in an almost constant width. Because it was thought that not all molecules between the two electrodes were polymerized, that is, the molecules were partially polymerized and many current paths were formed between two electrodes. We tried to find one of electric paths and measure its conductivity using a conductive metal-probe atomic force microscope (CP-AFM).
2.2 Molecular structure of TEN and CP-AFM Instrument

A molecule investigated in this study is TEN in Fig. 2(a). Figure 2(b) shows a schematic drawing of the conductivity measurement of a CAM in the lateral direction using the CP-AFM. To estimate the resistivity effect, we also formed a CAM on glass substrates with Pt electrodes, and measured currents between the Pt electrode and the metal coated cantilever through the CAM (metal-molecular-metal probe), as shown in Fig. 2(b).

![Molecular Structure of TEN](image)

Fig. 2. (a) The molecular used are 3-{6-{11-(Trichlorosilyl) undecanoyl} hexyl} thiophene (TEN). (b) The adsorbed monomolecular layer of TEN is strictly located only on the glass plate. Schematic for electric conduction path under current measurement after polymerization.

3. Results and Discussion

3.1 Measurement of a polymerized path using the CP-AFM

We utilized the CP-AFM. We are interested in the electrical properties of a metal–molecule–metal coated probe junction for future applications of molecular-based biosensors, in which the sensing molecules are expected to bridge 200 µm gap junctions. From the AFM image, it was confirmed that the edges of the Pt electrode, formed by photolithography, have an angle comparable to the tip apex. After the electrode-patterning and the adsorbing monolayer processes, the image of the TEN surfaces on the glass was observed by the AFM, and the current mode at 2mV. The AFM image of a TEN film on the Pt-patterned glass showing a flat surface with sparsely distributed small protrusions, due probably to the aggregations of TEN molecules. Figure 3 shows an example of a simultaneous an observed topographic image (Fig. 3(a)), current image (Fig. 3(b)) between the conductive cantilever and the Pt electrode by the CP-AFM technique. In the topographic and current image obtained by CP-AFM of (a), (b), a boundary between the polymerized portion of the TEN monomolecular layer and Pt electrode was shown. All area is polymerized portion of the TEN monomolecular layers in (b).

The poly thiophen-conjugated bonds contributing to the direction of the electric conduction paths are formed from one Pt electrode to another Pt electrode, because the electric paths grow rapidly to be perpendicular to each edge of the Pt electrode by the applied electric field in an electro-oxidative polymerization, and grow together into electric paths and Pt electrodes. For locating the electric paths in the monomolecular layer, directly measuring their individual resistances was important. A point of variable length of an electric path could be constructed using a microfabricated Au probe electrode contacting one electric path. Current-voltage (I-V) measurements are made in air as a function of the probe position by applying positive voltages to the Pt electrode while keeping the probe tip on the ground. We could obtain some I–V curves involving TEN molecules as shown in Fig. 3(c). Here, when the applied voltage between the Pt electrode and the metal coated tip was changed from 0 to 0.5 mV, the slop of the I/V trace was about 400 nA/mV. Here, it is notable that the I–V curves are very steep. Also in this bias range, the current is not obviously fluctuated. When those I–V measurements
were conducted, the z-feedback servo loop was turned off. When the contact is by chemical bonding, the contact resistance is essentially independent of a contact force.

![Image](a) ![Image](b) ![Image](c)

Fig. 3. Simultaneously observed topographic (a), current image (b), and obtained V-I curve (c). I-V characteristics of TEN molecules on glass substrate measured using Pt electrode by AFM with conductive cantilever at cross mark on (b).

The electric resistance between the Pt and the metal coated tip was approximately 2.5 kΩ. An electric conduction thickness (about 2 nm) for the current measurement is one piece of Tetrahydrothiophene in a monomolecular layer, as shown schematically in Fig. 2 (a). Since the cross section dimension of the current path is a width of 400 nm (observed width of tip apex with SEM), and its length 2 μm, it was calculated a conductivity at about 5.0 x 10^4 S/cm as the same as a Pt conductivity (9.4 x 10^4 S/cm). This conductivity is about 100-1000 times higher than those of organic films. This indicates that the electric resistance of the electric path is very low in comparison with the contact resistances between the polythiophen-conjugated bonds and the AFM tip covered with Au.

4. Conclusions

We prepared a TEN on a glass substrate where thiophen molecules were incorporated in the CAM. We conducted PC-AFM on this sample. Acquiring a 256 x 256 pixel topographic image, we could conduct I–V measurements at each of the corresponding pixels. A monomolecular layer containing thiophen groups at the surface was used between two Pt electrodes on a glass substrate by a chemical adsorption technique using TEN. We have confirmed the formation of electric paths in the TEN monomolecular layer. If an electric path is formed between any two points in a molecular device, this technique may be useful for the formation of a molecular wire in the molecular device. Finally, we would like to note the potential usefulness of the present method for studying the electronic properties of metal-molecule-metal probe junctions involved by conducting molecules which are embedded in a CAM.

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