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We fabricated a molecular electronic device which has a structure of Al/Al_2O_3/ ASA-15 LB monolayer/Ti/Al device. To study a charge transfer mechanism of molecular electronic devices, a current density-voltages (J-V) characteristics was measured at an increasing temperature range from 10 K to 300 K with an interval of 30 K. Strong temperature-dependent electrical property and tunneling through organic monolayer at low bias (below 0.5 V) were appeared. These experimental data was fitted by using a theoretical formula such as the Simmons model. In comparison between the theoretical and experimental results, it was verified that the fitting results of Simmons model about direct tunneling is fairly fitted below 0.5 V at both 300 K and 10 K. Hopping conduction is also dominant at all voltage range above 200 K due to charges trapped by defects located within the dielectric stack, including the Al_2O_3, organic monolayer and Ti interfaces.

Keywords: direct tunneling; hopping conduction; molecular electronic device; Simmons model; temperature-dependence

INTRODUCTION

Organic molecules have many properties that make them attractive for electronic applications. During the last decade, enormous progress has taken place in the device physics of organic molecular electronic devices, mainly in organic light emitting diode (OLED), organic

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thin-film-transistor (OTFT), and molecular memory [1–3]. Much attention has recently given to the investigation of highly ordered molecular nanostructures such as nano-scale molecular memory of metal/organic monolayer/metal structure created on the basis of Langmuir-Blodgett (LB) films [4–6]. Regarding to analyzing the charge transfer mechanism in the molecular electronic device, quantum mechanical tunneling through solid-state organic insulating barriers has been contrastively less studied than conventional case of solid-state inorganic insulators [7], due mainly to the difficulty of fabricating defect-free thin organic films. Preceding research on multilayer organic insulators confirmed the exponential decay of tunneling current with increasing thickness [8], but conductance and temperature properties remained fabrication dependent and explanation of the multiple dielectric layers difficult. Increasing interest in molecular electronics is driving new efforts to progress a robust appreciation of charge transport through organic layer in solid-state organic-inorganic hybrid systems [9]. So far, theory and experiment have focused mainly on two-terminal devices consisting of a single molecule or a molecular monolayer sandwiched between conducting metal electrodes. A range of interesting researches has been observed experimentally, including rectification behavior such as diode-like [10], negative-differential resistance (NDR) for logic and/or memory [11], switching behavior [12]. Theoretical interpretations have depended on standard temperature independent models of resonant and non-resonant quantum mechanical tunneling [13].

In this paper, to study the conduction mechanism of ASA-15 LB monolayer devices, we measured the current density-voltage (J-V) characteristics according to variable temperatures and calculated by using fitting formula such as Simmons model. From those results, we verified the dominant charge transport mechanism in molecular electronic device.

EXPERIMENT

ASA-15 ($C_{34}H_{46}N_2O_2$, molecular weight: 514.74) molecule, one of the amino-style derivatives, synthesized by our research group was sandwiched between top and bottom electrodes in metal/organic monolayer/metal junctions by Langmuir-Blodgett (LB) method. The molecular structure of the ASA-15 molecule and the device structure are shown in Figure 1. Details of device fabricating method including both LB monolayer deposition and fabrication of electrodes were well presented in previous studies [14].

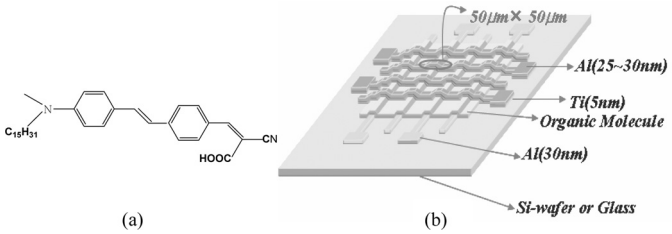


FIGURE 1 Schematics of (a) molecular structure of the ASA-15 molecule and (b) crossbar type device structure.

A Keithley 236 Source Measure Unit (SMU) interfaced with a computer using Labview program is used to measure the current density-voltage (J-V) characteristics of the two terminal molecular electronic devices in the cryogenic system (A CTI-Cryodyne refrigeration system Model 22, Helix Co.). To maintain the sample temperature, a Lakeshore electronically controlled heater is used, which can be used to regulate the helium gas temperature in the range from 10 K to 300 K. The actual sample temperature was monitored using a Lakeshore thermometer (Model 330) mounted on the sample stage.

RESULTS AND DISCUSSION

The strong temperature dependence of the charge transport through the ASA-15 LB monolayer is illustrated in Figure 2. Current density-voltage (J-V) curves of the ASA-15 LB monolayer devices show 100 times increase of current density from 10 K to 300 K. All J-V curves are quite symmetric about $V=0$, illustrated by inverting and superposing the negative bias curves at each temperature; the ratio $|J+|/|J-|<1.1$ at all voltage ranges. In this figures, we expected both tunneling behavior having not temperature dependence and thermal activation having temperature dependence.

First of all, having established direct tunneling as the conduction mechanism, we can now obtain the barrier height by comparing our experimental J-V data with theoretical calculations from a direct tunneling model. A model that has been used widely for thin film tunneling is the Simmons model [15]. This model considers the contribution of only one band, either the conduction band (LUMO), or the valence band (HOMO). In the following we use the Simmons model to characterize our experimental J-V data and we show that the Simmons model can be used on our metal-organic monolayer-metal junctions. From the Simmons model, the tunneling current density through a

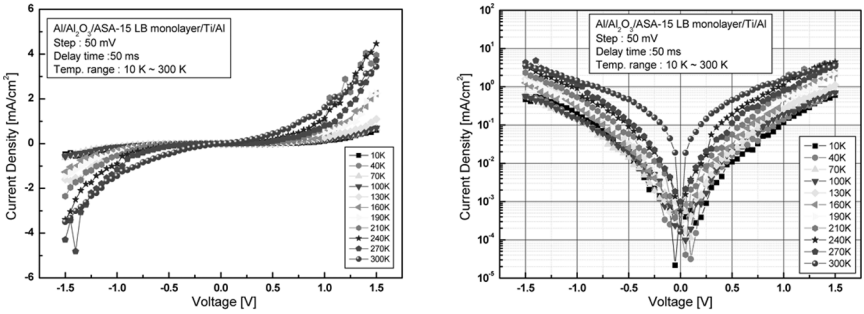
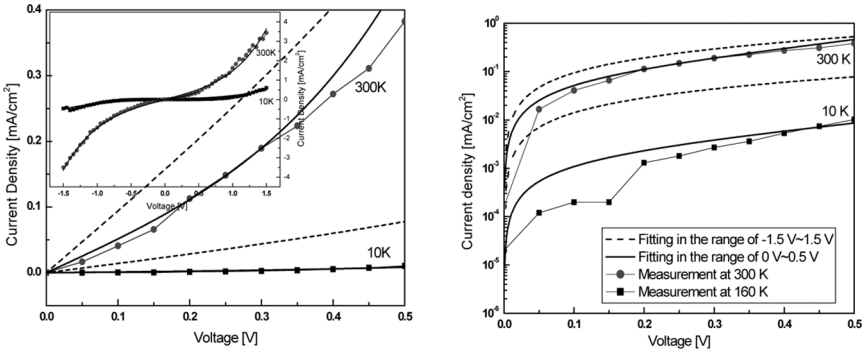


FIGURE 2 Current density-voltage (J-V) characteristics of $Al/Al_2O_3/ASA\text{-}15$ LB monolayer/Ti/Al device according to the temperature in a range of 10 K to 300 K. (a) Linear scale, (b) Semi-log scale.

barrier in the direct tunneling regime ($V < \Phi_B/e$) is given by [16]

$$J = \left(\frac{e}{4\pi^2\eta d^2}\right)\left\{\left(\Phi_B - \frac{eV}{2}\right)\exp\left[-\frac{2(2m)^{1/2}}{\eta}\alpha\left(\Phi_B - \frac{eV}{2}\right)^{1/2}d\right] - \left(\Phi_B + \frac{eV}{2}\right)\exp\left[-\frac{2(2m)^{1/2}}{\eta}\alpha\left(\Phi_B + \frac{eV}{2}\right)^{1/2}d\right]\right\} \quad (1)$$

where m is electron mass, d is barrier width, Φ_B is barrier height, V is applied bias, and α is a unitless adjustable parameter that is introduced to modify the simple rectangular barrier model or to account for an effective mass [15], $\alpha = 1$ corresponds to the case for a rectangular barrier and bare electron mass. From equation (1) by adjusting the parameter Φ_B and α, a nonlinear least square fitting can be performed to fit the measured ASA-15 LB monolayer J-V data [17] as shown in Figure 3. The best fitting parameters (minimized χ^2) for the ASA-15 LB monolayer J-V data were extracted to be $\Phi_B = 1.81 \pm 0.05$ eV and $\alpha = 0.43 \pm 0.01$ at 300 K and $\Phi_B = 2.33 \pm 0.09$ eV at 10 K. Using Φ_B and α, a calculated J-V for ASA-15 LB monolayer is plotted as a solid curve (fitted from 0 V to 0.5 V using Simmons model) and a dash curve (fitted from -1.5 V to 1.5 V using Simmons model) in Figure 3. From the Figure 3, we verified that bias range of direct tunneling for adequate fitting is verified between 0 V and 0.5 V. The data appear good fitting on a linear scale at inset of Figure 3(a), but are shown somewhat poor fitting when viewed on a magnified scale from 0 V to 0.5 V as shown in Figure 3(a) or at a logarithmic scale as shown in



(a) (b)

FIGURE 3 Temperature dependence of ASA-15 LB monolayer transport at both 10 K and 300 K in the bias range from 0 V to 0.5 V. Comparison to measured data and fitting data using Simmons model. (a) linear scale. (Inset) linear scale at both 10 K and 300 K in the bias range from −1.5 V to 1.5 V, (b) Semi-log scale.

Figure 3(b). Though slight different is presented, fitting results is fairly well fitted.

Also, although the physical meaning of α is not unambiguously defined, it provides a way of applying the tunneling model of rectangular barrier to tunneling either through a nonrectangular barrier [18], a proposed effective mass (m^*) of the tunneling electrons through the molecules [19], (i.e. for $\alpha = 0.43$, m^* would be $= 0.18\ m$ here), or a combination of both.

Direct tunneling happens when the applied bias is less than the barrier height ($V < \Phi_B/e$), while Fowler-Nordheim (FN) tunneling is dominant when the applied bias becomes larger than the barrier height ($V > \Phi_B/e$). These two tunneling mechanisms can be distinguished due to their distinct voltage dependencies. Analysis of *ln* (J^2/V) versus 1/V shows significant voltage dependence as shown in Figure 4, indicating obvious FN transport behavior in this bias range (0.5 V to 1.5 V) and thus determining that the barrier height is larger than the applied bias (i.e. $\Phi_B > 0.5$ V). The transition from direct tunneling to FN tunneling requires higher bias passing through barrier thickness. We confirmed that the data have nothing to do with temperature range. This phenomenon suggests that FN tunneling was dominant charge transfer mechanism, when Φ_B is approximately above 1 V at any temperature range.

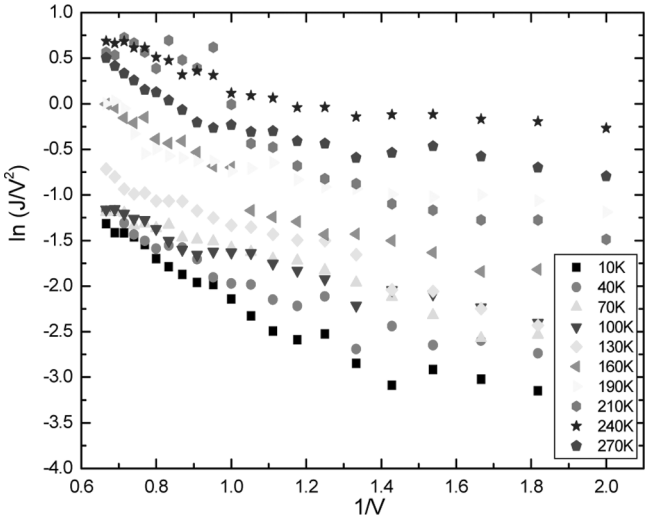


FIGURE 4 Fowler-Nordheim (FN) tunneling plot according to the bias voltage at all temperature range.

Hopping conduction plot is shown in Figure 5. The results of the data presented strong temperature dependence above 200 K and slight dependence below 200 K at all positive voltage. From appearance of

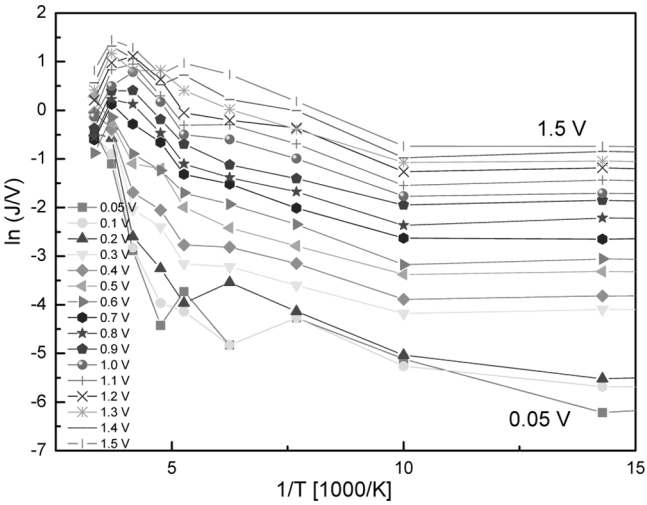


FIGURE 5 Hopping conduction plot according to the temperature at bias voltage from 0.05 V to 1.5 V.

the hopping conduction, we confirmed that the mechanism giving rise to the observed hysteretic behavior as our former results [13] is one based upon transport mediated by charges trapped by defects located within the dielectric stack, including the Al_2O_3 layer, molecules, and Ti interface in device structure. At negative biases, carrier flux may activate charge-trapping defects and create anomalous positive charge [20] in the dielectric stack. These positively charged traps can lead to the high current state via two possible mechanisms. First, the charge state of the defects will affect the height and shape of the tunneling barrier, with the positive charge leading to a lowering of the electron tunneling barrier and consequently greater tunneling current. Second, electrons can hop through the active trap states adding a new defect assisted contribution to the total current. At sufficient positive bias, electrons may be captured by the positively charged defects, neutralizing the defects and returning the device to the low current state. In this particular model, the defects in the low state are passive and charge neutral. A near identical model can be proposed for the case of negatively charged defects. The most likely location for charge trapping to occur is not within the molecular monolayer itself, but at the interfaces between the head groups of the LB monolayer and the alumina bottom electrode, and between the molecular film and the deposited Ti top electrode. When Ti is vacuum deposited onto

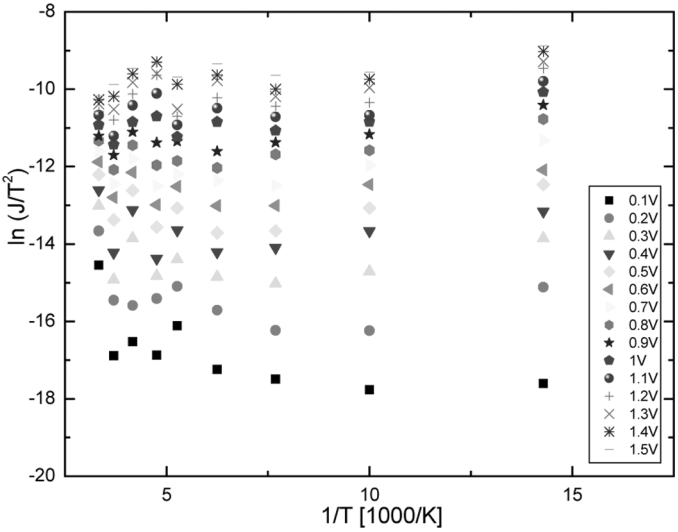


FIGURE 6 Both Poole-Frenkel conduction and Schottky emission plots according to the voltage from 0.1 V to 1.5 V.

molecular films there is a strong Ti/molecule interaction, as indicated by significant changes in the molecular vibration spectra [21]. Thus, both inorganic-organic interfaces are physically complex and remain poorly understood in these Al_2O_3 based molecular devices. Anyway, it is likely that one or both interfaces are the site of electrical defects and traps.

The Poole-Frenkel (PF) conduction and Schottky emission plot according to temperature dependence is shown in Figure 6. It shows no significant temperature dependent at all positive voltages. This means charge transfer was no connection with both PF conduction and Schottky emission mechanism. We are currently investigating about theoretical fitting about the hopping conduction, PF conduction, and Schottky emission dependent on the temperature and the FN tunneling independent on the temperature, will be discussed later.

CONCLUSIONS

In this paper, we investigated charge transport mechanism and electrical characteristics dependent temperature of the molecular electronic devices. When bias voltage was applied below 0.5 V, it is verified direct tunneling is dominant at all temperature range from results of both experimental data and theoretical fitting using Simmons model. When bias voltage was applied above 1 V, it is also confirmed Fowler-Nordheim tunneling is dominant at all temperature range. Moreover, hopping conduction have nothing to do with voltage range, is strongly dominant at temperature above 200 K. Such hopping conduction is due to charges trapped by defects located within the dielectric stack, including the Al_2O_3, molecules and Ti interfaces. As a consequence of this reason, our former results as hysteresis phenomena can be explained and demonstrated.

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