Determination of the NDR and Electron Transport Properties of Self-Assembled Nitro-Benzene Monolayers Using UHV-STM

Nam-Suk Lee*, Jeong-Soo Chang and Young-Soo Kwon†**

Abstract - We investigated the negative differential resistance (NDR) property of self-assembled 4,4-di(ethynylphenyl)-2′-nitro-1-(thioacetyl)benzene ("nitro-benzene"), which has been well known as a conducting molecule [1]. Self-assembly monolayers (SAMs) were prepared on Au (111), which had been thermally deposited onto pre-treated (H_2SO_4 : H_2O_2=3:1) Si. The Au substrate was exposed to a 1 mM solution of 1-dodecanethiol in ethanol for 24 hours to form a monolayer. After thorough rinsing of the sample, it was exposed to a 0.1 μM solution of nitro-benzene in dimethylformamide (DMF) for 30 min and kept in the dark during immersion to avoid photo-oxidation. Following 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 the electrical properties of SAMs using ultra high vacuum scanning tunneling microscopy (UHV-STM) and scanning tunneling spectroscopy (STS) [2]. As a result, we confirmed the properties of NDR in between the positive and negative region.

Keywords: Negative Differential Resistance (NDR), SAMs, Scanning Tunneling Spectroscopy (STS)

1. Introduction

Currently, molecular devices show the NDR property clearly. The property of NDR is decreased current when the applied voltage is increased [3]. The NDR property is defined by electronic components, including the Esaki diode and resonant tunneling diodes (RTD) [4, 5]. It is 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. Some examples of organic systems have been demonstrated.

Although there are several methods in the preparation of a thin film using an organic molecule, the self-assembly method is used by most researchers. We produced self-assembly monolayers (SAMs) using the self-assembly method that is able to make a molecular array. 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 outside intervention [6]. SAMs is a regularly well-arranged organic molecular layer, which is spontaneously coated onto the surface of a given substrate.

A scanning probe microscopy (SPM) system, which can support STM, is used to measure the properties of SAMs. STM uses the quantum mechanical tunneling phenomenon obtained by scanning a tip over the surface of a sample when a bias is applied between the sample and tip. STM and STM-related techniques are now widely used in the areas of physics, chemistry, material science, and biology. In earlier times, the main application of STM was to image the surface of a material. Nowadays, STM and STS techniques enable the study of electrical properties of nanoscale elements [7].

The purpose of this research is to study the application of molecules as a device using the NDR property. Expressly, analyze the electric property (I-V) of the nitro-benzene molecule to define the NDR property by STM. We fabricated SAMs by using 1-dodecanethiol and nitro-benzene. Because it blocks the aggregation of the nitro-benzene molecule, we used 1-dodecanethiol as the base material and measured intrinsic properties of nitro-benzene SAMs [2]. Nitro-benzene is also known as a conducting molecule [1]. Therefore, we used nitro-benzene to measure the property of NDR using a self-assembly method in STM In addition, this study produced the vertical junction structure of a STM tip/SAMs/Au (111) substrate using a STM tip. We used the Au (111) substrate as the base substrate and the surface morphology was investigated at the STM mode. Also, the current-voltage (I-V) or differential conductance (dI/dV) properties were measured while the electrical properties of the formed monolayer were scanned by using a STS [8].

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2. Experiment

2.1 Organic Materials

The chemical structures of 1-dodecanethiol and nitro-benzene prepared in this study are shown in Fig. 1. Materials used in this experiment are nitro-benzene that is composed in the Korea Research Institute of Chemical Technology (KRICT) [9]. This material could fabricate a SAMs easily because it contained a thioacetyl functional radical, which could perform a self-assembly onto the surface of Au (111).

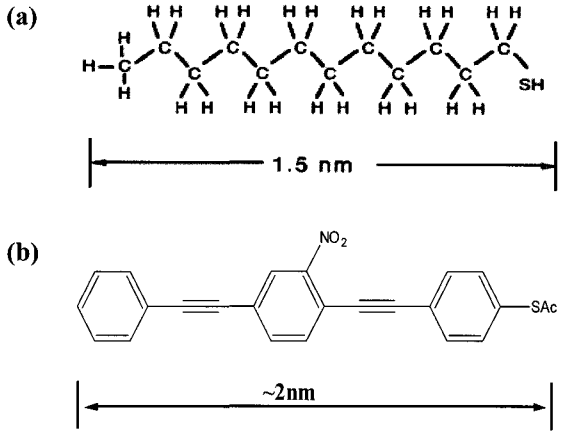

Fig. 1. The chemical structures of (a) 1-dodecanethiol, (b) nitro-benzene

2.2 SAM Preparation [10]

SAMs were prepared on Au (111), which had been thermally deposited onto freshly cleaved, heated Si. The Au substrate was exposed to a 1 mM solution of 1-dodecanethiol in ethanol for 24 hours to form a monolayer. After thorough rinsing of the sample, it was exposed to a 0.1 μM solution of nitro-benzene in DMF for 30 min. 1-dodecanethiol was used to prevent nitro-benzene from the vibration by applied voltage. Nitro-benzene and 1-dodecanethiol have a molecular length of 2 nm and 1.5 nm separately. 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.

2.3 Measurement of the STM

The STM measurement was performed at room temperature using a UHV-STM (UNISOKU, USM-1200). The vacuum condition is 6×10^{-8} Torr. The probe was a Pt/Ir tip. Scanning was applied under the condition that the sample was biased at -1.50 V, and had a 0.20 nA of tunneling current, which employed a constant current mode. The schematic of the STM measuring system is indicated in Fig. 2 (a). A highly oriented pyrolytic graphite (HOPG) surface was observed before the scanning of the sample's surface in order to investigate the normal state of the tip. The normal state of the tip was verified by investigating a nicely arranged pyrolytic graphite surface for a 10 nm × 10 nm scanning surface. Images of the SAMs were produced using a normal tip, and then the characteristics of I-V were measured at arbitrarily configured points on the surface of the sample. Measurement of I-V was performed by monitoring the tunneling voltages using varied voltage on the sample, from -2.0 V to +2.0 V.

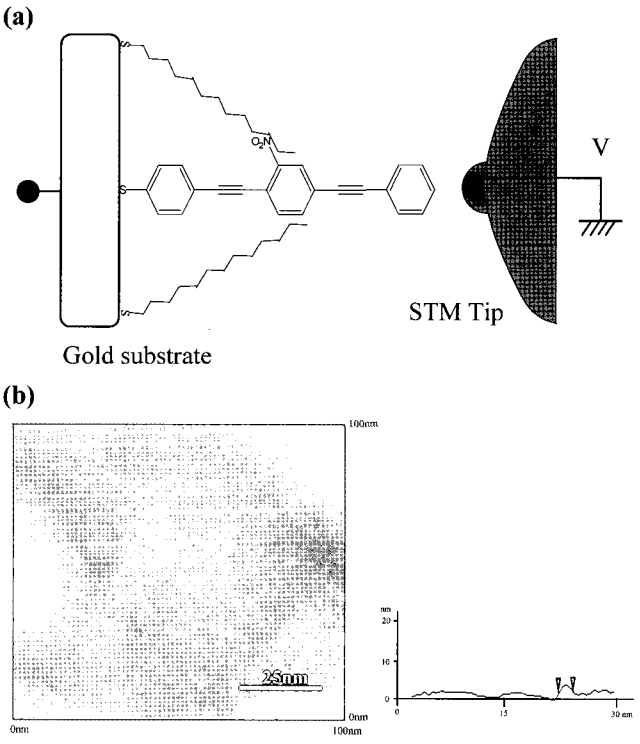

Fig. 2. (a) Self-assembly monolayers of 1-dodecanethiol and nitro-benzene on an Au (111) substrate (only one molecule of the monolayer is shown for clarity). Also shown schematically is an STM tip used to measure the current-voltage characteristics, (b) STM image of self-assembled nitro-benzene with 3 nm height, 2.5 nm width. Electrical property is measured by fixing the STM tip marked by an arrow.

3. Results and Discussion

The STM images of SAMs on the Au (111) substrate are presented in Fig. 2 (b). It shows an image of the STM observation of the morphology by scan size 100 nm × 100

nm. This is an STM image of Self-Assembled nitro-benzene with 3 nm height, 2.5 nm width. Electrical property is measured by fixing the STM tip marked by an arrow. Fig. 3 (a), (b) shows the characteristics of I-V and dI/dV for SAMs.

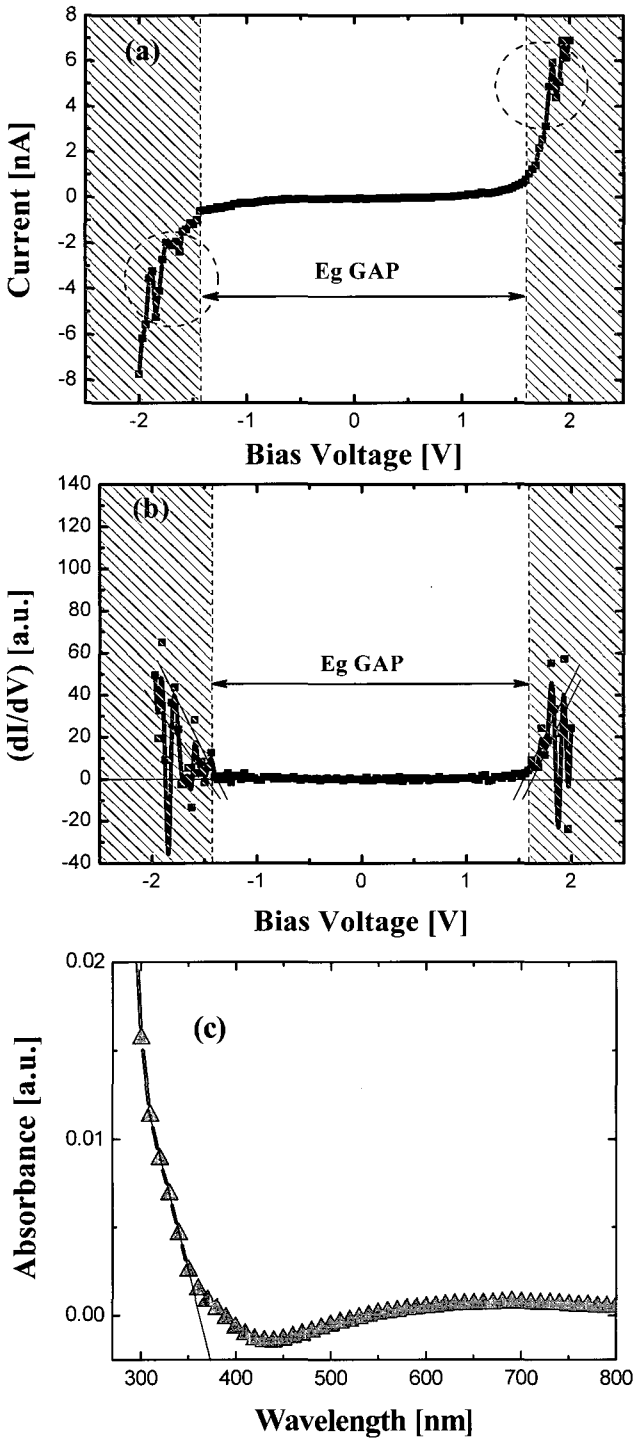

Fig. 3. (a) The characteristics of current-voltage (I-V) and (b) dI/dV, (c) UV/visible spectrophotometer data, energy gap (E_g) of nitro-benzene is 3.3 eV.

We measured I-V property using UHV STM in STS mode, I-V property also clearly shows current peaks between the negative bias region (-1.61 V) and the positive bias region (1.84 V). As illustrated in Fig. 3 (a), some regions show in the circle of I-V, and this is called NDR. This paper defines NDR voltage that has a maximum current in the region of the NDR. We measured the NDR and peak-to-valley current ratio. As results of measurements, R_{NDR} is <-106 MΩ (negative region), <-22 MΩ (positive region), according to Eq. (1).

$$|R_{NDR}| = \frac{V_V - V_P}{I_P - I_V} \tag{1}$$

And peak-to-valley current ratio (PVCR) is 1.14:1 (negative region), 1.30:1 (positive region), according to Eq. (2).

$$PVCR = \frac{I_P}{I_V} \tag{2}$$

Where R_{NDR} means a negative differential resistance, V_V is the voltage at the lowest point, V_P is the voltage of the highest point, I_V is the current of the lowest point, and I_P is the current of the highest point. Fig. 3 (a) shows the I-V property for the nitro-benzene sample. The I-V property shows some symmetry. Fig. 3 (b) presents the dI/dV property, on which are drawn the tangents to the density of states (DOS) and the intercepts that define the band edges [9]. This gives a energy gap (E_g) of 3.01 eV for this sample [11]. It is possible to study the movement of electrons which is caused by height variation because we can see the organic materials barrier height and STM tip by organic materials E_g. It is for this reason that E_g was studied by UV/visible spectroscopy. Fig. 3 (c) is the UV/visible spectrophotometer data. The energy is $E=h\nu$ ($\nu=c/\lambda$), wavelength is 372 nm where E is the energy, h is the Planck's constant, ν is the frequency, c is the velocity of light and λ is the wavelength. So, E_g value is 3.3 eV. Measured E_g is also illustrated from the diagram in Fig. 4 (a). When voltage is applied, Band value is a little bit reduced but almost equal to equilibrium state. The energy diagrams for STM tunneling of bias voltage are shown in Fig. 4 (b).

The phenomenon of NDR is characterized by decreasing current through a junction at increasing voltage. To explain the NDR, we proposed 'double barrier junction' by Gorman et al [3]. Between SAMs on Au and vacuum gap

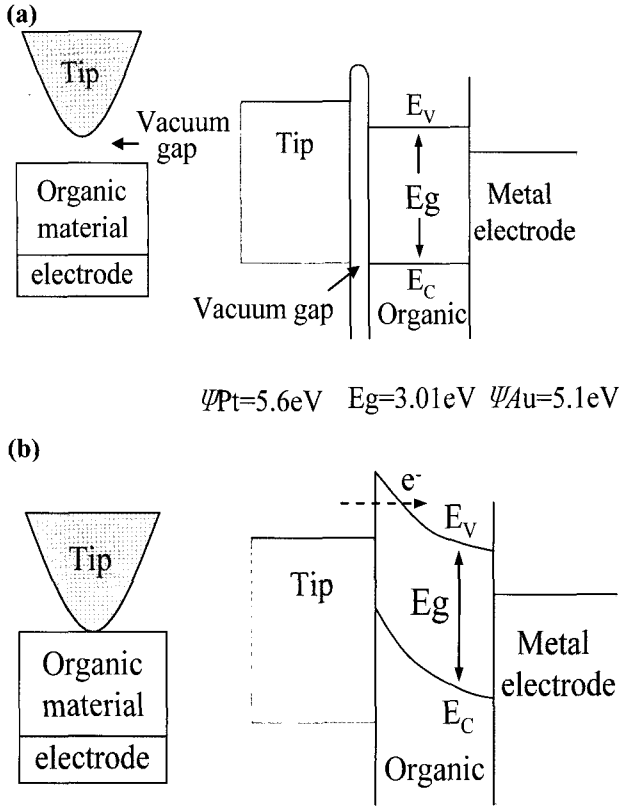

Fig. 4. The energy diagrams for STM tunneling (a) before bias voltage and (b) after bias voltage.

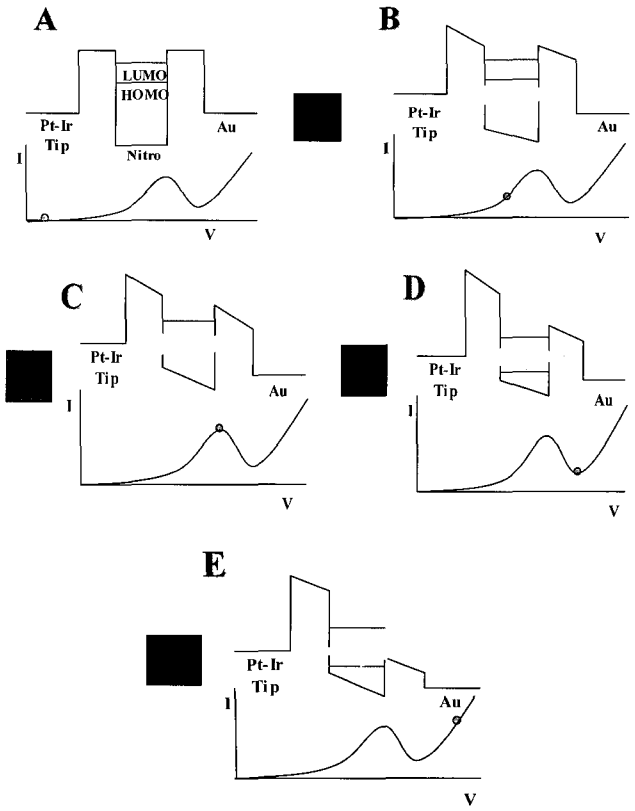

Fig. 5. Mechanism of tunneling current and NDR in the nitro-benzene SAMs

and between the molecule and STM tip exists double barrier junction. Fig. 5 shows the mechanism of tunneling current and NDR. A: In the case of zero voltage, being equilibrium, there is no electron transfer, because the energy level of the other part is closed and the current is zero. B: highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the organic molecule exist over than Fermi level of tip and gold electrode. In this case, if positive bias is applied on the gold electrode, molecular energy state inclines toward the state of the gold electrode. C: Current reaches to peak value (Vpeak) by tunneling in resonant state between tip and molecule. Resonant state means that local density of state (LDOS) of the tip and molecular energy state are piled up. D: After resonant ends, current decreases until the applied voltage is increased enough to make thermal electron emission. E: This is the flow of conductive current by the thermal electron emissions.

A candidate mechanism for NDR is a two-step reduction process that modifies charge transport through the molecule [12]. As the voltage is increased, the molecule initially undergoes a one-electron reduction, turning on the conduction channel; a further increase in voltage causes a second-electron reduction with subsequent blocking of the current [13]. The width of the I-V peak correlates well with the difference in the two-electron reduction potentials.

4. Conclusion

We fabricated the SAMs containing nitro-benzene and studied NDR phenomenon by using UHV-STM, at room temperature. The measured NDR voltage and the value of R_{NDR} are negative region -1.61 V, positive region 1.84 V and <-106 MΩ (negative region), <-22 MΩ (positive region), respectively. We found that this gives a E_g of 3.01 eV for this sample. Height was changed slightly by band bending when the voltage was applied between STM tip and electrode. Energy barrier height by band bending might relate with electro conductive property.

As a result, nitro-benzene to molecular devices and the NDR, which is a unique property of an organic molecule, will provide an important source of switching. Also, it is possible to logic a device by controlling the functions of an organic molecule.

Acknowledgements

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