

## Current-voltage (I-V) Characteristics of the Molecular Electronic Devices using Various Organic Molecules

Ja-Ryong Koo<sup>a</sup> and Sang-Woo Pyo

*Department of Electrical Information & Control Engineering & Center for Organic Materials and Information Devices (COMID), Hongik University, Sangsu-dong, Mapo-gu, Seoul 121-791, Korea*

Jun-Ho Kim

*Department of Electronic Engineering & Center for Organic Materials and Information Devices (COMID), Hongik University, Sangsu-dong, Mapo-gu, Seoul 121-791, Korea*

Jung-Soo Kim

*Korea Institute of Science and Technology Information (KISTI), Cheongnyangni 2-dong, Dongdaemun-gu, Seoul 130-742, Korea*

Doowon Gong and Young Kwan Kim

*Department of Information display & Center for Organic Materials and Information Devices (COMID), Hongik University, Sangsu-dong, Mapo-gu, Seoul 121-791, Korea*

<sup>a</sup>E-mail : [jrkoo9215@lycos.co.kr](mailto:jrkoo9215@lycos.co.kr)

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Organic molecules have many properties that make them attractive for electronic applications. We have been examining the progress of memory cell by using molecular-scale switch to give an example of the application using both nano scale components and Si-technology. In this study, molecular electronic devices were fabricated with amino style derivatives as redox-active component. This molecule is amphiphilic to allow monolayer formation by the Langmuir-Blodgett (LB) method and then this LB monolayer is inserted between two metal electrodes. According to the current-voltage (I-V) characteristics, it was found that the devices show remarkable hysteresis behavior and can be used as memory devices at ambient conditions, when aluminum oxide layer was existed on bottom electrode. The diode-like characteristics were measured only, when Pt layer was existed as bottom electrode. It was also found that this metal layer interacts with organic molecules and acts as a protecting layer, when thin Ti layer was inserted between the organic molecular layer and Al top electrode. These electrical properties of the devices may be applicable to active components for the memory and/or logic gates in the future.

*Keywords* : Langmuir-blodgett techniques, Metal/insulator interfaces, Memory, Hysteresis

### 1. INTRODUCTION

During the last decade, enormous progress has taken place in the device physics of organic molecular electronic devices, mainly in organic light emitting diodes (OLED), organic thin film transistors (OTFT) and molecular memory[1-3]. In devices with certain organic molecules, depending on the voltage sweep direction, the current-voltage (I-V) characteristics show the presence of high and low conducting states. The existence of these

states and the switching property between two states has been explained in terms of many possible mechanisms. The high conducting state (ON-state) observed in monolayer sandwiched structures has been explained in terms of traps, which are filled under high fields leading to high carrier mobility and filamentary effect[4-8]. It is now found that the current-voltage (I-V) characteristics of monolayered devices can also show a hysteresis behavior[9-11], which has been explained in space charge region at the organic monolayer/metal interfaces.

The devices with either the hysteresis or switching behavior can lead to data-storage applications. The Langmuir-blodgett (LB) method makes it possible to prepare a monolayer film with well-defined molecular orientation at a molecular scale. Because of this superior feature, we had carried out experiment about Zn-porphyrin derivative LB monolayer device[12] and have tried to use amino-style derivatives LB films as a switching material or a memory material applicable to data-storage. In this article, we have studied the possibility of the organic monolayer as a molecular-scale memory or a logic circuit. The device fabrication process using amino-style derivative LB monolayer was described and current-voltage characteristics of the amino-style derivatives LB monolayer devices were obtained and discussed in this study.

## 2. EXPERIMENTAL

In this study, ASBC-18 ( $C_{35}H_{53}IN_2S$ , M.W. : 660.78), ASDC-18 ( $C_{39}H_{51}N_3O$ , M.W. : 577.84), ASA-15 ( $C_{34}H_{46}N_2O_2$ , M.W. : 514.74) molecules, three of the amino-style derivatives were used and synthesized by our research group. Figure 1 shows the molecular structures of the amino-style derivatives used in this study. The surface pressure ( $\pi$ )-area (A) isotherm experiments and the deposition of monolayers were carried out with a Kuhn-type LB trough system (NIMA 611D), where deionized pure water (18.3  $M\Omega \cdot cm$ ) was used as the subphase. The measurement and the film deposition were performed with the compression speed of 25  $cm^2/min$  at room temperature and the deposition rate was 10  $mm/min$  at up stroke. The amino-style derivatives were dissolved in chloroform at a concentration of 0.5  $mM$  and this solution was spread on the water surface. The film was transferred onto the vertical dipping method at the surface pressure of 25  $mN/m$ , 15  $mN/m$ , 35  $mN/m$  respectively. Slide glass and Si-wafer on which LB film were deposited, were treated in concentrated  $H_2SO_4$  solution to have a hydrophilic property about a surface of the substrate following the washing with deionized water.

Al bottom electrode and Ti/Al top electrodes for electrical measurement were thermally vacuum-deposited at a pressure of  $10^{-6}$  Torr and Pt bottom electrode was deposited with DC magnetron sputtering method (Inostek Inc.). The thickness of top and bottom electrodes was approximately 30 nm and that of the protecting Ti layer was 5 nm and was controlled by the thickness monitor. Figure 2 shows the device structure using Pt electrode and the device structure using Al electrode was shown elsewhere[10]. The current-voltage (I-V) characteristics of the film were measured by using computer controlled Keithley 236 electrometer. The

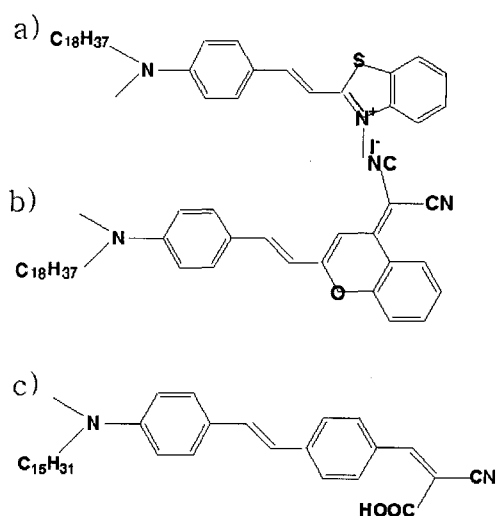


Fig. 1. Molecular structures of the amino-style derivatives used in this study. a) ASBC-18, b) ASDC-18, and c) ASA-15.

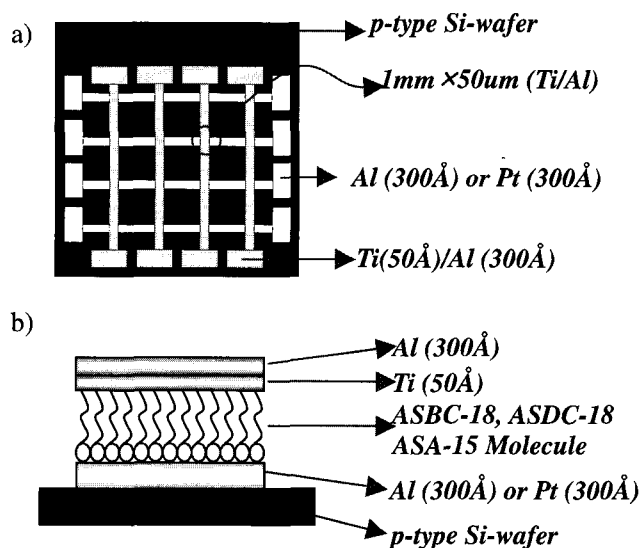


Fig. 2. Device structure fabricated in this study. a) top view and b) side view.

voltage was applied initially from -0.5 V to 0.5 V in an interval of 50 mV/50 ms to the bottom electrode and current was measured at that time. The voltage sweep was increased gradually from -0.5 V to -4 V and from 0.5 V to 4 V and was cycled repeatedly.

## 3. RESULTS AND DISCUSSION

For acquiring Langmuir-blodgett (LB) film deposition condition, we carried out surface pressure ( $\pi$ )-area (A)

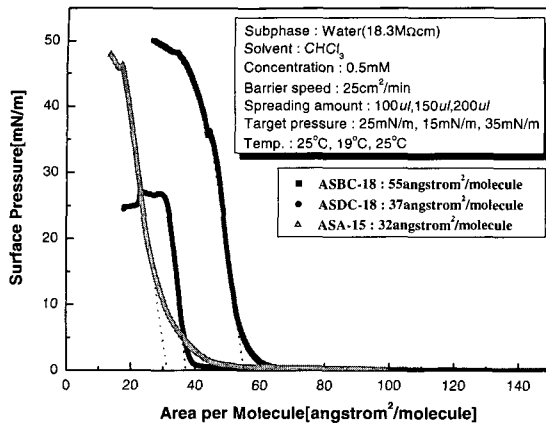


Fig. 3.  $\pi$ -A isotherm characteristics of the langmuir film of the amino-style derivatives.

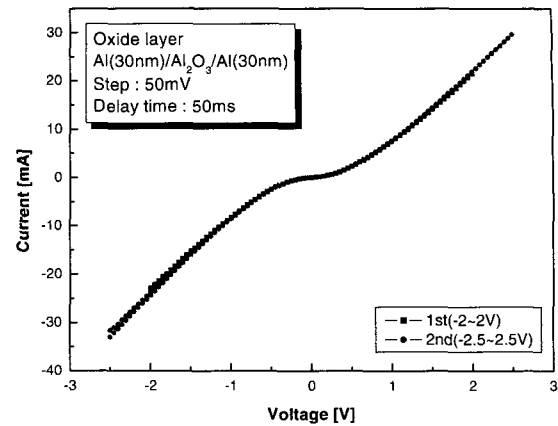


Fig. 5. Current-voltage characteristics of Al/Al<sub>2</sub>O<sub>3</sub>/Al device.

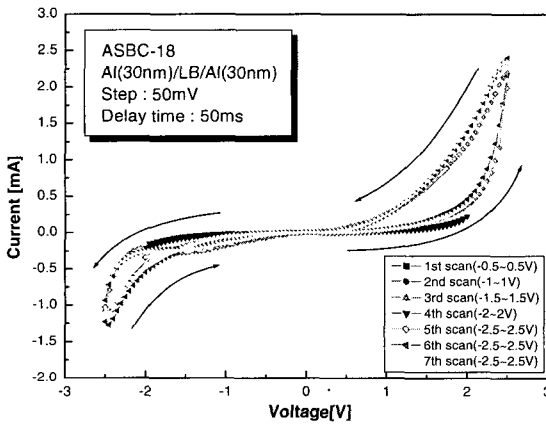


Fig. 4. Current-voltage characteristics of Al/ASBC-18 LB monolayer/ Al device.

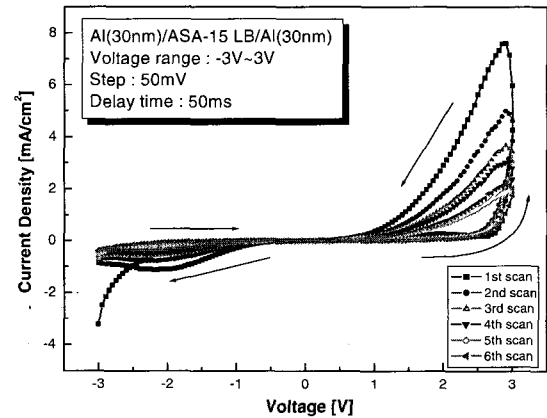


Fig. 6. Current-voltage characteristics of Al/ASA-15 LB monolayer/Al device.

isotherm experiment. Figure 3 shows  $\pi$ -A isotherm characteristics of the amino-style derivative Langmuir films. The area per molecule of ASBC-18, ASDC-18 and ASA-15 molecules were respectively  $55 \text{ \AA}^2$ ,  $37 \text{ \AA}^2$ ,  $32 \text{ \AA}^2$  and relatively low collapse pressure of  $47 \text{ mN/m}$ ,  $27 \text{ mN/m}$ ,  $45 \text{ mN/m}$  were shown in Fig. 3. In this study, the surface pressure of  $25 \text{ mN/m}$ ,  $15 \text{ mN/m}$  and  $35 \text{ mN/m}$  were chosen as an optimum film transfer pressure for film deposition, where the film transfer ratio was always approximately 100 % in case of Z-type.

The electrical performance of the devices is largely determined by the electrode materials used. The experimental results were obtained from four combinations of the electrode materials used in the MIM junction. When Al bottom electrode was used, native Al-oxide layer was surely created on the Al bottom electrode during LB process. In this experiment, when Al/Al<sub>2</sub>O<sub>3</sub> bottom electrode was used, ASBC-18, ASDC-

18, ASA-15 molecular devices showed interesting current-voltage characteristics. In the case of Al bottom electrode devices, i) 25 % of Al/ASBC-18/Al based on total 24 samples was short-circuited, but approximately 54 % of devices, 13 samples were hysteresis and 21 % of devices, 5 samples were diode-like characteristics even after several repeated measurements. ii) 36 % of Al/ASDC-18/Al based on total 14 samples was short-circuited, but approximately 50 % of devices, 7 samples were hysteresis and 14 % of devices, 2 samples were diode-like characteristics. iii) 12.5 % of Al/ASA-15/Al based on total 16 samples was short-circuited, but approximately 12.5 % of devices, 2 samples were hysteresis and 75 % of devices, 12 samples were diode-like characteristics. The short circuits are mainly due to the incapability to control the thickness of the top Al electrode, or due to the imperfections in the LB film.

Figure 4 shows the current-voltage (I-V) characteris-

tics of Al/ASA-18 LB monolayer/Al device measured initially with the bias scan range -0.5 V to 0.5 V at room temperature in air. In this figure, the voltage scan range was increased gradually in accordance with a scan sequence. During the initial successive 4 cycles, the plots were shown diode-like characteristics, but the next cycles were shown hysteresis characteristics.

Figure 5 shows the I-V characteristics of Al/Al control device. The ohmic characteristics is the same as the short-circuit characteristics and the current level of these device was 10 times higher than the amino-style derivatives inserted devices. The devices allow some Al atoms to crowd directly into the Al-oxide layer, because the device has not any organic molecule between the metal top and bottom electrode. Therefore, there is no doubt about that the hysteresis of the Fig. 4 is inherent property of the organic molecule.

Figure 6 shows the I-V characteristics of Al/ASA-15 LB monolayer/Al device. The voltage scan range is from -3 V to +3 V and from +3 V to -3 V. During 6 cycles, when a number of cycles were increased, the current value was decreased gradually. It is convinced that this decreased current value is because of degradation of organic molecule. But, the hysteresis was appeared obviously and was convinced of an inherent property of ASA-15 molecule.

For increasing the yield of the organic device, Ti protecting layer[13] was inserted between the amino-style LB monolayer and Al top layer. In the case of using Al bottom electrode, the yield is roughly not different from that of non-using Ti-protecting layer. In order to compare with influence of an oxide layer, Pt bottom electrode as oxide free metal was used. In the case of the structure as the Pt/amino-style LB monolayer/Al, all samples were short-circuits. We guess that such results are due to penetrate Al atoms of the top electrode into the organic monolayer. But, when Ti protecting layer was inserted between the amino-style LB monolayer and the Al top layer, approximately 80 % was short-circuits and 20 % was diode-like characteristics.

Figure 7 shows I-V characteristics of Pt/ASA-15 LB monolayer/Ti/Al device measured initially with the bias scan range -2 V to 2 V. In the same voltage range from 4th cycle to 7th cycle, the current value was gradually decreased and the I-V curve was a little asymmetry. From this results we believe that the inserted Ti layer must be protect the organic monolayer and the device is reproducible.

From our experimental data, we believe that the origin of the conduction is due to asymmetric tunneling through an ordered monolayer and the origin of the short-circuit samples is due to the formation of filaments of top Al electrode that interspersed between the alkyl chains of adjacent amino-style molecules. Though Ti protecting layer was inserted between an organic layer and the top

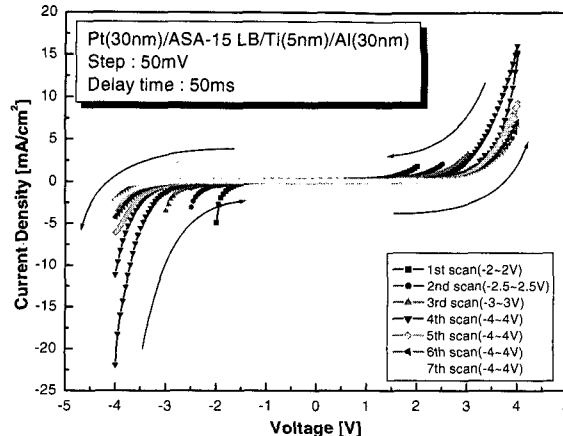


Fig. 7. Current-voltage characteristics of Pt/ASA-15 LB monolayer /Ti/Al device.

metal layer, the uniformity of the Ti layer was so poor as having a void.

#### 4. CONCLUSION

We fabricated metal/amino-style derivative LB monolayer/metal junctions with an asymmetric tunneling barrier and measured the I-V characteristics of these device structures. From the results of the I-V characteristics, amino-style derivative LB monolayer devices using the Al bottom electrode were shown a reproducible switching and a hysteresis property. Also, the LB monolayer device using oxide-free Pt bottom electrode were slightly shown a diode-like characteristic but a yield of the sample was worse than that using the Al bottom electrode. To increase the yield of device, we had introduced a thin Ti protecting layer between the LB monolayer and Al top electrode. Nevertheless, the yield was not increased. It was due to created diffusion into the LB monolayer of Ti atoms because of increasing strong intermolecular interactions between the alkyl group of the amino-style LB monolayer and atoms of Ti protecting layer. Finally, the amino-style LB monolayer devices having a hysteresis and a switching property may be applicable to memory and logic gate in the future if the yield of the device and the reliability of repetitive operations will be settled.

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