Molecular self-assembly of conducting polymer by Conducting Probe Technique in Atomic Force Microscope

Shin-ichi Yamamoto
Department of Electrical Engineering, Kobe City College of Technology, 8-3, Gakuenhigashi-machi, Nishi-ku, Kobe 651-2194, Japan

Kazufumi Ogawa
Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, 2217-20, Hayashi-cho, Takamatsu 761-0396, Japan

shin1@kobe-kosen.ac.jp

Abstract. A polypyrrole derivative monolayer was investigated for the application as a wire. First, a pyrrole derivative monolayer was prepared by chemically adsorbing (self-assembling) monolayer (CAM) of 6-pyrrolylhexyl-12,12,12-trichloro-12-siladecanoate (PEN) on a glass substrate. Then, the monolayer was polymerized in the presence of pure water by electro-oxidation. The surface characterization of the molecular interaction was investigated by measuring the properties of CAMs attached to the glass substrate in the lateral direction. We formed PEN having polypyrrolyl groups, using Pt-patterned electrodes on glass surfaces and measured the conductance under a small bias voltage, using a conductive cantilever of atomic force microscopy (AFM). The polypyrrole derivative monolayer thus synthesized was covalently bonded to the glass substrate and showed conductivity as high as $3.05 \times 10^3$ S/cm after electro-oxidized. The method of preparing a conductive polymer monolayer by the combining chemical adsorption and electro-oxidation leads to a lot molecular wire to perpendicular to the Pt electrodes, and it is one of the key technologies for molecular devices.

1. Introduction
In recent years, atomic force microscopy (AFM) using a conductive cantilever has become a good candidate for direct measurement of the electrical conduction of organic monolayers such as self-assembled monolayers (SAMs) [1-4]. In the present paper, we investigated direct conductivity measurements of an electric path in the lateral direction with two Pt electrodes using a conductive probe of an AFM, which may contain super long polypyrrolyl-conjugated bonds. We successfully searched the conjugated path and unconjugated area of the surface of the transparent monomolecular layer with the conductive probe. The samples with the electric path were prepared by a chemical adsorption technique with 6-pyrrolylhexy 1-12,12-trichloro-12-siladecanoate (PEN) on a glass substrate, followed by electro-oxidative polymerization with water. We detected the highly conductive image of an electric path in the lateral direction as a super-long polypyrrolyl-conjugated polymer between the edges of two Pt electrodes in the air with the conductive probe under a small bias voltage. In this study, we also carried out macroscopic measurements of the conductivity of Chemically
adsorbed monolayer (CAM) under controlled atmosphere using samples made on substrates with interdigitated (comb) electrodes.

2. Experiments

For the ‘side-contact process’ (see in Fig. 1) we chose to measure the conductivity of CAM in the lateral direction not to cause any damage to the Chemically absorbing monolayer (CAM) on the glass substrates with the Pt patterned electrode. Glass substrates were chosen as the substrate for CAM, because it is an insulator. To remove contamination, the substrate was exposed to UV (Ultra Violet) irradiation for 30 min followed by blow-drying with N₂. This cleaning process was repeated at least twice. Then the metal patterned glass was immersed in the solution of CAM materials, PEN in expectation of a larger conductivity. The Pt metal-patterned substrate was immersed in the solution for 180 min at room temperature to form a PEN layer. After being taken out, the film was rinsed twice with chloroform followed by blow-drying with N₂. The substrate was withdrawn from the solution after 60 min, washed with ethanol twice, and finally blown dry with N₂. Generally, it is not easy to form CAM on patterned substrates, because their formation is quite sensitive to the nature of the substrate surface, its chemical properties, contamination, and roughness. However, by a careful cleaning process, residuals from the process of forming electrodes were thoroughly removed with aqua regia, and CAM of the same quality as those on a pristine surface could be formed.

Fig. 1. Schematic drawing of the deposition process of CAMs

In this case, it was also thought that the conjugated bonds of the polyprolyl group contributing to electric conduction might have formed many path (self-assembly) from the edge of the positive electrode on the substrate perpendicular to the edge of two Pt electrodes, upon applying the electric
field. 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 an atomic force microscope (AFM) combined with the current mode [5].

3. Results and Discussion

3.1 Molecular structure of PEN

Figure 2 shows a schematic drawing of the conductivity measurement of CAM in the lateral direction using AFM. Here we used a conductive cantilever (stiffness: 0.14 N/m) made of a highly doped Si coated with Cr and Au (thickness: 80 nm). For the electrode metals, we chose Au to avoid the problem of strong adhesion between same metals. With this setup, we could select sample areas in the vicinity of the patterned electrode.

![Schematic for electric conduction path under current measurement after polymerization.](image)

**Fig. 2.** The adsorbed monomolecular layer of PEN is strictly located only on the glass plate. Schematic for electric conduction path under current measurement after polymerization. The direction of the current flow only in the top section from the tip is shown by a broken line.

The minimum distance between the tip and the edge of the electrode in this study was estimated to be about 20 nm for the 50 nm-thick electrodes, since the original tip radius of 20 nm and the 80 nm-thick Au coating restrict the minimum distance and the spatial resolution. From the current-voltage (I-V) characteristics, the electrical properties of CAM in the lateral direction could be estimated. In particular, the current measured at a certain point is integral to the current from all parts of the Pt electrode to the tip, and should be analyzed carefully. The net resistivity of the CAM could be estimated from the current measured at a distance from the edge of the Pt electrode. To estimate the resistivity effect, we also formed CAM on glass substrates with Pt electrodes, and measured currents between Pt electrodes and the cantilever through the CAM, as shown in Fig. 2.

3.2 Measurement of an electric path using conductive AFM

From the AFM image, it was confirmed that the edges of the Pt electrodes formed by photolithography have an angle comparable to the tip apex. After the electrode-patterning and adsorbing monolayer processes, the images of the PEN surface on the glass was observed by AFM, FFM, and the Current mode. The AFM image of a PEN film on the Pt-patterned glass showing a flat surface with sparsely distributed small protrusions, due probably to aggregations of PEN molecules.
Figure 3. Simultaneously observed topographic (a), friction force (b), and current images (c) of Pt patterned glass substrate by electro-oxidative polymerization

Figure 3 shows an example of simultaneously an observed topographic (Fig. 3(a)), friction force (FFM) (Fig. 3(b)) and current images (Fig. 3(c)) between the conductive cantilever and Pt electrode by the AFM technique. The data were recorded along the scanning direction from left to right at a speed of 0.5 s/line, while the bandwidth of the current amplifier was 1 kHz.

Firstly the topographical (a) and FFM (b) images were taken simultaneously. In the topographic and FFM image obtained by conductive AFM shown the left side of (a), (b), a boundary of the polymerized portion of the PEN monomolecular layer ① and the un-polymerized portion of the PEN monomolecular layer ② could not be distinguished by topography and FFM. Prior to observing the current image, we checked the film surface quality was satisfactory by AFM; for example, no pinholes appeared, and the roughness of the surface was less than 0.1 nm, from about 50 nm² (especially, with magnification). In the topographical image, no pinholes and domains were seen either. On the other hand, on the current image of the isolated electrical path shown in Fig. 3(c), which was obtained using the AFM tip covered with Au, the boundary of the polymerized portion of the PEN monomolecular layer ①’ and the un-polymerized PEN monomolecular layer ②’ could be distinguished clearly.

The surface shapes of polymerized and un-polymerized portions are not considered to be identical, whereas the observed height differences in the topographic image were less than 0.2 nm. The above results in Fig. 3(c) indicate that the polymerization was caused by one Pt positive electrode. The poly pyrrolyl-conjugated bonds contributing to the direction of the electric conduction paths are formed from one Pt positive electrode to the other Pt negative electrode, because the electric paths grow rapidly to be perpendicular to the two Pt electrodes by the applied electric field in electro oxidative polymerization, and grow together into electric paths and Pt electrodes.

The cross-sectional view along the scan line of Figs. 3 (c) is displayed in Fig. 4. The conductivity of CAM can be characterized by the distance from the electrode where the dashed line of measurable current. Figure 4 shows the cross-sectional current profile in the transition area, i.e., the area between the onset of the current and the point where the tip comes into contact with the flat substrate (the current of 200 nA is the saturated current of the amplifier of this system), together with the curve measured from an untreated substrate.
3.3 Conductance of the point on the electric path using conductive AFM

For locating the electric paths in the monomolecular layer and directly measuring their individual resistances, AFM was also used. 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. The three similar V-I curves were obtained, as shown in Fig. 5 (a), (b), and (c). Slopes of the three V-I curves (a), (b), and (c) obtained were very steep. When the applied voltage between the Pt electrode and the AFM tip covered with Au was 1 mV, the current was about 200 nA at the cross ‘A1, A2, and A3’ on the image of Fig. 5 (d). When the applied voltage between the Pt electrode and Au-coated AFM tip was changed from 0 to 2 mV, however, no current was obtained at A0 because of un-polymerization. That is, electric resistance at the ‘A1, A2, and A3’ point was about 3.3 kΩ, 6.1 kΩ, 6.0 kΩ, respectively. At the A1 point the dimension of the electric path were about 40 nm² (cross-sectional area of the electric path and tip of the cantilever; tip diameter:100 nm, thickness of the conjugated bonds:0.2 nm)×20 μm (length from the Pt electrode to the tip at the cross A1 in image in Fig. 5 (d)), calculated conductivity at about $3.1 \times 10^3$ S/cm. This conductivity is about 100-1000 times higher than those of organic films.
Fig. 5. Obtained three similar V-I curves. I-V characteristics of PEN CAM on glass substrate measured using Pt electrode by AFM with conductive cantilever at A1 (a), A2 (b), A3 (c).

(d): Schematic drawing of the experiment for measurement of CAM on a glass substrate with Pt electrodes using AFM with a conductive cantilever. No current obtained at A0 after polymerization.

On the other hand, when the measurement points (indicated by the crosses) were changed from A1 to A2, A3, the lengths measured from the Pt positive electrode on the cross in A2 and A3 were about 100 μm and 190 μm, respectively. The net conductivity of the CAM could be estimated from the current measured as a function of the distance from the edge of the Pt electrode. The A2, and A3 in image in Fig. 5(d) calculated conductivity at about 8.1×10^3 S/cm and 1.6×10^4 S/cm, respectively. This indicates that the electric resistance of the electric path is very low in comparison with the contact resistances between the polypyrrolyl-conjugated bonds and the AFM tip covered with Au, and/or contact resistance of side contact between the polypyrrolyl-conjugated bonds and the Pt electrode. It should be noted that the measured conductivity contains not only the conductance of the film in the lateral direction, but also that of the interface between the electrode and the film, and between film and cantilever. For further discussion, it is essential to improve the contacts and reduce the contact resistances.

4. Conclusions

A monomolecular layer containing pyrrolyl groups at the surface was used between two Pt electrodes on a glass substrate by a chemical adsorption technique using PEN. We have confirmed the formation of electric paths in the PEN monomolecular layer. The resistance of one path is 3.3 kΩ at A1 point, for example, without any dopants for a measurement volume of about 0.2 nm (the thickness of an electric path in the monomolecular layer) × 200 μm (the average width of an electric path) × 100 μm (the distance between Pt positive electrode and the Au-covered AFM tip). 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.

References

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