A Study on the Negative Differential Resistance in Dipyridinium Self-Assembled Monolayers Using STM

Nam-Suk Lee*, Hoon-Kyu Shin* and Young-Soo Kwon†

Abstract - Organic monolayers were fabricated onto Au(111) substrate by self-assembly method using dipyridinium. Also, organic single molecule in the organic monolayers was selected to measure the current-voltage (I-V) curves by using the ultrahigh vacuum scanning tunneling microscopy (UHV-STM). The organic molecule used in the experiment was dipyridinium dithioacetate, which contains thiol functional group and can be self-assembled easily onto Au(111) substrate. The concentration of dipyridinium dithioacetate for self-assembly procedure was 1 [mM/L]. To confirm the formation of self-assembled monolayers (SAMs), the differences of thickness of the self-assembled organic monolayers were observed by using an ellipsometer, and the morphology and I-V curves of the SAMs were investigated by using UHV-STM. The applied voltages were from -2 [V] to +2 [V], temperature was 300 [K]. The vacuum for measuring current of the organic single molecule was 6×10^{-8} [Torr]. As a result, properties of the negative differential resistance (NDR) in constant voltage were found.

Keywords: negative differential resistance, self-assembled monolayers, UHV-STM

1. Introduction

The discovery of negative differential resistance (NDR) in single molecule opened a new chapter in molecular electronic devices[1]. The phenomenon of NDR is characterized by decreased current when the applied voltage is increased. The NDR property is defined by electronic components, including the Esaki diode and, resonant tunnelling diodes (RTD)[2]. Recently, a kind of molecular devices which shows NDR property clearly was found. Some examples of organic systems have been demonstrated. In order to understand NDR phenomenon in single molecule, we need further work.

This study produced a self-assembled monolayer using a self-assembly method in order to investigate the electrical properties of single molecule[3,4]. Self-assembly is a phenomenon in which atom, molecules, or groups of molecules arrange themselves spontaneously into regular patterns and even relatively complex systems without external equipment. The research suggests that they can make a molecular arrangement, and image of the surface of an the organic monolayers by using a ultrahigh vacuum scanning tunneling microscopy (UHV-STM). Moreover, the method of the measurement of the Current-Voltage (I-V) properties can be used by scanning the electrical properties of the formed organic monolayers by using a scanning tunneling spectroscopy (STS).

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2. Experiment

2.1 Materials

The specimen used in this study was an organic molecule of [4-{4[4-(4-{1-[4-(4-acetylsulfanyl-phenylethynyl)-pheny l]-2,6-diphenyl-pyridinium-4-yl}-pheynyl)-2,6-diphenyl-py ridinium-1-yl]-phenylethynyl}-phenylthioacetate] (dipyridi nium dithioacetate) which was synthesized by the Korea Research Institute of Chemical Technology. The chemical structure of dipyridinium dithioacetate used in this study was shown in Fig. 1.

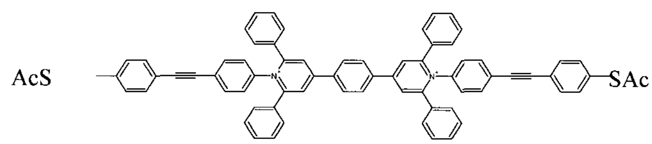


Fig. 1 Chemical structure of dipyridinium dithioacetate

2.2 Au(111) Substrates

A single-crystal silicon wafer was cut into 5 [mm] × 5 [mm] sheets and then cleaned for 30 [min.] in a hot (40 [℃]) fresh acidic peroxide (H_2SO_4:H_2O_2=3:1) solution, rinsed with flowing distilled water, ethanol, and acetone, and the pieces of Si were dried in flowing ultrahigh purity N_2 gas[3]. The Au films were deposited by thermal evaporation of 100 [nm] thick Au onto the Si sheets at a rate of 0.1 [Å/S] under a vacuum of 1.8×10^{-6} [Torr] and annealing for 8 [h.] at 550 [℃]. The Au samples were finally stored in a N_2 atmosphere. Before use the Au substrates were cleaned by a UV/O_3 cleaner (NL-UV253) for 10 [min.] in order to remove organic contamination, followed by ultrasonic cleaning in ethanol for 20 [min.] to remove the resulting Au oxide layer, rinsing with ethanol and acetone, and then drying in flowing N_2. Fig. 2 shows the schematic diagram of fabrication of Au(111) substrates.

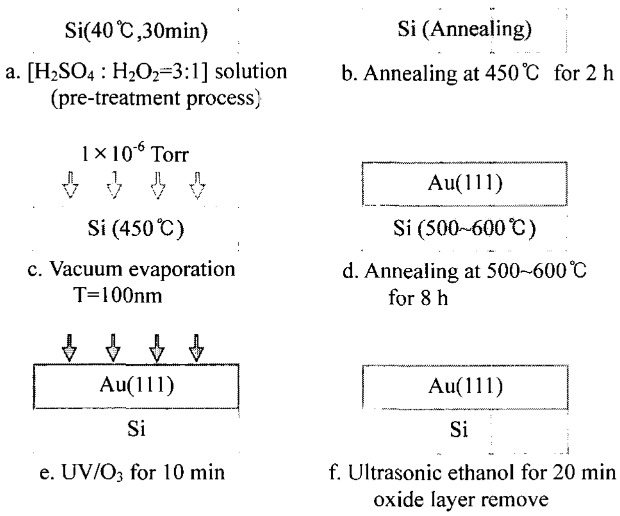


Fig. 2 Schematic diagram of process for the Au(111) substrate

2.3 SAM Preparation

The dipyridinium (3.4 [mg]) was dissolved in a solvent, DMF in a 3 [mL] vial. A clean gold substrate was then immersed into the solution at room temperature for a period of 24 [h.] and kept in the dark during immersion to avoid photo-oxidation[4]. After the assembly, the samples were removed from the solutions, rinsed thoroughly with methanol, acetone, and CH_2Cl_2, and finally blown dry with N_2. Under these conditions, we measured electrical properties of SAMs using UHV-STM.

Table 1 Chemical Self-Assembly of Conjugated Thiol-acetylated dipyridinium in DMF

compound	solvent	time(h)	thickness (nm) exptl ^{a}	thickness (nm) calcd ^{b}
dipyridinium	DMF	24	3.21	3.61

^{a} The value measured by ellipsometry. ^{b} The theoretical thickness calculated by molecular mechanics without the consideration of the tilt angle of molecule in SAM.

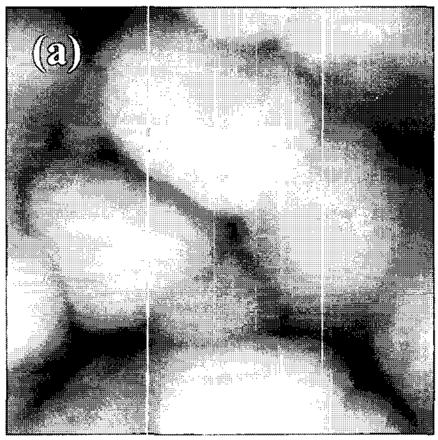
2.4 Apparatus and Measurements

We can observe electrical properties in 6×10^{-8} [Torr] vacuum conditions. In the STS Plot modes, the tip was positioned at a point on the surface, and a spectroscopic plot was acquired and displayed in a scope format. Electronic measurements were performed consisting of Pt-Ir/SAM/Au structure. STM measurement was carried out with UHV-STM system at room temperature (T=300 [K])[5].

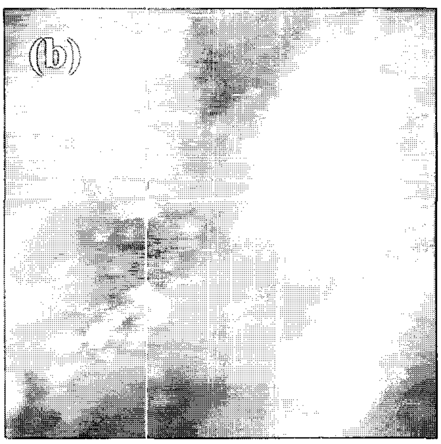
3. Results and Discussion

3.1 Tunneling Microscopy Data

Fig. 3 (a) shows an image of the STM observation for the surface of the A(111) substrate before the self-assembly of the specimen of dipyridinium dithioacetate. Fig. 3 (b) is an image of the STM observation of the morphology through self-assembly with the concentration of 1 [mM/L] of dipyridinium dithioacetate onto the Au(111) substrate. It shows an image of the STM observation of the morphology by scan size 100 [nm] × 100 [nm].



(a) Typical STM image of the Au(111) surface



(b) STM image of the surface to the SAMs

Fig. 3 Typical STM images of the Au(111) surface and the SAMs at the concentration of 1 [mM/L]; scan size: 100 [nm] × 100 [nm]

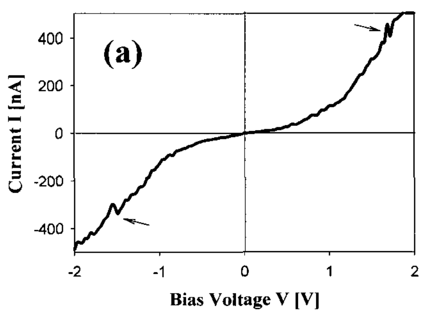
It is clear that the SAMs were formed and were checked by means of the STM images of Fig. 3 (a), and (b). It can also be seen that the surface of the Au(111) substrate is more flat before the self-assembly. On the other hand, the surface of self-assembled Au(111) substrate by the concentration of 1 [mM/L] has small particles.

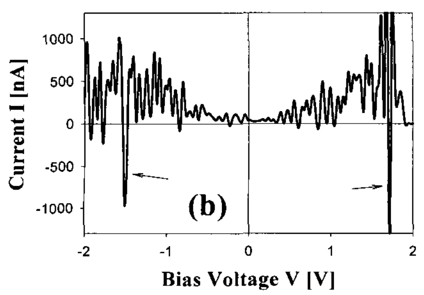
3.2 Tunneling Spectroscopy Data

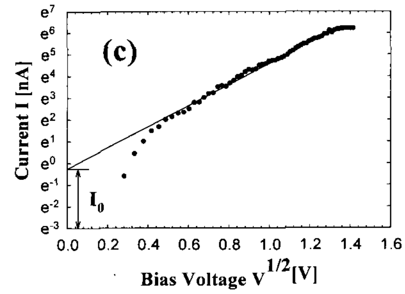
All STM data were obtained for the morphology and I-V curve using a constant current mode[6]. As shown in Fig. 4 (b), some regions show a negative value of dI/dV, and this is called a NDR. The occurrence of regions with NDR was indicated by arrows in Fig. 4 (a) and Fig. 4 (b). This paper defines a NDR voltage that has a maximum current in the region of NDR. According to the definition of NDR, the NDR voltages of dipyridinium dithioacetate were 1.68 [V] in the positive bias region and -1.49 [V] in the negative bias region, respectively by Fig. 4 (a). Moreover, the conductivity of dipyridinium dithioacetate were 2.7×10^{-7} [S/cm] in the positive bias region and 2.3×10^{-7} [S/cm] in the negative bias region respectively. Fig. 4 (c) shows Schottky plot. We have calculated barrier height between Au(111) and SAMs.

$$\phi_D = \left(KT \cdot \ln \frac{AT^2}{I_0 \cdot S} \right) / e \qquad (1)$$

Where ϕ_D means a barrier height of between Au(111) and SAMs, A is 120×10^4 [Am^{-2}/deg^{-2}], T is 300 [K], S is 0.25 [cm^2]. Moreover, the value of ϕ_D originating from the defined equations (1) was 0.69 [eV][7].







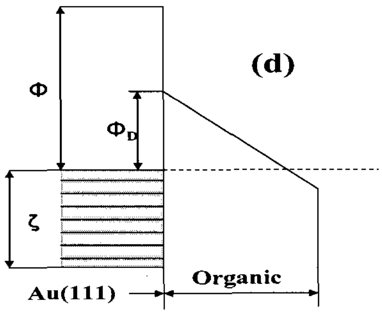


Fig. 4 Graph of a typical I-V curve of the dipyridinium SAMs (a) and dI/dV curve (b) and Schottky current for the dipyridinium monolayers (c) barrier height between Au(111) and SAMs (d)

The schematic diagram of barrier height between Au(111) and SAMs calculated by Schottky plot was shown in Fig. 4 (d). Where ζ is Fermi level, ϕ is Work function of Au(111), ϕ_D is barrier height.

4. Conclusion

Organic monolayers containing a dipyridinium were fabricated and NDR of the organic molecular was measured. The measured NDR and conductivity at the positive region were 1.68 [V] and 2.7×10^{-7} [S/cm], respectively and also were -1.49 [V] and 2.3×10^{-7} [S/cm] at the negative region. Also, SAMs image was confirmed by STM. I-V characteristics showed the symmetry. Finally, it was expected that the NDR property is a unique property of an organic molecule and might present important applications in designing molecular switching and logic devices[8].

Acknowledgements

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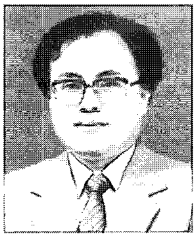

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