

Statistical Analysis of Electronic Transport Through Chemisorbed Versus Physisorbed Alkanethiol Self-Assembled Monolayers

Tae-Wook Kim, Gunuk Wang, and Takhee Lee

Abstract—We fabricate microscale via-hole structure molecular electronic devices using various lengths of alkanemonothiol and alkanedithiol self-assembled monolayers (SAMs) and characterize their charge transport properties. From the statistical analysis of the transport properties of these SAMs, we have found that the conductance of alkanedithiols is higher about an order of magnitude than that of alkanemonothiols, which is due to the different nature of metal–molecule contacts, i.e., physisorbed versus chemisorbed contacts. However, the transport decay coefficients that can be obtained from the length-dependent transport characterization are almost identical for the two molecular systems.

Index Terms—Electronic transport, molecular electronics, self-assembled monolayer.

I. INTRODUCTION

MOLECULAR electronics promises to deliver low-cost and ultrahigh-density electronic devices [1]–[3]. However, understanding the charge transport mechanism through molecules is important before any applications [4]. For example, alkyl-chain thiol molecular systems have been extensively studied because they form robust self-assembled monolayers (SAMs) on Au surface [5]–[7]. In vertical metal–molecule–metal (M–M–M) junctions where the molecules are sandwiched between Au electrodes, the alkanemonothiol ($\text{HS} - (\text{CH}_2)_{n-1} - \text{CH}_3$) molecular junctions have one chemisorbed contact via thiol–Au reaction (S–Au) and the other physisorbed contact ($\text{CH}_3 - \text{Au}$), whereas the alkanedithiol molecular junctions has thiol–Au chemisorbed contacts at both sides [5], [8]. It has been shown the current density through alkanedithiols is higher than that of alkanemonothiols due to their different nature of metal–molecule contact properties (chemisorbed versus physisorbed contact) at Au–molecule contacts [9]. However, the charge transport study for statistically meaningful number of molecular “working” devices has not been quite attempted. The electronic transport properties statistically obtained from enough number of devices can provide more accurate characteristics of molecular systems.

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In this study, we investigate the electronic transport properties of alkanemonothiol and alkanedithiol SAMs using M–M–M molecular devices with microscale via-hole structures. We fabricated $\sim 30\,000$ molecular devices and subsequently characterized all of these mass-fabricated devices. We obtained the statistical distribution of conductance for different lengths of alkanemonothiol and alkanedithiol SAMs and determined transport decay coefficients from length-dependent transport characterization. And we compared these characteristics for the two molecular systems.

II. EXPERIMENTAL METHODS

The alkanethiol (alkanemonothiol and alkanedithiol) M–M–M junction devices were fabricated on a p-type (100) Si substrate covered with a thermally grown 3000 Å thick layer of SiO_2 . The conventional optical lithography method was used to pattern bottom electrodes that were prepared with Au (1000 Å)/Ti (50 Å) using an electron beam evaporator. A SiO_2 layer (700 Å thick) was deposited on the patterned bottom by plasma enhanced chemical vapor deposition. Reactive ion etching (RIE) was then performed to create microscale via-holes of 2 μm diameter through SiO_2 layer to expose the Au surfaces of the bottom electrodes. Six different ~ 5 mM alkanethiol solutions were prepared by adding ~ 10 μL alkanethiols to ~ 10 mL anhydrous ethanol (from Aldrich Chem. Co.). The chips were left in the solution for 24–48 h for the alkanethiol SAMs to assemble on the Au surfaces exposed by RIE in a nitrogen-filled glove box with an oxygen level of less than ~ 10 ppm. Alkanemonothiols (from Aldrich Chem. Co.) of three different lengths: octanemonothiol ($\text{CH}_3(\text{CH}_2)_7\text{SH}$, denoted as C8, for the number of alkyl units), dodecanemonothiol ($\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, C12), hexadecanemonothiol ($\text{CH}_3(\text{CH}_2)_{15}\text{SH}$, C16), and alkanedithiols (from Tokyo Chem. Industry) of three different lengths: octanedithiol ($\text{HS}(\text{CH}_2)_8\text{SH}$, DC8), nonanedithiol ($\text{HS}(\text{CH}_2)_9\text{SH}$, DC9), and decanedithiol ($\text{HS}(\text{CH}_2)_{10}\text{SH}$, DC10) were used to form the active molecular components. These six molecules were chosen to vary molecular length and the property of metal–molecule contact. The molecular structures are shown in Fig. 1(b). After the alkanethiol SAMs were formed on the exposed Au surfaces, top Au electrode was made by thermal evaporation to form M–M–M junctions. This evaporation was done with a shadow mask on the chips with a liquid nitrogen cooled cold stage in order to minimize thermal damage to the active molecular component under a pressure of $\sim 10^{-6}$ torr. For the same reason,

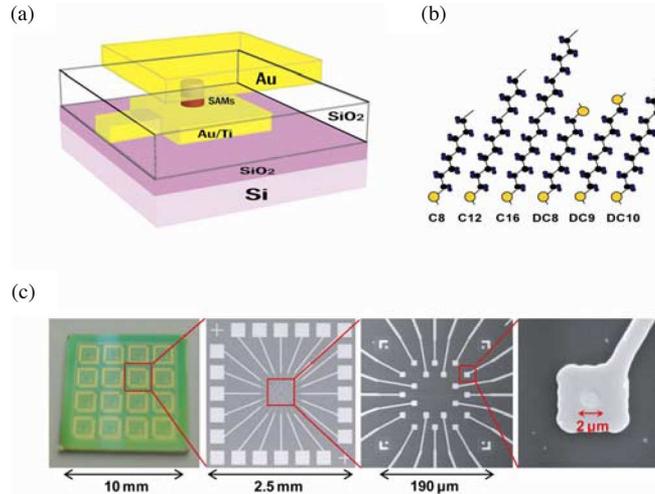


Fig. 1. (a) Schematic diagram of an M–M–M device with microscale via-hole structure. (b) Chemical structures of alkanemonthiols (C8, C12, and C16) and alkanedithiols (DC8, DC9, and DC10). (c) Optical and SEM images of M–M–M devices.

the deposition rate for the top Au electrode was kept very low, typically $\sim 0.1 \text{ \AA/s}$ until the total thickness of the top Au electrode reached $\sim 500 \text{ \AA}$. Fig. 1(a) shows the schematic diagram of a microscale M–M–M junction device, and Fig. 1(c) shows a series of optical and scanning electron microscopy (SEM) images of the fabricated M–M–M devices before the top electrode metallization. From left to right in Fig. 1(c), a $1 \text{ cm} \times 1 \text{ cm}$ unit piece contains 16 dies, and each die contains 20 individual molecular M–M–M devices, thus each unit piece has total 320 molecular devices. The room temperature current–voltage (I – V) characteristics of all of the fabricated devices were evaluated using a HP4155A semiconductor parameter analyzer.

III. RESULTS AND DISCUSSION

There have been many efforts to understand the charge transport through alkanethiol SAMs; however, due to the low yield problem of molecular electronic devices that is mainly because of the electrical shorts [7], [10], [11], systematic studies on the intrinsic properties of alkanethiols are still undergoing. In our previous report, we provided a criterion for determining “working” molecular electronic devices from statistically meaningful number of alkanemonthiol molecular electronic devices [12]. The working devices were defined if the current values are within a certain range in the histogram of the current distribution. That range can be arbitrarily chosen, for example, as the interval (3σ range) between $m + 3\sigma$ and $m - 3\sigma$ where m and σ are the mean value and standard deviation of the current distribution [12]. Alternatively, another interval of the 1σ range between $m + \sigma$ and $m - \sigma$ can also be used, although the 1σ range contains fewer working molecular devices than the 3σ range. Fig. 2 shows an example of the current histogram of C8 devices with working devices contained within the 1σ range marked with dashed lines. Similar statistical analysis was carried out for other molecules, and the statistical results are summarized in Table I.

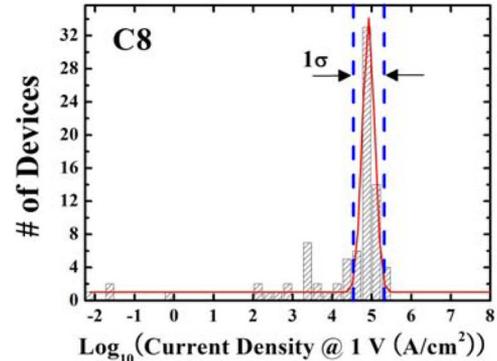


Fig. 2. Histogram of C8 devices with working devices contained within the 1σ range.

Fig. 3 shows plots of the resistance (R) of all the different length alkanemonthiol and alkanedithiol molecular devices of which current values are within the 1σ range of the current distributions. The resistance of each device was calculated from the linear fitting at the low bias ohmic regime from 0 to 0.3 V. In spite of some fluctuations of resistance values in each alkanemonthiol, there are unique resistance ranges for different molecules, as shown in Fig. 3(a). The mean values of resistances of C8, C12, and C16 molecular devices can be determined from $\log(R)$ values of all the working devices, and were found as $\sim 9.3 \times 10^2$, 1.4×10^5 , and $1.5 \times 10^7 \Omega$, respectively. As the molecular length of alkanemonthiols increases, the resistance also increases exponentially with the length, indicating the length-dependent charge transport behavior. Similarly, the resistances of alkanedithiol devices also showed the exponential length dependence, as shown in Fig. 3(b), and the mean values of resistance of DC8, DC9, and DC10 molecular devices were found as 1.2×10^2 , 4.0×10^2 , and $1.1 \times 10^3 \Omega$, respectively. Note that Fig. 3(a) and (b) are plotted with a different scale in y-axis and the degree of the distribution in

TABLE I
SUMMARY OF STATISTICAL ANALYSIS ON THE ALKANEMONOTHIOL AND ALKANEDITHIOL DEVICES. THE DEVICE YIELD, THE NUMBER OF WORKING DEVICES, AND THE MEAN (m) AND STANDARD DEVIATION (σ) OF $\log(J)$ WITH THE 1σ RANGE ARE LISTED FOR EACH MOLECULAR TYPE

	Working Devices					
	C8	C12	C16	DC8	DC9	DC10
# of working device	50	30	59	64	89	93
Yield	0.37 %	0.22 %	0.44 %	0.44%	0.62%	1.94%
m (Log (J))	4.87	3.15	0.533	5.66	5.29	4.81
σ (Log (J))	0.23	0.29	0.527	0.27	0.6	1.09

The device yield, the number of working devices, and the mean (m) and standard deviation (σ) of $\log(J)$ with the 1σ range are listed for each molecular type.

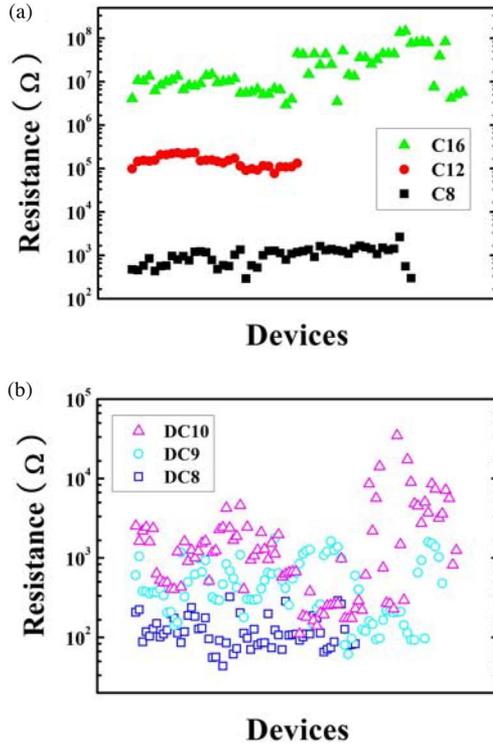


Fig. 3. Statistical distribution of resistances of: (a) alkanemonothiols and (b) alkanedithiols for all the M–M–M working devices chosen from the 1σ range.

resistances of alkanemonothiols and alkanedithiols is actually similar.

To compare the mean resistances for alkanemonothiols and dithiols, we introduce the normalized resistances (R_N) of each molecule as relative to the mean resistance of C8, as $R_N = \log R_{\text{Molecules}} / \log R_{C8}$. The R_N values for C8, C12, C16, DC8, DC9, and DC10 were found as 1, 1.72, 2.46, 0.70, 0.91, and 1.12, respectively, and plotted in Fig. 4(a). The relative resistances indicate that the resistances of C12, C16, DC8, DC9, and DC10 can be expressed as $R_{C8}^{1.72}$, $R_{C8}^{2.46}$, $R_{C8}^{0.70}$, $R_{C8}^{0.91}$, and $R_{C8}^{1.12}$, respectively. Although C8 and DC8 have very similar molecular structure [see Fig. 1(b)], the difference of C8 resistance and DC8 resistance is large, which is because of the different nature of metal–molecular contacts. DC8 has both chemisorbed contacts (S–Au) at both sides whereas C8 has one chemisorbed contact and one physisorbed contact (CH₃–Au).

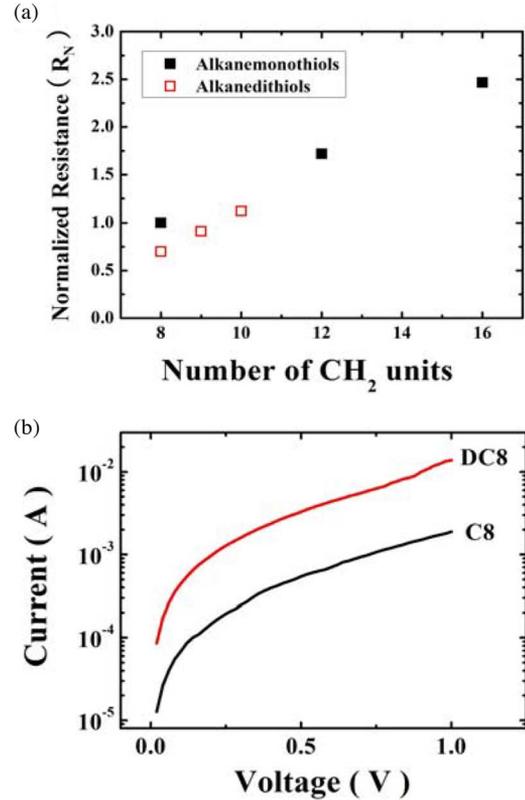


Fig. 4. (a) Normalized resistance (R_N) of alkanemonothiols and alkanedithiols relative to the resistance of C8. (b) Representative I – V characteristics of C8 and DC8 devices.

It is well known that the charge transport for alkanedithiol devices is more efficient than alkanemonothiol devices due to the stronger coupling through the chemisorbed contacts at both sides [9]. Fig. 4(b) shows the I – V curves of “representative” C8 and DC8 devices; for example, the representative C8 device was chosen from the position of the mean value in Fig. 2. DC8 device shows about an order higher current density at 1 V than that of the C8 device. Using the statistical representative devices, the length-dependent I – V characterization of alkanemonothiol and alkanedithiol devices can be further performed. Fig. 5(a) shows a semilog plot of tunneling current densities (at each bias) as a function of the molecule length for various alkanemonothiols and alkanedithiols. The current densities J show exponential dependence on molecular length d , as $J \propto \exp(-\beta_{\text{Body}} d)$, where

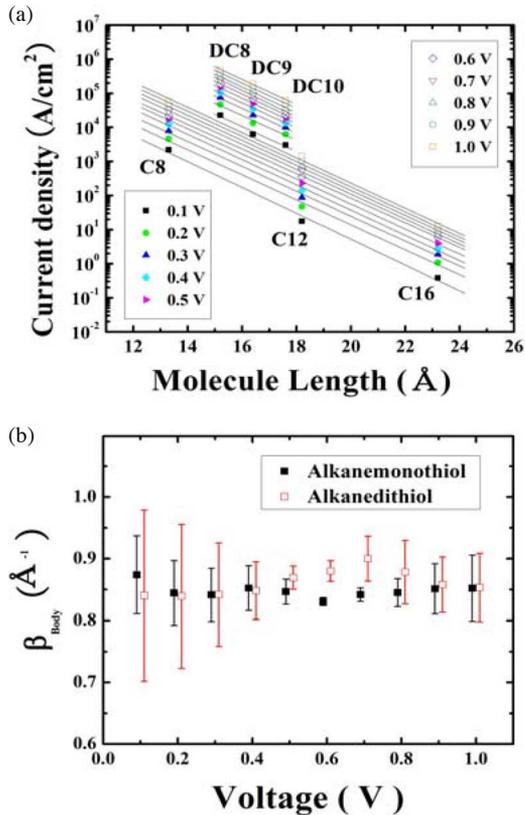


Fig. 5. (a) A semilog plot of current densities at each bias versus molecule lengths, obtained from the representative devices. The lines are exponential fittings. (b) Transport decay coefficient β_{Body} values of alkanemonothiol (open squares) and alkanedithiol (solid squares) obtained from the slope of exponential fitting in (a). For clarity, β_{Body} values were plotted as shifted by ± 0.01 V.

β_{Body} is transport decay coefficient [6]. The molecular lengths of alkanemonothiol and alkanedithiol devices used in this plot are 13.3, 18.2, 23.2, 15.2, 16.4, and 17.6 Å for C8, C12, C16, DC8, DC9, and DC10, respectively, which were determined by adding one (alkanemonothiol) or two (alkanedithiol) Au-thiol bonding length to the length of molecules. The β_{Body} values of alkanemonothiol and alkanedithiol were deduced from the slopes at each bias and are plotted in Fig. 5(b). The error values were obtained by linear fitting errors. The error values were obtained by linear fitting errors. The β_{Body} values were found to be almost identical; ~ 0.85 Å⁻¹ for alkanemonothiol and alkanedithiol. This result is evident in Fig. 5(a) because the slopes of two molecular systems are very similar, which suggests that the β_{Body} values obtained from the length-dependent analysis depend on the molecular structures, not on the details of metal–molecule contacts. This result is consistent with the previous report on the electronic properties of alkanethiol [9].

IV. CONCLUSION

We investigated the charge transport through different length alkanemonothiol and alkanedithiol using microscale via-hole

structure devices. From the statistical analysis of the transport properties for $\sim 30\,000$ fabricated molecular devices, we found that the conductance of alkanedithiol is higher than that of alkanemonothiol, which is due to the different nature of metal–molecule contacts. However, the transport decay coefficients obtained from the length-dependent transport characterization were almost identical for the two molecular systems.

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