

A Study on the Current-Voltage Characteristics of Self-Assembled Organic Molecules by using STM

Seung-Un Kim*, Hoon-Kyu Shin** and Young-Soo Kwon[†]

Abstract - Currently, molecular devices are reported utilizing active self-assembled monolayers (SAMs) containing the nitro group as the active component, which has active redox centers [1]. SAMs are ordered molecular structures formed by the adsorption of an active surfactant on a solid surface. The molecules will be spontaneously oriented toward the substrate surface and form an energetically favorable ordered layer. During this process, the surface-active head group of the molecule chemically reacts with and chemisorbs onto the substrate. In this paper, the electrical properties of the 4,4'-di(ethynylphenyl)-2'-nitro-1-benzenethiolate was confirmed. This material is well known as a conducting molecule having possible application to molecular level negative differential resistance (NDR) device. To deposit the self-assembly monolayers onto the gold electrode, the prefabricated Au(111) substrates were immersed into 0.5[mM/l] self-assembly molecule in THF solution. Then, the electrical properties and surface morphologies of 4,4'-di(ethynylphenyl)-2'-nitro-1-benzenethiolate were measured by using the ultra-high vacuum scanning tunneling microscopy (UHV-STM).

Keywords: self-assembled monolayers, NDR, UHV-STM

1. Introduction

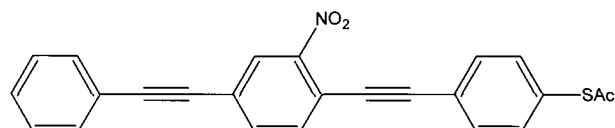
The ability to utilize single molecules that function as self-contained electronic devices has motivated researchers around the world for years, concurrent with the continuous drive to minimize electronic circuit elements in semiconductor industry. The molecular electronics is conceptually different from conventional solid-state semiconductor electronics[2-4]. It allows chemical engineering of organic molecules with their physical and electronic properties tailored by synthetic methods, bring a new dimension in design flexibility that does not exist in typical inorganic electronic materials. Chemical synthesis makes it possible to make large quantities of nanometer size molecules with the same uniformity but at significantly less cost, compared to other batch-fabrication processes such as microolithography. 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[3]. In this study, we characterized electrical properties of 4,4'-di(ethynylphenyl)-2'-nitro-1-benzenethiolate and measured negative differential resistance(NDR), peak-to-valley ratio, using UHV STM system. Recently, the multiple peak current-voltage(I-V) characteristics based on negative

differential resistance (NDR) devices have been widely used in various applications because they are expected to greatly reduce circuit complexity [5-7] and achieve high-speed operation [8, 9] in the integrated circuits.

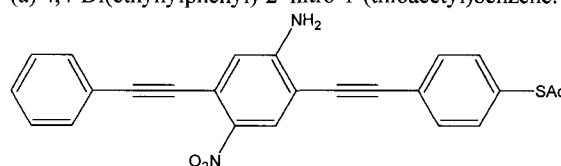
2. Experiment

2.1 Organic Molecules

The organic molecules used in the experiment were composed in Korea Research Institute of Chemical Technology (KRICT). Self-assembly of these molecules takes possible thioacetyl or methyl sulfide functional group and can form self-assembled organic thin film easily on the gold electrode surface. In this paper, molecule dynamics procedure painted molecule in computer using HYPERCHEM.



(a) 4,4'-Di(ethynylphenyl)-2'-nitro-1-(thioacetyl)benzene.

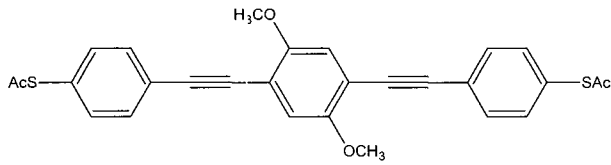


(b) 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-benzenethiolate

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Received April 11, 2005 ; Accepted May 17, 2005



(c) 4-[[2,5-dimethoxy-4-phenylethynyl]phenyl]ethynyl-phenylethanoate

Fig. 1 Chemical structure of organic molecules.

Fig. 1 shows organic molecules used in this experiment. (a) is molecule having nitro functional group and (b) is amino-nitro functional group. And, (c) is molecule that has methoxy functional group.

2.2 Fabrication of Device and Self-assembled Organic Thin Film

Substrate causes definite effect in adsorption process of self-assembled organic thin film. To investigate electrical properties of organic molecule, oxidized silicon wafer (Si<100>) was used. And, as a bottom electrode, Au was evaporated by using Ion Beam Sputtering (IBS) techniques.

When the Au electrode was put into thiol solution which has suitable concentration, the chemical adsorption between molecules was occurred in ten minutes. Specimens, which have Si/SiO₂/Cr/Au/SA film structure, were cleaned for 10 minutes in piranha solution (H₂SO₄:H₂O₂ = 3:1) before the measurements. Chemical equations for the process are as follows [10, 11].

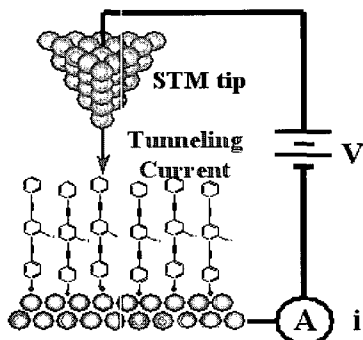
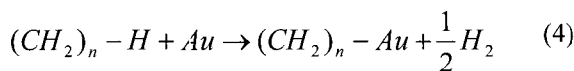
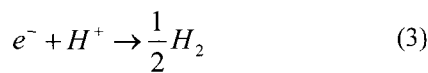
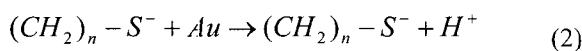
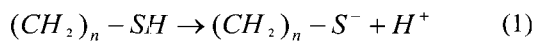


Fig. 2 Schematic of STM measurement system.

By the result of interaction in chemical attraction between adsorption molecular alkyl chains, highly ordered self-assembled organic thin film was formed.

In this paper, we fabricated the STM measurement system such as Fig. 2 and measured electrical properties of self-assembled organic molecule.

3. Results and Discussion

Fig. 3 shows surface images of SAM formation on Au. We could observe electrical properties in 10⁻¹⁰[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.

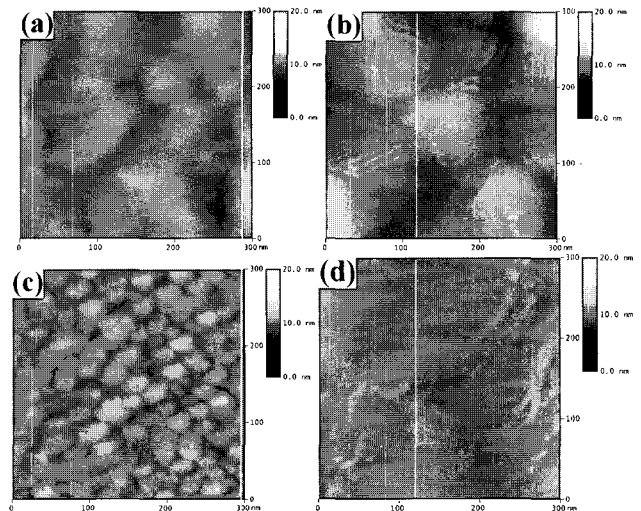


Fig. 3 STM images of self-assembled monolayers. (a) Surface image of Au(111) substrate. (b) Surface image of nitro organic molecule on Au. (c) Surface image of amino-nitro organic molecule on Au. (d) Surface image of methoxy organic molecule on Au.

Electronic measurements were performed consisting of Pt-Ir/SAMs/metal structure. All STM data were obtained using a constant height mode (servo max: 18nm). As a result, NDR phenomenon that current decreases when voltage increase observed partially. Fig. 4,5 and Fig. 6 are showing the voltage-current characteristic curves of each organic molecules. And, the NDR and peak to valley current ratio (PVCR) were calculated, according to Eq. (5), (6).

$$|R_{NDR}| = \frac{V_V - V_P}{I_P - I_V} \quad (5)$$

$$PVCR = \frac{I_P}{I_V} \quad (6)$$

From Eq. (5), we calculated nitro organic molecular negative differential resistance. The NDR at the negative region was less than $-2.9564[\text{m}\Omega/\text{cm}^2]$, and NDR at the positive region was less than $-3.1244[\text{m}\Omega/\text{cm}^2]$. Also, from Eq. (6), PVCr of 1.29:1 at the negative region, and 1.30:1 at the positive region were calculated. Table 1 shows NDR and PVCr value for nitro, nitro-amino, methoxy organic molecules.

Table 1 NDR and PVCr value for nitro, nitro-amino, methoxy organic molecules.

Compound	NDR $[\text{m}\Omega/\text{cm}^2]$	PVCr
Amino group	(-) < -2.9564	1.29:1
	(+) < -3.1244	1.30:1
Amino-nitro group	(+) < -17.285	15.74:1
Methoxy group	(-) < -0.396	1.41:1
	(+) < -0.201	96.43:1

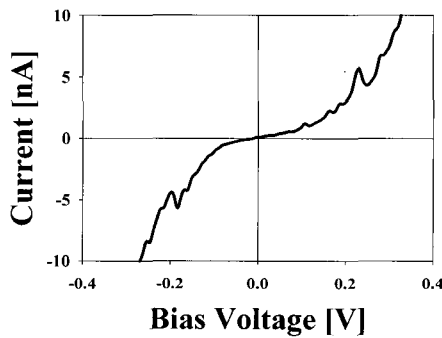


Fig. 4 I-V curves of nitro organic molecule.

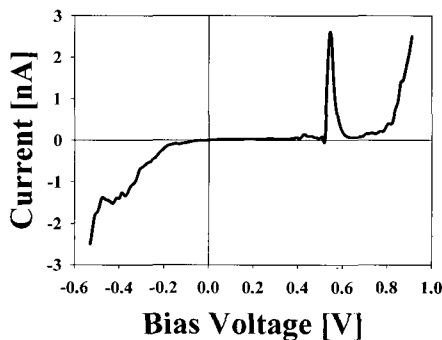


Fig. 5 I-V curves of amino-nitro organic molecule.

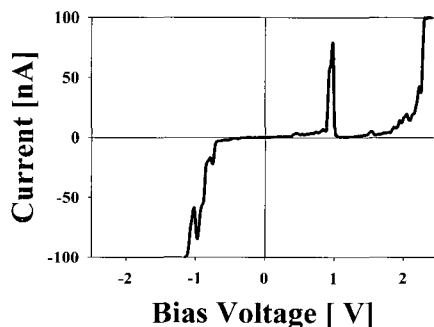


Fig. 6 I-V curves of methoxy organic molecule.

Fig. 7 shows 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 other part is closed and current is zero. (b): HOMO and LUMO of the organic molecule exist over than Fermi level of probe and gold electrode. At the case, if positive bias is applied on the gold electrode, molecular energy state inclines toward the state of gold electrode. (c): Current reaches to peak value (V_{peak}) by tunneling in resonant state between probe and molecule. Resonant state means that LDOS (local density of state) of probe 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. Since these organic molecules that show NDR phenomenon have applicability for switching device, high-frequency oscillator, mixer, multiplier, logic and A/D converter etc., industry is expecting that the molecules are going to cause many effects generally.

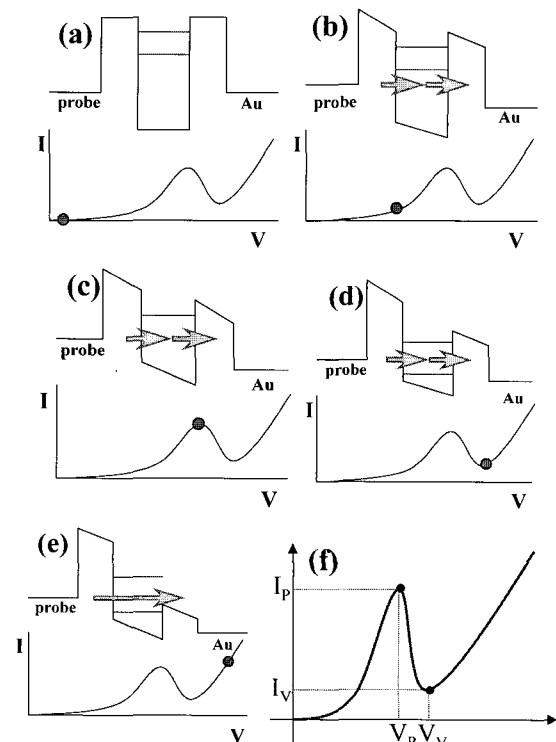


Fig. 7 Principle of tunneling current and NDR.

4. Conclusion

Organic thin films containing redox center were fabricated and the resonant tunneling processes in potential barriers were studied at room temperature. As a result, we obtained NDR and PVCR value of each molecule by using UHV-STM. The negative differential resistance behavior was measured at a tip/SAM/Au substrate junction. The possibility for the development of molecular devices using the NDR mechanism of the organic molecules was presented.

Acknowledgements

This work was supported by the KOSEF through the CIIPMS at Dong-A University.

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