Mechanism of Electron Conduction in Self-Assembled Alkanethiol Monolayer Devices

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ABSTRACT: Electron tunneling through self-assembled monolayers (SAMs) of alkanethiols was investigated using nanometer scale devices that allow temperature-dependent current–voltage, \( I(V,T) \), measurements. The \( I(V,T) \) measurement results show, for the first time, temperature-independent electron transport characteristics, proving direct tunneling as the transport mechanism in alkanethiol SAMs. The measured tunneling currents can be fitted with theoretical calculations using the modified rectangular barrier model of direct tunneling with a barrier height \( \Phi_B = 1.42 \pm 0.04 \text{eV} \) and a non-ideal barrier factor \( \alpha = 0.65 \pm 0.01 \) (that may correspond to effective mass of 0.42\( m \)). From the length-dependent conduction measurement on different alkanethiols of various lengths, the tunneling current exhibits exponential dependence on the molecular length, \( d \), as \( I \propto \exp(-\beta d) \), where \( \beta \) is a decay coefficient that was found to be bias-dependent and agrees with the existing theory of direct tunneling. A zero field decay coefficient \( \beta_0 \) of \( 0.79 \pm 0.01 \text{Å}^{-1} \) was obtained.

KEYWORDS: self-assembled monolayer; alkanethiol; tunneling

INTRODUCTION

Understanding the transport mechanism in organic molecular layers has gained particular interest recently due to their potential applications in nanometer scale electronic systems.\(^1-5\) One of the molecular systems that have been studied extensively is alkanethiol (\( \text{CH}_3(\text{CH}_2)_n\text{SH} \)) because it forms a robust self-assembled monolayer (SAM) on Au surfaces.\(^6\) A few groups have used scanning tunneling microscopy,\(^7\) conducting atomic force microscopy,\(^8,9\) or mercury-drop junctions\(^10\) to investigate electron transport through alkanethiols at room temperature and they claim that the transport mechanism is tunneling. Although the electron conduction mechanism is expected to be tunneling when the Fermi levels of contacts lie within the HOMO-LUMO gap (HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital) of a short length molecule, as for the case of these alkanethiols,\(^11\) without temperature-dependent current–voltage \( (I(V,T)) \) characteristics other conduction mechanisms (for example, thermionic or impurity conduction) cannot be ruled out.

In this study, electron transport through alkanethiol self-assembled monolayers is investigated using a nanometer scale device that enables \( I(V,T) \) measurements. The
measured $I(V)$ data are compared with theoretical calculations. $I(V)$ measurements on different alkanethiols of various molecular lengths are also performed so as to study length-dependent conduction behavior.

**EXPERIMENTAL**

Electronic transport measurements on alkanethiol SAMs were performed using a device structure similar to one reported elsewhere. In this device, as illustrated in Figure 1, a number of molecules (several thousands) are sandwiched between two metallic contacts. This technique provides a stable device structure and makes cryogenic measurements possible. Device fabrication starts with a high resistivity silicon wafer with low stress Si$_3$N$_4$ film deposited on both sides by low pressure chemical vapor deposition (LPCVD). By standard photolithography processing, a suspended Si$_3$N$_4$ membrane (size 40µm × 40µm and thickness about 70nm) is fabricated on

![Figure 1](image)

**FIGURE 1.** Schematics of a nanometer scale device used in this study. Top schematic is the cross section of a silicon wafer with a nanometer scale pore etched through a suspended silicon nitride membrane. Middle and bottom schematics show a Au/SAM/Au junction formed in the pore area. The structure of octanethiol is shown as an example.
the topside of the wafer. Subsequent e-beam lithography and reactive ion etching creates a single pore with a diameter of tens of nanometers through the membrane. In the next step, 150nm gold is thermally evaporated onto the topside of the wafer to fill the pore and form one of the metallic contacts. The device is then transferred into a molecular solution to deposit the SAM layer. For our experiments, an approximately 5mM alkanethiol solution is prepared by adding about 10µL alkanethiols into 10mL ethanol. The deposition is done in solution for 24 hours inside a nitrogen filled glove box with an oxygen level of less than 100ppm. Three molecules of different molecular lengths: octanethiol (CH$_3$(CH$_2$)$_7$SH; denoted by C8, for the number of alkyl units), dodecanethiol (CH$_3$(CH$_2$)$_{11}$SH; denoted by C12), and hexadecanethiol (CH$_3$(CH$_2$)$_{15}$SH; denoted by C16) were used to form the active molecular components. As a representative example, the chemical structure of octanethiol is shown in Figure 1. To statistically determine the pore size, test patterns (arrays of pores) were created under similar fabrication conditions. Figure 2 shows a scanning electron microscope (SEM) image of such test pattern arrays. This indirect measurement of device size is performed since SEM examination of the actual device can cause hydrocarbon contamination of the device and subsequent contamination of the monolayer. From regression analysis of 298 pores, the device sizes of the C8, C12, and C16 samples are predicted as 46 ± 2nm, 45 ± 2nm, and 45 ± 2nm diameter, respectively, (99% confidence interval). The sample is then transferred under ambient conditions to an evaporator that has a cooling stage to deposit the opposing Au contact. During the thermal evaporation (under a pressure of about 10$^{-8}$Torr), liquid nitrogen is kept flowing through the cooling stage in order to avoid thermal damage to the molecular layer. This technique reduces the kinetic energy of evaporated Au atoms at the surface of the monolayer, thus preventing Au atoms from punching through the monolayer. For the same reason the evaporation rate is kept very low. For the first 10nm gold evaporated, the rate is less than 0.1Å/sec. Then the rate is 

![FIGURE 2. A scanning electron microscopic image of a representative array of pores used to calibrate device size. The scale bar is 500 nm.](image)
increased slowly to 0.5 Å/sec for the rest of the evaporation and a total of 200nm gold is deposited to form the contact. The device is subsequently packaged and loaded into a Janis cryostat. The sample temperature is varied from 300K to 77K by flowing cryogen vapor onto the sample (and thermometer) using a closed loop temperature controller. Two-terminal DC \( I(V) \) measurements are performed using a HP4145B semiconductor parameter analyzer.

**RESULTS**

**Temperature-Dependent Current–Voltage \((I(V, T))\) Measurements**

In Table 1, possible conduction mechanisms are listed with their characteristic current-, temperature-, and voltage-dependencies. \(^{13}\) (The models listed in Table 1 apply to solid state insulators with one band.) Based on whether thermal activation is involved, the conduction mechanisms fall into two distinct categories: (1) thermionic or hopping conduction, which has temperature-dependent \( I(V) \) behavior, and (2) direct tunneling or Fowler–Nordheim tunneling, which does not have temperature-dependent \( I(V) \) behavior. For example, thermionic and hopping conduction have been observed for 4-thioacetylbiphenyl SAMs\(^ {2} \) and 1,4-phenelyene diisocyanide SAMs.\(^ {14} \) On the other hand, the conduction mechanism through alkanethiols is expected to be direct tunneling because the Fermi levels of contacts lie within the large HOMO-LUMO gap (approximately 8eV) of the alkanethiols with short molecular lengths (approximately 1–2.5nm).\(^ {11} \) Previous work on Langmuir–Blodgett alkane monolayers\(^ {15,16} \) exhibited a large impurity-dominated transport component, complicating the analysis. \( I(V) \) measurements on self-assembled alkanethiol monolayers have also been reported\(^ {7–10,17–19} \); however, all of these measurements were performed at a fixed temperature (300K) which is insufficient to prove tunneling as the dominant mechanism. Without temperature-dependent current–voltage \((I(V,T))\) characterization, other conduction mechanisms (such as, thermionic or hopping

<table>
<thead>
<tr>
<th>Conduction Mechanism</th>
<th>Characteristic Behavior</th>
<th>Temperature Dependence</th>
<th>Voltage Dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Tunneling(^ b )</td>
<td>( J \sim \frac{V^2e}{d} )</td>
<td>none</td>
<td>( J \sim V )</td>
</tr>
<tr>
<td>Fowler–Nordheim Tunneling</td>
<td>( J \sim \frac{eV^{3/2}}{\eta h} )</td>
<td>none</td>
<td>( \ln \left( \frac{J}{V^{2}} \right) - \frac{1}{V} )</td>
</tr>
<tr>
<td>Thermionic Emission</td>
<td>( J \sim \frac{\Phi - q\sqrt{d/4 \pi e}}{kT} )</td>
<td>( \ln \left( \frac{J}{V^{2}} \right) - \frac{1}{T} )</td>
<td>( \ln(J) \sim V^{1/2} )</td>
</tr>
<tr>
<td>Hopping Conduction</td>
<td>( J \sim \frac{\Phi}{kT} )</td>
<td>( \ln \left( \frac{J}{V} \right) - \frac{1}{T} )</td>
<td>( J \sim V )</td>
</tr>
</tbody>
</table>

\(^{a}\)Table adapted from Reference 13.

\(^{b}\)This characteristic of direct tunneling is valid for the low bias regime (see Eq. \((3a)\)).
conduction) cannot be excluded. Reported here for the first time are $I(V)$ measurements in a sufficiently wide temperature range (300 to 80K) and resolution (10K) to determine the mechanism of self-assembled alkanethiol molecular systems.

Figure 3 shows a representative $I(V,T)$ characteristic of dodecanethiol (C12) measured with the device structure shown in Figure 1. Positive bias corresponds to electrons injected from the physisorbed Au contact (bottom contact in FIG. 1) into the molecules. By using a contact area of $45 \pm 2 \text{nm}$ diameter, a current density of about $1,500 \pm 200 \text{A/cm}^2$ at 1.0volt was determined. No significant temperature dependence of the characteristics (from $V = 0$ to 1.0volt) was observed over the range from 300 to 80K. An Arrhenius plot ($\ln(I)$ versus $1/T$) of this is shown in Figure 4A, exhibiting little temperature dependence in the slopes of $\ln(I)$ versus $1/T$ at different bias and thus indicating the absence of thermal activation. Therefore, we conclude that the conduction mechanism through alkanethiol is tunneling, either direct or Fowler–Nordheim. Direct tunneling happens when the applied bias is less than the barrier height ($V < \Phi_B/e$), whereas Fowler–Nordheim 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 two distinct voltage dependencies (see Table 1). Analysis of $\ln(I^2/V)$ versus $1/V$ (FIG. 4B) shows no significant voltage dependence, indicating no obvious Fowler–Nordheim transport behavior in this bias range (0 to 1.0volt) and thus determining that the barrier height is larger than the applied bias; that is, $\Phi_B > 1.0\text{eV}$. This study is restricted to applied biases not greater than 1.0volt. The transition from direct tunneling to Fowler–Nordheim tunneling requires higher bias, and is under study at present. Having established

**FIGURE 3.** Temperature-dependent $I(V)$ characteristics of dodecanethiol (C12). $I(V)$ data at temperatures from 300 to 80K in 20K steps are plotted on a log scale. **Inset** is linear plot for 0–0.2V.
direct tunneling as the conduction mechanism, we can now obtain the barrier height by comparing our experimental $I(V)$ data with theoretical calculations from a direct tunneling model.

**Tunneling Characteristics through Alkanethiols**

To describe the transport through a molecular system having HOMO and LUMO energy levels, one of the applicable models is the Franz two-band model.\(^{20-25}\) This model provides a non-parabolic energy–momentum $E(k)$ dispersion relationship by considering the contributions of both the conduction band (corresponding to the LUMO) and valence band (corresponding to the HOMO).\(^{20}\)

\[
k^2 = \frac{2m^*}{\hbar^2} E \left( 1 + \frac{E}{E_g} \right),
\]  

(1)
where \( k \) is the imaginary part of wave vector of electrons, \( m^* \) is the electron effective mass, \( h = 2\pi\hbar \) is Planck’s constant, \( E \) is the electron energy, and \( E_g \) is the band gap. From this non-parabolic \( E(k) \) relationship, the effective mass of the electron tunneling through the SAM can be deduced by knowing the barrier height of the metal–SAM–metal junction.21

When the Fermi level of the metal is aligned close enough to one band, the effect of the other distant band on the tunneling transport is negligible, and the widely used Simmons model26 is an excellent approximation.27,28 In the following we use the Simmons model to characterize our experimental \( I(V) \) data, and later compare it to the Franz model to examine the validity of the approximation.

The Simmons model expresses the tunneling current density through a barrier in the direct tunneling regime (\( V < \Phi_B/e \)) as

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

(2)

where \( m \) is electron mass, \( d \) is barrier width, \( \Phi_B \) is barrier height, \( V \) is applied bias, and \( \alpha \) is a unitless adjustable parameter that is introduced to modify the simple rectangular barrier model or to account for an effective mass.9,10,26 The value \( \alpha = 1 \) corresponds to the case for a rectangular barrier and bare electron mass, and has been previously shown not to fit \( I(V) \) data well for some alkanethiol measurements at fixed temperature (300K).10

From Eq. (2), by adjusting two parameters \( \Phi_B \) and \( \alpha \), a nonlinear least square fitting can be performed to fit the measured C12 \( I(V) \) data. (Nonlinear least square fittings were performed using Microcal Origin 6.0.) By using a device size of 45nm diameter, the best fitting parameters (minimized \( \chi^2 \)) for the room temperature C12 \( I(V) \) data were found to be \( \Phi_B = 1.42 \pm 0.04 \text{ eV} \) and \( \alpha = 0.65 \pm 0.01 \) (C12, 300K), where the error ranges of \( \Phi_B \) and \( \alpha \) are dominated by potential device size fluctuations of 2nm. A second, independently fabricated device with C12 gave values of \( \Phi_B = 1.37 \pm 0.03 \text{ eV} \) and \( \alpha = 0.66 \pm 0.01 \). Likewise, a data set was obtained and fitting was done for hexadecanethiol (C16), which yielded values of \( \Phi_B = 1.40 \pm 0.03 \text{ eV} \) and \( \alpha = 0.68 \pm 0.01 \) (C16, 300K).

In addition to the nonlinear least square fittings, to visualize the variations of fitting as a function of \( \Phi_B \) and \( \alpha \), contour plots of \( \Delta(\Phi_B, \alpha) = (\Sigma I_{\text{exp},V} - I_{\text{cal},V})^2 \) were generated, where \( I_{\text{exp},V} \) denotes experimental current values at various bias and \( I_{\text{cal},V} \) are calculated values using Eq. (2). Figure 5 is such a contour plot generated for the C12 \( I(V) \) data (300K). In this plot, darker regions correspond to a more accurate fit. The best fitting condition from this contour plot was determined to be \( \Phi_B = 1.42 \text{ eV} \) and \( \alpha = 0.65 \) by taking the median of \( \Phi_B \) and a values for minimized \( \Delta(\Phi_B, \alpha) \) (specifically, less that \( 4.5 \pm 10^{-9} \), the most accurate 0.04% of the sample).

Using \( \Phi_B = 1.42 \text{ eV} \) and \( \alpha = 0.65 \), a calculated \( I(V) \) for C12 is plotted as a solid curve on a linear scale in Figure 6A and on a logarithmic scale in Figure 6B. A calculated \( I(V) \) for \( \alpha = 1 \) and \( \Phi_B = 0.65 \text{ eV} \) (which gives the best fit at low bias range) is shown as the dashed curve in the same figure, illustrating that, with \( \alpha = 1 \), only limited regions of the \( I(V) \) can be fit (specifically here, for \( V < 0.3 \text{ V} \)). Although the
physical meaning of \( \alpha \) is not unambiguously defined, it provides a way of applying the tunneling model of a rectangular barrier to tunneling either through a non rectangular barrier, a proposed effective mass \( (m^*) \) of the tunneling electrons through the molecules, or a combination of both. Note that the \( I(V) \) data can be fit to arbitrary accuracy over the entire bias range by allowing a slight bias dependence of \( \alpha \) (or \( \Phi_B \)).

Nonlinear least square fittings on C12 \( I(V) \) data at all temperatures allow us to determine \( \{\Phi_B, \alpha\} \) over the entire temperature range and show that \( \Phi_B \) and \( \alpha \) values are temperature-independent in our temperature range (300 to 80K). For the first C12 sample reported, a value of \( \Phi_B = 1.45 \pm 0.01 \text{eV} \) and \( \alpha = 0.64 \pm 0.01 \) was obtained (1\( \sigma \)M, standard error).

**Length Dependence of Tunneling through Alkanethiols**

Equation (2) can be approximated in two limits: low bias and high bias as compared with the barrier height \( \Phi_B \). For the low bias range, (2) can be approximated by

\[
J = \left( \frac{(2m\Phi_B)^{1/2}e^2}{\hbar^2d} \right) \frac{2(2m)^{1/2}}{\hbar} \frac{\alpha(\Phi_B)^{1/2}}{d}. \tag{3a}
\]

To determine the high bias limit, we compare the relative magnitudes of the first and second exponential terms in Eq. (2). At high bias, the first term is dominant and thus the current density can be approximated by
FIGURE 6. Measured C12 $I(V)$ data ($\bullet$) is compared with calculated values (solid curve) using the optimum fitting parameters $\Phi_B = 1.42 \text{ eV}$ and $\alpha = 0.65$. Calculated $I(V)$ from the simple rectangular model ($\alpha = 1$) with $\Phi_B = 0.65 \text{ eV}$ is also shown as a dashed curve. Current is plotted A on linear scale and B on log scale.
According to the Simmons model, in the low bias regime the tunneling current depends on the barrier width \( d \) as
\[
J = \left( \frac{e}{4\pi^2\hbar d^2} \right) \left( \Phi_B - \frac{eV}{2} \right) e^{-\frac{2(2m)^{1/2}}{\hbar}(\Phi_B - \frac{eV}{2})^{1/2}d}.
\]
(3b)

At high bias \( \beta_V \) decreases as bias increases (4b), which results from barrier lowering effect due to the applied bias.

We define the high bias range somewhat arbitrarily by comparing the relative magnitudes of the first and second exponential terms in (2). Using \( \Phi_B = 1.42 \) eV and \( \alpha = 0.65 \) obtained from nonlinear least square fitting of the C12 \( R(V) \) data, the second term becomes less than about 10% of the first term at about 0.5 volt that is chosen as the boundary of low and high bias ranges.

To determine the \( \beta \) values for alkanethiols used in this study, three alkanethiols with different molecular lengths, octanethiol (C8), dodecanethiol (C12), and hexa decanethiol (C16) were investigated to generate length-dependent \( R(V) \) data. Figure 7 is a log plot of tunneling current densities multiplied by molecular length \( (Jd \text{ at low bias and } Jd^2 \text{ at high bias}) \) as a function of the molecular length for these

![Figure 7](image_url)
alkanethiols. (Both bias values were used for the C8 data to compensate for an observed asymmetry and are plotted in Figure 7.) The molecular lengths used in this plot are 13.3, 18.2, and 23.2 Å for C8, C12, and C16, respectively (each molecular length was determined by adding an Au–thiol bonding length to the length of molecule\(^8\)). Note that these lengths implicitly assume “through-bond” tunneling, that is, along the tilted molecular chains between the metal contacts.\(^9\)

As can be seen in Figure 7, the tunneling current shows exponential dependence on molecular length. The \(\beta\) values can be determined from the slope at each bias and are plotted in Figure 8. The error bar of an individual \(\beta\) value in this plot was obtained by considering both the device size uncertainties and the linear fitting errors.

According to (4b), \(\beta_v^2\) depends on bias \(V\) linearly in the high bias range. The inset in Figure 8 is a plot of \(\beta_v^2\) versus \(V\) in this range (0.5 to 1.0 volt) along with linear fitting of the data. From this fit, \(\Phi_B = 1.32 \pm 0.18\) eV and \(\alpha = 0.63 \pm 0.03\) were obtained from the intercept and the slope, respectively, consistent with the more precise values obtained from the nonlinear least square fitting in the previous section. The \(\Phi_B\) (square symbols) and \(\alpha\) (circular symbols) values obtained by the C12 and C16 \(I(V)\) data fittings and \(\beta_v^2 - V\) linear fitting are summarized in Figure 9. The combined values are \(\Phi_B = 1.39 \pm 0.01\) eV (1\(\sigma_M\)) and \(\alpha = 0.65 \pm 0.01\) (1\(\sigma_M\)). Using Eq. (4a), we can derive a zero field decay coefficient \(\beta_0\) value of 0.79 \(\pm 0.01\) Å\(^{-1}\).

For alkanethiols the \(\beta\) values obtained by various experimental techniques are reported elsewhere.\(^7\)–\(^10\),\(^17\)–\(^19\) However, these \(\beta\) values are based upon the approximation\(^11\),\(^29\)

\[
G = G_0 e^{-\beta_d}
\]  

\(5\)
FIGURE 9. Summary of $\Phi_B$ (■) and $\alpha$ (○) values obtained from alkanethiol $I(V)$ fittings and the $\beta_v^2-V$ fitting.

FIGURE 10. $E(k)$ relationship (symbols) generated from the length-dependent measurement data for alkanethiols. Solid and open symbols correspond to electron and hole, respectively. The insets show the corresponding energy band diagrams. The solid curve is the Franz two-band expression for $m^* = 0.38\, m$.
and are generally be different from those determined from a more precise relationship \( J \propto d^{-1} \exp(-\beta_0 d) \) or \( J \propto d^{-2} \exp(-\beta_1 d) \), deduced from the Simmons model. However, to compare with these previously reported \( \beta \) values, we also performed length-dependent analysis on our experimental data according to Eq. (5). This gave a \( \beta \) value from 0.83 to 0.72 Å\(^{-1}\) in the bias range from 0.1 to 1.0 volt, which is comparable to results reported previously; for example, Holmlin \textit{et al.} reported a \( \beta \) value of 0.87 Å\(^{-1}\) by mercury drop experiments,\(^{10}\) and Wold \textit{et al.} reported a \( \beta \) value of 0.94 Å\(^{-1}\) and Cui \textit{et al.} reported a \( \beta \) value of 0.64 Å\(^{-1}\) for various alkanethiols by using a conducting atomic force microscopy technique.\(^{8,9}\) These reported \( \beta \) were treated as bias-independent quantities, contrary to the results reported here and that observed in a slightly different alkane system (ligand-encapsulated nanoparticle/alkane-dithiol molecules).\(^{30}\)

### Franz Model

We analyzed our experimental data using a Franz two-band model.\(^{20,22–25}\) Since there is no reliable experimental data on the Fermi level alignment in these metal–SAM–metal systems, \( \Phi_B \) and \( m^* \) are treated as adjustable parameters. We performed a least squares fit on our data with the Franz non-parabolic \( E(k) \) relationship (Eq. (1)) using an alkanethiol HOMO-LUMO gap of 8 eV.\(^{31–34}\) FIGURE 10 shows the resultant \( E(k) \) relationship\(^{22–25}\) and the corresponding energy band diagrams. The zero of energy was chosen as the LUMO energy. The best fitting parameters obtained by minimizing \( \chi^2 \) were \( \Phi_B = 1.55 \pm 0.59 \text{ eV} \) and \( m^* = 0.38 \pm 0.20 \text{ m} \), where the error ranges of \( \Phi_B \) and \( m^* \) are dominated by the error fluctuations of \( \beta \) (\( -k^2 = (\beta/2)^2 \)). Both electron tunneling near the LUMO and hole tunneling near the HOMO can be described by these parameters. \( \Phi_B = 1.55 \text{ eV} \) indicates that the Fermi level is aligned close to one energy level in either case, therefore, the Simmons model is a valid approximation. The previous best fits obtained from Simmons model of \( \Phi_B = 1.39 \text{ eV} \) and \( \alpha = 0.65 \) (corresponding to \( m^* = 0.42 \text{ m} \) for the rectangular barrier case) are in reasonable agreement.

### CONCLUSIONS

From temperature-dependent current–voltage measurements, direct tunneling is unambiguously shown to be the dominant transport mechanism for the first time in alkanemonothiol SAMs (for \( V < \Phi_B/e \)), with a barrier height \( \Phi_B = 1.39 \pm 0.01 \text{ eV} \) and a non-ideal barrier factor \( \alpha = 0.65 \pm 0.01 \) (combined values from \( I(V) \) fittings and the \( \beta V^2 \) fitting). Exponential length dependence is observed with a bias-dependent decay coefficient (contrary to previous reports\(^{7–10,17–19}\)) with a zero field decay coefficient \( \beta_0 \) of 0.79 ± 0.01 Å\(^{-1}\).

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REFERENCES

31. Although the HOMO-LUMO gap of alkyl chain type molecules has been reported (see References 35–37), there is no experimental data on the HOMO-LUMO gap for Au/alkanethiol SAM/Au system. 8 eV is commonly used as HOMO-LUMO gap of alkanethiol.