4.16 Electronic Properties of Alkanethiol Molecular Junctions: Conduction Mechanisms, Metal–Molecule Contacts, and Inelastic Transport

G Wang, T-W Kim, and T Lee, Gwangju Institute of Science and Technology, Gwangju, Korea
W Wang, University of Wyoming, Laramie, WY, USA
M A Reed, Yale University, New Haven, CT, USA

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4.16.1 Introduction

Molecular electronics utilizing functional molecules as the ultimate nanoscale electronic components has recently generated considerable interest in both the basic transport physics of molecular systems and potential technological applications in a variety of functional electronic device components for ultra-high density future electronics [1–4].

However, despite the numerous potential advantages of molecular electronics as compared to traditional silicon-based electronics, there are many issues and challenges that need to be overcome to apply molecules to actual electronic circuits. For example, some reports of molecular mechanisms in electronic devices [3a,5,6a,b] have shown to be premature due to filamentary conduction [3c,7], highlighting the fabrication sensitivity of molecular structures and the need to institute reliable controls and methods to validate true molecular transport [8].

A related problem is the characterization of molecules in the active device structures, including their configuration, bonding, and indeed even their very presence. In addition, metal–molecule contact is important not only for understanding the transport properties of molecular devices but also for realizing reproducible molecular electronic devices due to its role in controlling metal–molecule interfaces [9,10].

Here we present results on well-understood molecular assemblies, which exhibit an understood classical transport behavior, and which can be used as a control for eliminating (or understanding) fabrication variables. Utilizing tunneling spectroscopic methods, we present the unambiguous evidence of the presence of molecules in the junction. Using the statistical analysis on the current–voltage
characteristics of molecular junctions, we investigate the effect of metal–molecule contacts and present the contact resistances of the junctions.

A molecular system whose structure and configuration are sufficiently well characterized such that it can serve as a standard is the extensively studied alkanethiol self-assembled monolayer (SAM) [11]. There are two kinds of alkanethiols: alkanemethiols (CH$_n$(CH$_2$)$_m$–SH), where there is one thiol at an end of molecule; and alkanedithiols (HS(CH$_2$)$_m$SH), where there are thiols at both end of molecule. This molecule system is useful as a control since properly prepared SAMs form single van der Waals crystals [11,12], and presents a simple classical metal–insulator–metal (M-I-M) tunnel junction when fabricated between metallic contacts due to the large gap of approximately 8 eV [13–15] between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

Various surface analytical tools have been utilized to investigate the surface and bulk properties of the alkanethiol SAMs, such as X-ray photoelectron spectroscopy [16], Fourier transform infrared spectroscopy (FTIR) [17], Raman spectroscopy [18], scanning tunneling microscopy (STM) [12], etc. For example, studies have shown that the bonding of the thiolate group to the gold surface is strong with a bonding energy of ≈1.7 eV [11]. STM topography examinations revealed that alkanethiols adopt the commensurate crystalline lattice characterized by a c(4×2) superlattice of a ($\sqrt{3}$×$\sqrt{3}$)R30° [12,19]. FTIR investigation showed that the orientation of the alkanethiol SAMs on Au(111) surfaces are tilted $\approx$30° from the surface normal [20].

Electronic transport through alkanethiol SAMs have also been characterized by STM [21,22], conducting atomic force microscopy [23–26], mercury-drop junctions [29–30], cross-wire junctions [31], and electrochemical methods [32–34]. These investigations are exclusively at ambient temperature – clearly useful – but insufficient for an unambiguous claim that the transport mechanism is tunneling (of course expected, assuming that the Fermi levels of the contacts lie within the large HOMO–LUMO gap). However, in the absence of temperature-dependent current–voltage ($I(V,T)$) characteristics, other conduction mechanisms (e.g., thermionic, hopping, or filamentary conduction) cannot be excluded complicating the analysis, and thus such a claim is premature.

Utilizing a solid-state device structure that incorporates alkanethiol SAMs, we demonstrate devices that allow $I(V,T)$ and structure-dependent measurements [35,36] with results that can be compared with accepted theoretical models of M-I-M tunneling. The use of this fabrication approach is not special in any way (other than that we have so far found it to be successful) – indeed we stress that any successful device fabrication method should yield the results described below if one is characterizing the intrinsic molecular transport properties.

The electronic transport is further investigated with the technique of inelastic electron tunneling spectroscopy (IETS) [36]. IETS was developed in the 1960s as a powerful spectroscopic tool to study the vibrational spectrum of organic molecules confined inside metal–oxide–metal junctions [37–41]. In our study, IETS is utilized for the purpose of molecule identification, chemical bonding, and conduction mechanism investigations of the ‘control’ SAMs. The exclusive presence of well-known vibrational modes of the alkanes used is direct evidence of the molecules in the device structure, something that has to date only been inferred (with good reason, but nonetheless not unambiguously). The vibrational modes, exclusively identified as alkanes (as well as contact modes) are difficult to interpret in any other way other than as components in the active region of the device. The inelastic tunneling spectra also demonstrate that electronic tunneling occurs through the molecules, confirming the conduction mechanism obtained by $I(V,T)$ characterizations. The specific spectral lines also yield intrinsic linewidths that may give insight into molecular conformation, and may prove to be a powerful tool in future molecular device characterization.

We also present the influence of metal–molecule contacts in molecular junctions using a proposed multibarrier tunneling (MBT) model where the metal–molecule–metal junction can be divided into three parts: the molecular-chain body with metal–molecule contacts on either side of molecule [9,10]. The MBT model will help introduce an insight for studying charge transport mechanisms, focused on the metal–molecule contacts in molecular electronic devices or other nanoscale devices.

4.16.2 Experiment

Electronic transport measurements on alkanethiol SAMs were performed using two different device structures. The first device structure is similar to the nanoscale device structure reported previously, the so-called ‘nanopore’ devices [3a,35,36,42–44].
Another device structure is vertical metal–molecule–metal device structure with microscale via-holes [9,10,45].

In the nanopore devices, as illustrated in Figure 1(a) (not drawn to scale in the relative thickness), a number of molecules (several thousands) are sandwiched between two metallic contacts. This technique provides a stable device structure and makes cryogenic measurements possible. The device fabrication starts with a high-resistivity silicon wafer with low-stress Si₃N₄ film deposited on both sides by low-pressure chemical vapor deposition (LPCVD). By standard photolithography processing, a suspended Si₃N₄ membrane (size of 40 μm x 40 μm and thickness of ~70 nm) is fabricated on 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. As the next step, 150 nm 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, a ~5 mM alkanethiol solution is prepared by adding ~10 μl alkanethiols into 10 ml ethanol [46]. The deposition is done in solution for 24 h inside a nitrogen-filled glove box with an oxygen level of less than 100 ppm. Alkanemonothiols and alkanedithiols of different molecular lengths: octanemonothiol (CH₃(CH₂)₇SH, C8), dodecanemonothiol (CH₃(CH₂)₁₁SH, C12), hexadecanemonothiol (CH₃(CH₂)₁₅SH, C16), octanedithiol (HS(CH₂)₈SH, DC8), nonanedithiol (HS(CH₂)₉SH, DC9), and decanedithiol (HS(CH₂)₁₀SH, DC10) were used to form the active molecular components in molecular devices [46]. As representative examples, the chemical structures of octanethiol and octanedithiol are shown in Figure 1(c).

In order to statistically determine the pore size in nanopore devices, test patterns (arrays of pores) were created under similar fabrication conditions. This indirect measurement of device size is done 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, C16, and C8-dithiol samples are determined as 50 ± 8, 45 ± 2, 45 ± 2, and 51 ± 5 nm in diameters, respectively. A more ideal (less parasitic) C8 sample supercedes that of previous reports [35], and derived parameters from the two data sets agree to within a standard error. We will use these device areas as the effective contact areas. Although one could postulate that the actual area of metal that contacts the molecules may be different, there is little reason to propose that it would be different as a function of length over the range of alkanethiols used, and at most would be a constant systematic error.

The other device structure is shown in Figure 1(b), that is, a vertical metal–molecule–metal junction device structure having a microscale via-hole in which the molecules are self-assembled. The sample is then transferred in ambient conditions to an evaporator that has a cooling stage to deposit the opposing Au contact in case of both device structures. During the thermal evaporation (under the pressure of 10⁻⁷–10⁻⁸ Torr), liquid
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nitrogen is kept flowing through the cooling stage in order to avoid thermal damage to the molecular layer [35,47]. 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. The deposition rate is typically 0.1–0.5 Å s⁻¹. A total of 50–200 nm gold is deposited to form the contact.

The device is subsequently packaged and loaded into a low-temperature cryostat. The sample temperature is varied from 300 to 4.2 K by flowing cryogen vapor onto the sample (and thermometer) using a closed-loop temperature controller. Two-terminal direct current (DC) I(V) measurements are performed using a semiconductor parameter analyzer. Inelastic electron tunneling spectra are obtained via a standard lock-in second harmonic measurement technique [37,38]. A synthesized function generator is used to provide both the modulation and the lock-in reference signal. The second harmonic signal (proportional to d²I/dV²) is directly measured using a lock-in amplifier, which is checked to be consistent with a numerical derivative of the first-harmonic signal (proportional to dI/dV). Various modulation amplitudes and frequencies are utilized to obtain the spectra. The alternating current (AC) modulation is added to a DC bias using operational amplifier-based custom circuitry [48].

4.16.3 Theoretical Basis

4.16.3.1 Possible Conduction Mechanisms

In Table 1, possible conduction mechanisms are listed with their characteristic current, temperature, and voltage dependencies [49] (we do not discuss filamentary tunneling mechanisms, which are easier to categorize [50a–c]). Based on whether thermal activation is involved, the conduction mechanisms fall into two distinct categories: (i) thermionic or hopping conduction, which has temperature-dependent I(V) behavior and (ii) 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-thioacetyl biphenyl SAMs [42] and 1,4-phenylene disiocyanode SAMs [43b]. On the other hand, the conduction mechanism is expected to be tunneling when the Fermi levels of contacts lie within the large HOMO–LUMO gap for short-length molecule, as for the case of alkanethiol molecular system [13–15]. Previous work on Langmuir–Blodgett alkane monolayers [51a,b] exhibited a significant impurity-dominated transport component, complicating the analysis. The I(V) measurements on self-assembled alkanethiol monolayers have also been reported [21–31,52]; however, all of these measurements were performed at fixed temperature (300 K), which is insufficient to prove tunneling as the dominant mechanism.

4.16.3.2 Tunneling Models

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 [53–56]. This model provides a nonparabolic energy–momentum E(k) dispersion relationship by considering the contributions of both the HOMO and LUMO energy levels [53]:

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

Table 1 Possible conduction mechanisms

<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</td>
<td>( J \sim V \exp \left( \frac{-2d}{\hbar} \sqrt{2m^*} V \right) )</td>
<td>None</td>
<td>( J \sim V )</td>
</tr>
<tr>
<td>Fowler–Nordheim tunneling</td>
<td>( J \sim V^2 \exp \left( \frac{-4d \sqrt{2m^* g^2 \hbar^2}}{3qV} \right) )</td>
<td>None</td>
<td>( \ln \left( \frac{J}{V^2} \right) \sim \frac{1}{V} )</td>
</tr>
<tr>
<td>Thermionic emission</td>
<td>( J \sim T^2 \exp \left( \frac{\Phi - q \sqrt{V/4 \pi e d}}{kT} \right) )</td>
<td>( \ln \left( \frac{J}{V^2} \right) \sim \frac{1}{T} )</td>
<td>( \ln (J) \sim V^{1/2} )</td>
</tr>
<tr>
<td>Hopping conduction</td>
<td>( J \sim V \exp \left( \frac{\Phi}{kT} \right) )</td>
<td>( \ln \left( \frac{J}{V} \right) \sim \frac{1}{T} )</td>
<td>( J \sim V )</td>
</tr>
</tbody>
</table>

* This characteristic of direct tunneling is valid for the low bias regime (see equation 3a).

where $k$ is the imaginary part of wave vector of electrons, $m^*$ the electron effective mass, $b = (2\pi\hbar)$ the Planck’s constant, $E$ the electron energy, and $E_g$ the HOMO–LUMO energy gap. From this nonparabolic $E(k)$ 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.

When the Fermi level of the metal is aligned close enough to one energy level (either HOMO or LUMO), the effect of the other distant energy level on the tunneling transport is negligible, and the widely used Simmons model [57] is an excellent approximation. Simmons model expressed the tunneling current density through a barrier in the tunneling regime of $V < \Phi_B/e$ as [27,57]

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

$$- \left( \Phi_B + \frac{eV}{2} \right) \exp \left[ - \frac{2(2m)^{1/2}}{\hbar} \alpha \left( \Phi_B + \frac{eV}{2} \right)^{1/2} \right]$$

(2)

where $m$ is the electron mass, $d$ the barrier width, $\Phi_B$ the barrier height, and $V$ the applied bias. For molecular systems, the Simmons model has been modified with a parameter $\alpha$ [27,35]. Here $\alpha$ is a unitless adjustable parameter that is introduced to provide either a way of applying the tunneling model of a rectangular barrier to tunneling through a nonrectangular barrier [27], or an adjustment to account for the effective mass ($m^*$) of the tunneling electrons through a rectangular barrier [27,35,56,58], or both. Here $\alpha = 1$ corresponds to the case for a rectangular barrier and bare electron mass. By fitting individual $I(V)$ data using equation 2, $\Phi_B$ and $\alpha$ values can be obtained.

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, equation 2 can be approximated as [57]

$$J \approx \left( \frac{2(2m)^{1/2}}{\hbar^2d} \right) \frac{e^\alpha}{b} V \exp \left[ - \frac{2(2m)^{1/2}}{\hbar} \alpha \left( \Phi_B \right)^{1/2} \right]$$

(3a)

To determine the high bias limit, we compare the relative magnitudes of the first and second exponential terms in equation 2. At high bias, the first term is dominant and thus the current density can be approximated as

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

(3b)

The tunneling currents in both bias regimes are exponentially dependent on the barrier width $d$. In the low-bias regime the tunneling current density is $J \propto (1/d)^0 \exp(-\beta_d d)$, where $\beta_d$ is bias-independent decay coefficient:

$$\beta_d = \frac{2(2m)^{1/2}}{\hbar} \alpha (\Phi_B)^{1/2}$$

(4a)

while in the high-bias regime, $J \propto (1/d)^2 \exp(-\beta_V d)$, where $\beta_V$ is bias-dependent decay coefficient:

$$\beta_V = \frac{2(2m)^{1/2}}{\hbar} \alpha (\Phi_B)^{1/2} = \beta_d \left(1 - \frac{eV}{2\Phi_B}\right)^{1/2}$$

(4b)

At high bias, $\beta_V$ decreases as bias increases, which results from barrier-lowering effect due to the applied bias.

4.16.4 Results

4.16.4.1 Tunneling Current–Voltage Characteristics

4.16.4.1.1 Temperature–variable current–voltage ($I(V,T)$) measurement

In order to determine the conduction mechanism of self-assembled alkanethiol molecular systems $I(V)$ measurements in a sufficiently wide temperature range (300 to 80 K) and resolution (10 K) were performed. Figure 2(a) shows a representative $I(V,T)$ characteristic of dodecanemonothiol (C12) measured with the device structure as shown in Figure 1(a). Positive bias corresponds to electrons injected from the physisorbed Au contact (bottom contact in Figure 1(a)) into the molecules. By using the contact area of $45 \pm 2$ nm in diameter determined from SEM study, a current density of $1500 \pm 200$ A cm$^{-2}$ at 1.0 V is determined. No significant temperature dependence of the characteristics (from $V = 0–1.0$ V) is observed over the range from 300 to 80 K. An Arrhenius plot ($\ln(I)$ versus $1/T$) of this is shown in Figure 2(b), 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 contingent on demonstrating a correct molecular length dependence.
The tunneling through alkanethiol SAMs has been assumed as ‘through-bond’ tunneling, that is, along the tilted molecular chains between the metal contacts [24,25,34,59a,b]. Based on the applied bias as compared with the barrier height (Φ_B), the tunneling through an SAM layer can be categorized into either direct (V < Φ_B/ε) or Fowler–Nordheim (V > Φ_B/ε) tunneling. These two tunneling mechanisms can be distinguished due to their distinct voltage dependencies (see Table 1). Analysis of ln(I/V^2) versus 1/V [in Figure 2(c)] shows no significant voltage dependence, indicating no obvious Fowler–Nordheim transport behavior in this bias range (0 to 1.0 V) and thus determining that the barrier height is larger than...

**Figure 2**  (a) Temperature-dependent I(V) characteristics of dodecanethiol (C12). I(V) data at temperatures from 300 to 80 K with 20 K steps are plotted on a log scale. (b) Arrhenius plot generated from the I(V) data in (a), at voltages from 0.1 to 1.0 V with 0.1 V steps. (c) Plot of ln(I/V^2) versus 1/V at selected temperatures.
the applied bias, that is, $\Phi_B > 1.0 \text{ eV}$. This study is restricted to applied biases $\leq 1.0 \text{ V}$ and the transition from direct to Fowler–Nordheim tunneling requires higher bias.

The importance of variable temperature measurements to validate tunneling is demonstrated in Figure 3. Here the $I(V)$ of an octanemonothiol (C8) device is shown (Figure 3(a)), whose $I(V)$ shape looks very similar to Figure 2 (i.e., direct tunneling), and indeed can be fit to a Simmons model. However, further $I(V, T)$ measurements display an obvious temperature dependence (Figure 3(b)), which can be fit well to a hopping conduction model (Table 1) with a well-defined activation energy of 190 meV (Figure 3(c)). This and other similar impurity-mediated transport phenomena (such as Coulomb blockade) are observed in a subset of devices and is indicative of the unintentional incorporation of a trap or defect level in those devices. This study instead focuses on devices that do not show any defect-mediated transport and probes the intrinsic behavior of the molecular layer.

Having established tunneling as the conduction mechanism in a device, we will now obtain the barrier height by comparing experimental $I(V)$ data with theoretical calculations from tunneling models.

### 4.16.4.1.2 Tunneling characteristics through alkanethiols

From the modified Simmons model (equation 2) by adjusting two parameters $\Phi_B$ and $\alpha$, a nonlinear least-squares fitting can be performed to fit the measured C12 $I(V)$ data (calculation assuming $\alpha = 1$ has been previously shown not to fit $I(V)$ data well for some alkanethiol measurements at fixed temperature (300 K)) [27]. By using a device size of 45 nm in diameter, the best-fitting parameters (minimizing $\chi^2$) for the room temperature C12 $I(V)$ data were found to be $\Phi_B = 1.42 \pm 0.04 \text{ eV}$ and $\alpha = 0.65 \pm 0.01$, where the error ranges of $\Phi_B$ and $\alpha$ are dominated by potential device size fluctuations of 2 nm. Likewise, data sets were obtained and fittings were done for octanethiol (C8) and hexadecanethiol (C16), which yielded values ($\Phi_B = 1.83 \pm 0.10 \text{ eV}$ and $\alpha = 0.61 \pm 0.01$) and ($\Phi_B = 1.40 \pm 0.03 \text{ eV}$, $\alpha = 0.68 \pm 0.01$), respectively.

Using $\Phi_B = 1.42 \text{ eV}$ and $\alpha = 0.65$, a calculated $I(V)$ for C12 is plotted as a solid curve in a linear scale (Figure 4(a)) and in a semi-log scale (Figure 4(b)). 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 $V < 0.3 \text{ V}$). For the case of a rectangular barrier, the $\alpha$ parameter fit presented above corresponds to an effective mass $m^* (\approx \alpha^2 m)$ of 0.42 $m$.

In order to investigate the dependence of the Simmons model fitting on $\Phi_B$ and $\alpha$, a fitting minimization analysis was undertaken on the individual $\Phi_B$
and $\alpha$ values as well as their product form of $\alpha \Phi_B^{1/2}$ in equation 4a. The quantity $\Delta(\Phi_B, \alpha) = \left( \sum |I_{exp, V} - I_{cal, V}|^2 \right)^{1/2}$ was calculated and plotted where $I_{exp, V}$ is the experimental current–voltage values and $I_{cal, V}$ is calculated using equation 2. Seven thousand five hundred different $\{\Phi_B, \alpha\}$ pairs were used in the fittings with $\Phi_B$ ranging from 1.0 to 2.5 eV (0.01 eV increment) and $\alpha$ from 0.5 to 1.0 (0.01 increment). Figure 5(a) is a representative contour plot of $\Delta(\Phi_B, \alpha)$ versus $\Phi_B$ and $\alpha$ values generated for the C12 $I(V)$ data, where darker regions correspond to smaller $\Delta(\Phi_B, \alpha)$ and various shades represent half order of magnitude $\Delta(\Phi_B, \alpha)$ steps. The darker regions represent better fits of equation 2 to the measured $I(V)$ data. In the inset in Figure 5(a) one can see there is a range of possible $\Phi_B$ and $\alpha$ values yielding minimum fitting parameters. Although the tunneling parameters determined from the previous Simmons tunneling fitting ($\Phi_B = 1.42$ eV and $\alpha = 0.65$) lie within this minimum region in this figure, there is a distribution of other possible values.

A plot of $\Delta(\Phi_B, \alpha)$ versus $\alpha \Phi_B^{1/2}$ for the same device reveals a more pronounced dependence, and is shown in Figure 5(b). This plot indicates the fitting to the Simmons model sharply depends on the product of $\alpha \Phi_B^{1/2}$. For this plot the $\Delta(\Phi_B, \alpha)$ is minimized at $\alpha \Phi_B^{1/2}$ of 0.77 (eV)$^{1/2}$ corresponding to a $\beta_0$ value of 0.79 Å$^{-1}$ from equation 4a. The C8 and C16 devices showed similar results, indicating the Simmons tunneling model has a strong $\alpha \Phi_B^{1/2}$
dependence. For the C8 device, although \( \Phi_B \) obtained from the fitting is a little larger, combined \( \alpha \) and \( \Phi_B \) gives a similar \( \beta_0 \) value within the error range as the C12 and C16 devices (Table 2).

### 4.16.4.1.3 Length-dependent tunneling through alkanethiols

Three alkanemonothiols of different molecular length (C8, C12, and C16) were investigated to study the length-dependent tunneling behavior. Figure 6 is a semi-log plot of tunneling current densities multiplied by molecular length (\( Jd \) at low bias and \( Jd^2 \) at high bias) as a function of the molecular length for these alkanethiols. 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 [24]. Note that these lengths assume through-bond tunneling [24,25,34,59a,b]. The high- and low-bias regimes are defined somewhat arbitrarily by comparing the relative magnitudes of the first and second exponential terms in equation 2. Using \( \Phi_B = 1.42 \) eV and \( \alpha = 0.65 \) obtained from nonlinear least-squares fitting of the C12 \( J(V) \) data, the second term becomes less than \( \sim 10 \% \) of the first term at \( \sim 0.5 \) V that is chosen as the boundary of low- and high-bias ranges.

As seen in Figure 6, the tunneling current shows exponential dependence on molecular length, which is consistent with the Simmons tunneling model (equation 3). The \( \beta_0 \) values can be determined from the slope at each bias and are plotted in Figure 7. The error bar of an individual \( \beta_0 \) value in this plot was obtained by considering both the device size uncertainties and the linear-fitting errors.

The \( \beta_0 \) values determined are almost independent of bias in the low-bias range (\( V < \sim 0.5 \) V), and an average \( \beta_0 = 0.77 \pm 0.06 \) Å\(^{-1}\) in this region (from 0 to 0.5 V) can be calculated from Figure 7. Table 3 is a summary of previously reported alkanethiol transport parameters obtained by different techniques. The current densities (\( J \)) listed in Table 3 are for C12 monothiol or dithiol devices at 1 V, which are extrapolated from published results of other length alkane molecules. The large variation of \( J \) of these reports can be attributed to the uncertainties in device contact geometry and junction area, as well as complicating inelastic or defect contributions. The \( \beta_0 \) value (\( 0.77 \pm 0.06 \) Å\(^{-1}\) \( \sim 0.96 \pm 0.08 \) per methylene) for alkanethiols reported here is comparable

### Table 2

Summary of alkanethiol tunneling parameters in this study

<table>
<thead>
<tr>
<th>Molecules</th>
<th>( J ) at 1 V (A cm(^{-2}))</th>
<th>( \Phi_B ) (eV)</th>
<th>( \alpha )</th>
<th>( m^2 ) (m)</th>
<th>( \beta_0 ) (Å(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8</td>
<td>31 000 ± 10 000</td>
<td>1.83 ± 0.10</td>
<td>0.61 ± 0.01</td>
<td>0.37</td>
<td>0.85 ± 0.04</td>
</tr>
<tr>
<td>C12</td>
<td>1500 ± 200</td>
<td>1.42 ± 0.04</td>
<td>0.65 ± 0.01</td>
<td>0.42</td>
<td>0.79 ± 0.02</td>
</tr>
<tr>
<td>C16</td>
<td>23 ± 2</td>
<td>1.40 ± 0.03</td>
<td>0.68 ± 0.01</td>
<td>0.46</td>
<td>0.82 ± 0.02</td>
</tr>
<tr>
<td>C8-dithiol</td>
<td>93 000 ± 18 000</td>
<td>1.20 ± 0.03</td>
<td>0.59 ± 0.01</td>
<td>0.35</td>
<td>0.66 ± 0.02</td>
</tr>
</tbody>
</table>

\( \beta_0 \) values were calculated using equation 4a.

### Figure 6

Log plot of tunneling current densities multiplied by molecular length \( d \) at low bias and by \( d^2 \) at high bias (symbols) versus molecular lengths. The lines through the data points are linear fittings.
to previously reported values as summarized in Table 3. This \( \beta \) value agrees with the value of 0.79 Å\(^{-1}\) \( (\beta_0) \) calculated via equation 4a from fitting individual \( I(V) \) characteristic of the C12 device. The calculated \( \beta_0 \) of C8 and C16 devices also have similar values, as summarized in Table 2. According to equation 4b, \( \beta_0 \) depends on bias \( V \) linearly in the high-bias range. The inset in Figure 7 is a plot of \( \beta_0 \) versus bias in this range (0.5 to 1.0 V) along with linear fitting of the data. From this fitting, \( \Phi_b = 1.35 \pm 0.20 \) eV and \( \alpha = 0.66 \pm 0.04 \) were obtained from the intercept and the slope, respectively, consistent with the values (\( \Phi_b = 1.42 \) eV and \( \alpha = 0.65 \)) obtained from the nonlinear least-squares fitting in the previous section.

The \( \beta \) values for alkanethiols obtained by various experimental techniques have previously been reported and are summarized in Table 3 [21-41,52]. In order to compare with these reported \( \beta \) values, we also performed a length-dependent analysis on our experimental data according to the generally used equation [22–30,35]:

\[
G = G_0 \exp(-\beta d)
\]

This gives a \( \beta \) value from 0.84 to 0.73 Å\(^{-1}\) in the bias range from 0.1 to 1.0 V, which is comparable to results reported previously. For example, Holmlin et al. [27] reported a \( \beta \) value of 0.87 Å\(^{-1}\) by mercury drop experiments and Wold et al. [24] have reported \( \beta \) of 0.94 Å\(^{-1}\) and Cui et al. [25] reported \( \beta \) of 0.64 Å\(^{-1}\) for various alkanethiols by using a conducting atomic force microscope technique. These reported \( \beta \) were treated as bias-independent quantities, contrary to the results reported here and that observed in Table 3

**Table 3 Summary of alkanethiol tunneling characteristic parameters**

<table>
<thead>
<tr>
<th>Junction</th>
<th>( \beta (\text{Å}^{-1}) )</th>
<th>( J(\text{A cm}^{-2}) ) at 1 V</th>
<th>( \Phi_b ) (eV)</th>
<th>Technique</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bilayer) monothiol</td>
<td>0.87 ± 0.1</td>
<td>25–200(^a)</td>
<td>2.1(^b)</td>
<td>Hg-junction</td>
<td>[25]</td>
</tr>
<tr>
<td>(Bilayer) monothiol</td>
<td>0.71 ± 0.08</td>
<td>0.7–3.5(^a)</td>
<td>1.4(^b)</td>
<td>Hg-junction</td>
<td>[27]</td>
</tr>
<tr>
<td>Monothiol</td>
<td>0.79 ± 0.01</td>
<td>1500 ± 200(^a)</td>
<td>1.4(^b)</td>
<td>Solid M-I-M</td>
<td>[33]</td>
</tr>
<tr>
<td>Monothiol</td>
<td>1.2</td>
<td></td>
<td></td>
<td>STM</td>
<td>[19]</td>
</tr>
<tr>
<td>Dithiol</td>
<td>0.8 ± 0.08</td>
<td>3.7–5 × 10(^5)(^c)</td>
<td>5 ± 2(^d)</td>
<td>STM</td>
<td>[20]</td>
</tr>
<tr>
<td>Monothiol</td>
<td>0.73–0.95</td>
<td>1100–1900(^d)</td>
<td>2.2(^e)</td>
<td>CAFM</td>
<td>[21]</td>
</tr>
<tr>
<td>Monothiol</td>
<td>0.64–0.8</td>
<td>10–50(^d)</td>
<td>2.3(^e)</td>
<td>CAFM</td>
<td>[23]</td>
</tr>
<tr>
<td>Dithiol</td>
<td>0.46 ± 0.02</td>
<td>3–6 × 10(^5)(^c)</td>
<td>1.3–1.5(^e)</td>
<td>CAFM</td>
<td>[24]</td>
</tr>
<tr>
<td>Monothiol</td>
<td>1.37 ± 0.03</td>
<td></td>
<td>1.8(^f)</td>
<td>Tuning fork AFM</td>
<td>[49]</td>
</tr>
<tr>
<td>Monothiol</td>
<td>0.97 ± 0.04</td>
<td></td>
<td></td>
<td>Electrochemical</td>
<td>[30]</td>
</tr>
<tr>
<td>Monothiol</td>
<td>0.85</td>
<td></td>
<td></td>
<td>Electrochemical</td>
<td>[31]</td>
</tr>
<tr>
<td>Monothiol</td>
<td>0.91 ± 0.08</td>
<td></td>
<td></td>
<td>Electrochemical</td>
<td>[32]</td>
</tr>
<tr>
<td>Monothiol</td>
<td>0.76</td>
<td>2 × 10(^4) (at 0.1 V)(^c)</td>
<td>1.3–3.4(^g)</td>
<td>Theory</td>
<td>[58]</td>
</tr>
<tr>
<td>Monothiol</td>
<td>0.76</td>
<td></td>
<td></td>
<td>Theory</td>
<td>[59]</td>
</tr>
<tr>
<td>Monothiol</td>
<td>0.79</td>
<td></td>
<td></td>
<td>Theory</td>
<td>[56]</td>
</tr>
</tbody>
</table>

\(^a\) The junction areas were estimated by optical microscope.

\(^b\) The junction areas were estimated by SEM.

\(^c\) The junction areas were estimated by assuming single molecule.

\(^d\) The junction areas were estimated by assuming Hertzian contact theory.

\(^e\) Barrier height \( \Phi_b \) values were obtained from Simmons equation.

\(^f\) Barrier height \( \Phi_b \) values were obtained from bias dependence of \( \beta \).

\(^g\) Barrier height \( \Phi_b \) values were obtained from a theoretical calculation.

Notes: Some decay coefficients \( \beta \) were converted into the unit of Å\(^{-1}\) from the unit of per methylene. Current densities \( J \) for C12 monothiol or dithiol at 1 V are extrapolated from published results for other length molecules by using conductance \( \propto \exp(-|d|) \) relationship.
a slightly different alkane system (ligand-encapsulated nanoparticle/alkane-dithiol molecules) [26]. We also caution against the use of parameters that have not been checked with a temperature-dependent analysis, since small nontunneling components can dramatically affect derived values of $\beta$.

4.16.4.1.4 Franz model

We have analyzed our experimental data using a Franz two-band model [53–56]. Since there are 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 nonparabolic $E(k)$ relationship (equation 1) using an alkanethiol HOMO–LUMO gap of 8 eV [14,15]. Figure 8 shows the resultant $E(k)$ relationship and the corresponding energy band diagrams. The zero of energy in this plot was chosen as the LUMO energy. The best-fitting parameters obtained by minimizing $\chi^2$ were $\Phi_B = 1.49 \pm 0.51$ eV and $m^* = 0.43 \pm 0.15 m$, 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. The value of $\Phi_B = 1.49$ 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 $\Phi_B$ and $m^*$ values obtained here are in reasonable agreement with the previous results obtained from the Simmons model.

Figure 8 $E(k)$ relationship (symbols) generated from the length-dependent measurement data for alkanethiols. Solid and open symbols correspond to electron and hole tunneling, respectively. The insets show the corresponding energy-band diagrams. The solid curve is the Franz two-band expression for $m^* = 0.43m$.

4.16.4.2 Metal–Molecule Contacts for Alkanethiols Junction

4.16.4.2.1 Statistical analysis of contact properties through alkanethiols

The yield of molecular electronic devices of even these robust alkanethiol molecular systems, however, is very low, mainly because of electrical shorts caused by the penetration of the top electrode through the molecular layer and making contact with the bottom electrode [8,60a,b]. A recent study, with the objective of preventing electrical shorts by using a layer of a highly conducting polymer resulted in a significant improvement in the yield of molecular electronic devices [61]. However, studies on the device yield of simple M-M-M junctions have not been extensive. In particular, systematic studies with the goal of defining ‘working’ molecular devices, device yield, and even selecting ‘representative’ devices have not been reported. Furthermore, determining the average transport parameters from a statistically meaningful number of molecular working devices is important, because the statistically averaged transport parameters can provide more accurate and meaningful characteristics of molecular systems. Statistical measurement has been performed, for example, to extract the electrical conductance of single molecules using mechanically controllable break junctions [62]. As mentioned above, the yields of the molecular electronic devices are very low, mainly due to electric short problems [8,60a,b,61]. However, thorough and systematic studies on what ‘working’ devices are and on the yields of the molecular electronic devices have not been reported. Typically, working devices might be defined as a device showing nonlinear $I(V)$ behavior and not being electrical open and short. Electrical open and short devices can be readily recognized. Open devices are noisy with a current level typically in the pA range and short devices show ohmic $I(V)$ characteristics with a current level larger than a few mA [63]. However, criteria are needed for determining working devices more precisely. Although the choice of such a criterion is not universal, current density can be a good criterion for determining working devices, because $I(V)$ data are major characteristics that are measured initially and the current directly reflects the conductivity of different lengths (or contacts) of alkanethiols or different molecular systems.

We fabricated and characterized a significantly large number of microscale molecular devices shown as Figure 1(b) (27 840 devices in total) to statistically analyze the molecular electronic
The working devices displaying molecular proper-

\[ \text{properties of a sufficient number of 'working' molecular electronic devices (427 devices) [9,45].} \]

The working devices displaying molecular properties were determined based on the statistical distribution of the current densities of the fabricated devices. Note that we selected the 99.7% of the devices by using the normal distribution function (Gaussian function) from the overall population, which are included in the interval of the 3\( \sigma \) range between \( \mu + 3\sigma \) and \( \mu - 3\sigma \), where \( \mu \) is the average and \( \sigma \) is the standard deviation. When current densities are within the 3\( \sigma \) range (indicated as dotted lines in Figure 9), they are defined as working molecular electronic devices, whereas the others are defined as 'nonworking' devices when the current densities are out of this range. Figure 9 shows an example of a histogram plot for logarithmic current densities of all C8 candidate devices. Similarly, we are able to define the working device ranges of alkanemonothiols and alkanedithiols devices. Basically, working molecular electronic devices were extracted from devices showing a majority of current densities in the statistical distribution. As summarized in Table 4, the numbers of C8, C12, C16, DC8, DC9, and DC10 working devices were 63, 33, 60, 84, 94, and 93, respectively, among the total 27 840 fabricated devices. Then, the device yields were found as \( \sim 1.2\% \) (156/13 440) for monothiol and \( \sim 1.9\% \) (271/14 440) for dithiol devices. Since the device yield (\( \sim 175\% \)) of DC8 dithiol devices is not much different from that of C8 monothiol devices (\( \sim 141\% \)), this result may suggest that device yield is not much affected by metal–molecule contact, but rather affected more by the device structures, fabrication condition, and quality of the self-assembled monolayers. In this study, the use of a statistical approach is very significant, as the analysis of a large number of devices increases the ability to develop more accurate and meaningful characteristics of molecular systems. Figures 10(a)–10(f) present the statistical histograms of current densities in logarithmic scale for different lengths of alkanemonothiols (C8, C12, and C16) and alkanedithiols (DC8, DC9, and DC10) at 1.0 V with the mean positions as representative devices indicated with arrows from the fitting results by Gaussian functions. The current densities for these representative devices were found to be \( \sim 8.3 \times 10^4 \), \( 1.2 \times 10^3 \), 3.5, \( 4.9 \times 10^3 \), \( 2.0 \times 10^3 \), and \( 6.3 \times 10^3 \) \( \text{A cm}^{-2} \) at 1.0 V for C8, C12, C16, DC8, DC9, and DC10, respectively. The current densities–voltage (\( \mathcal{J}–V \)) characteristics for these six representative devices are plotted in Figure 10(g). The conductance and \( \mathcal{J}–V \) characteristics are clearly dependent on the molecular length and metal–molecule contacts (i.e., monothiol vs. dithiol). This observation is supported by previous reports of M–M–M junctions that have shown that the current density for alkanedithiol is higher than that for alkanemonothiol due to their different natures of metal–molecule contact properties (chemisorbed vs. physisorbed contact) at Au–molecule contacts [64,65]. The histograms in Figures 10(a)–10(f) show the distribution of the logarithmic current densities, indicating the existence of fluctuation factors causing the exponential distribution in the current densities. The variation of junction area may exist, but the area fluctuation does not produce exponential distribution in current, instead fluctuation in the tunneling path is probably responsible for the distribution data of Figures 10(a)–10(f). Some fluctuations in molecular configurations in the self-assembled monolayers in the device junctions are possible, such as fluctuations in molecular configuration or microstructures in metal–molecule contacts [66,67].

4.16.4.2.2 Contact/length-dependent decay coefficients by multibarrier tunneling model

To investigate the effect of metal–molecule contacts on the electronic transport, we propose a multibarrier tunneling (MBT) model, which generalizes the Simmons tunneling model, a widely-used model for describing a rectangular tunneling barrier [9,10,57]. As compared to the Simmons tunneling model, where the tunneling barrier is represented by a single barrier, the M–M–M junction in MBT model can be divided into three parts: a molecular-chain body and metal–molecule contacts on either side of molecule, represented as three individual conduction barriers, as schematically illustrated in Figure 11(a). In the
Table 4  Summary of results for the fabricated devices

<table>
<thead>
<tr>
<th>Number of fabricated devices</th>
<th>Working&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fab. failure</td>
</tr>
<tr>
<td>Monothiol</td>
<td>13,440 (100%)</td>
</tr>
<tr>
<td>Dithiol</td>
<td>14,400 (100%)</td>
</tr>
</tbody>
</table>

<sup>a</sup> CS correspond to monothiol and DCs to dithiol.

Note: working and nonworking devices were defined by statistical analysis with Gaussian fitting on the histogram of the logarithmic scale current densities.
Electronic Properties of Alkanethiol Molecular Junctions

**Figure 10** The statistical histograms of log($J$) measured at 1.0 V for C8 (a), C12 (b), C16 (c), DC8 (d), DC9 (e), and DC10 (f). The line curves are fitting results obtained from the histograms with Gaussian functions, and the mean positions are indicated with arrows. (g) Current density–voltage characteristics of representative devices chosen from the mean positions of the fitted Gaussian functions.

**Figure 11** (a) (Left) An illustration of MBT model; (Right) a schematic of barrier widths for C8 and DC8. Schematics of MBT model for an alkanedithiol M-M-M junction (b) and for an alkanemonothiol M-M-M junction (c).
Electronic Properties of Alkanethiol Molecular Junctions

Alkanedithiol M-M-M junction, there is one molecular-chain body barrier \([(CH_2)_n]\) (n is the number of carbon units), and two chemisorbed contact barriers \([Au-S-C]\) on either side. Conversely, the alkanemonothiol M-M-M junction with the same a molecular-chain body barrier \([(CH_2)_n]\) as the alkanedithiol junction has one chemisorbed contact barrier \([Au-S-C]\) and one physisorbed contact barrier \([CH_3/Au]\). Please retain square brackets. This approach of separation of metal–molecule contact and molecular body from alkanedithiol M-M-M junction is reasonable, since hybridization of the metal–molecule wave function decays rapidly into the junction for alkanedithiol devices \([68,69]\).

In the typical nonresonant tunneling case, the resistance is exponentially dependent on the molecular length \(R = R_0 e^\beta d\). The widths of the barrier for \(d_1\), \(d_{body}\), and \(d_2\) in alkyl molecular system represent the length of the chemisorbed contact on the molecule \([Au–S–C]\), the molecular body region \([[(CH_2)_n]\), and the physisorbed contact on the molecule \([CH_3/Au]\), respectively. Here, we assume \(d_{body}\) is the projected length along the molecular body with the incremental length per carbon atom \((\Delta d_{body}[CH_2])\) of \(\approx 1.25 \AA\) and the contact lengths \((d_1\) and \(d_2\)) are the vertical distances between contact sites of molecule and electrode. The length \(d_{body}\) is identical for \(n\)-alkanemonothiol and \(n\)-alkanedithiol with the same \(n\) value. For example, octanemonothiol (C8) and octanedithiol (DC8) have an identical length, \(d_{body}[((CH_2)_8]\), \(\approx 8.75 \AA\). And, \(d_1\) ([Au–S–C]) is \(\approx 3.2 \AA\) and \(d_2\) ([CH3/Au]) is \(\approx 1.4 \AA\) \([70]\).

For small-length molecules with a large HOMO–LUMO energy gap, such as alkyl chain molecules, coherent tunneling is the main conduction mechanism of the electronic charge transport at relatively low bias regime \([35]\). As mentioned above, the tunneling current density in low-bias regime can be approximated as equation 4a. From equation 4a, \(\beta\) is the decay coefficient in a low-bias regime, which reflects the degree of decrease in wave function of the tunneling electron through the molecular tunnel barrier. A higher decay coefficient implies a faster decay of the wave function, that is, lower electron tunneling efficiency.

In MBT model, it is possible to describe the overall slope of wave function decay through the barriers based on the magnitude of the \(\beta\) value, and this overall decay can be further decomposed to three individual decays through three individual barriers, as shown in Figure 11. The \(\beta\) can be expressed as equation 6 for alkanemonothiol (alkanedithiol) junctions from the consideration of geometric configurations.

\[\beta = \frac{\beta_C d_1 + \beta_{body} d_{body} + \beta_{C(P)} d_{(2)}}{d_1 + d_{body} + d_{(2)}}\] (6)

One can see that \(\beta\) converges to \(\beta_{body}\) for a very long molecule. Also, \(\alpha(\Phi_B)^{1/2}\) can be expressed as equation 7 by combining equations 4a and 6:

\[\alpha(\Phi_B)^{1/2} = \frac{\hbar}{2(2m)^{1/2}} \frac{\beta_C d_1 + \beta_{body} d_{body} + \beta_{C(P)} d_{(2)}}{d_1 + d_{body} + d_{(2)}}\] (7)

As mentioned above, because the main conduction mechanism is coherent (elastic) tunneling at low-bias regime (and at room temperature), it is assumed that the energy of electron tunneling through the molecular barriers does not decrease, as expressed by the horizontal dashed line in Figure 11(a). Furthermore, due to the different nature of the metal–molecule contact properties, electron transmission for the chemisorbed contact \([Au–S–C]\) is found to be more efficient than that for the physisorbed contact \([CH_3/Au]\). As a result, the slope \((\beta)\) for alkanemonothiol junctions is steeper than that for alkanedithiol junctions, as illustrated by the dashed lines in Figure 11. In this MBT model, it was possible to define \(\beta_C\) (\(\beta_P\)) as the components of the decay coefficients corresponding to the chemisorbed (physisorbed) contact barrier width \(d_1\) (\(d_2\)), as expressed by the solid lines in Figure 11. Similarly, \(\beta_{body}\) is the decay coefficient component for the molecular-chain body barrier (center solid lines).

Figure 12 shows the statistical distribution of \(\beta\) values obtained for different-length alkanemonothiol and alkanedithiol M-M-M devices. In this plot, \(\beta\) values were determined from fitting the \(I-V\) data of all the 'statistically defined working' molecular...
Electronic Properties of Alkanethiol Molecular Junctions

Table 5: A summary of the experimental and calculated values for decay coefficients, contact resistances, and specific contact resistances

<table>
<thead>
<tr>
<th></th>
<th>$\beta_{\text{Body}}$ (Å⁻¹)</th>
<th>$\beta_{d}$ (Å⁻¹)</th>
<th>$\beta_{o}$ (Å⁻¹)</th>
<th>$R_{\Omega}$ (Ω)</th>
<th>$R_{\sigma}$ (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanemonothiol</td>
<td>Calculated value 0.92</td>
<td>0.05</td>
<td>1.89</td>
<td>0.19</td>
<td>0.58 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>Experimental value 0.93 ± 0.03</td>
<td>0.34 ± 0.30</td>
<td>1.08 ± 0.94 × 10⁻⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkanedithiol</td>
<td>Calculated value 0.92</td>
<td>0.05</td>
<td>0.03</td>
<td>0.98 × 10⁻⁹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Experimental value 0.92 ± 0.08</td>
<td>0.04 ± 0.03</td>
<td>1.13 ± 0.98 × 10⁻⁹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 13  (a) Semilog plot of the resistance $R$ versus the molecular-chain body length $d_{\text{body}}$ for alkanemonothiol and alkanedithiol junctions. The solid lines are exponential fitting results, giving the molecular-chain body decay coefficient $\beta_{\text{body}}$. (b) Experimental and calculated specific contact resistance $R_C$. The blue arrows represent the range of the estimated $R_C$ values from the contact resistances reported in literature [24,64,71a,b].

experimental and theoretical values for $R_C$ for our alkanemonothiol and alkanedithiol devices at a low-bias regime. Here, the specific contact resistance $R_C = R_o \times A$ can be obtained by multiplying the contact resistance ($R_o$) with the contact junction area ($A$) ($\sim 3.14 \times 10^{-8} \text{cm}^2$ for our molecular devices). The contact resistance ($R_o$) was found by extrapolating the observed resistance (Figure 13(a)) to a zero molecular-chain body length ($\sim 0.34 \pm 0.3 \Omega$ for alkanemonothiol, and $\sim 0.04 \pm 0.03 \Omega$ for alkanedithiol). Then, $R_C$ was calculated as $\sim 1.08 \pm 0.94 \times 10^{-8} \Omega \text{cm}^2$ for alkanemonothiol and $\sim 1.13 \pm 0.98 \times 10^{-8} \Omega \text{cm}^2$ for alkanedithiol. Using MBT model, $R_C$ could also be estimated as $\sim 0.58 \times 10^{-8} \Omega \text{cm}^2$ for alkanemonothiol and $\sim 0.98 \times 10^{-8} \Omega \text{cm}^2$ for alkanedithiol, both of which are in good agreement with the experimental values we obtained. Table 5 summarizes the experimental and calculated quantities of decay coefficients and contact and specific contact resistances for our measurements.

Note that our analysis with MBT model does not consider the details of the Fermi level alignment and molecular binding sites, which will generally influence the charge transport of molecular devices. Furthermore, the transport properties values obtained from our experimental results with microscale molecular junctions are an ensemble average effect with various microstructures of metal–molecule contacts and binding sites, and thus should not be compared with single-molecular measurement results, due to the contribution from the probability amplitude of multiple reflections and the possibility of cooperative effects between individual molecules in ensemble of molecules.

4.16.4.2.3 Contact properties through various electrodes by multi-barrier tunneling model

Similarly, using equation 4a, the contact decay coefficients $\beta_{C(P)}$ for Au contacts can be expressed as

$$\beta_{C(P)} = \frac{2(2m)^{1/2}}{h} \alpha_{C(P)}(\Phi_{C(P)})^{1/2}$$  (10)

where $\Phi_{C(P)}$ is the contact barrier height at zero bias and $\alpha_{C(P)}$ the $\alpha$ value through the contact barrier. These two value can be obtained from $\alpha$ and $\Phi_B$ in Au–alkyl molecule contacts, which can be deduced from the molecular body decay coefficients ($\beta_{\text{body}}$) and widths ($d_1$,$d_2$, and $d_{\text{body}}$) of each barrier part.

Furthermore, the decay coefficients and specific contact resistance can be determined for molecular junctions with various metal contacts other than Au. If molecular monolayers are sandwiched between other metals (Ag and Cu), the contact barrier heights can be expressed as $\Phi_{C(\text{other metals})} = \Phi_{C(Au)} + \Delta \Phi_{(Au\text{-other metals})}$ and $\Phi_{P(\text{other metals})} = \Phi_{P(Au)} + \Delta \Phi_{(Au\text{-other metals})}$ for chemisorbed contact and physisorbed contact, respectively, by assuming the tunneling around HOMO levels (i.e., a hole type tunneling). Note that $\Delta \Phi_{(Au\text{-other metals})}$ is the difference between the work function of Au and that of the other metal. From equation 10 with using $\Phi_{C}$, $\Phi_{P}$, $\alpha_{C}$, and $\alpha_{P}$, the contact decay coefficient $\beta_{C(P)|\text{Ag and Cu}}$ can be calculated as $\beta_{C(Ag)} = 0.51 \ \text{Å}^{-1}$ and
Figure 14 shows the $R_C$ values of various metal–molecule contacts (Ag, Cu, and Au) in alkyl M-M-M junctions obtained from experiment, reported studies, and the MBT model, by assuming tunneling around HOMO, that is, a hole type tunneling. In this Figure 7, the labels are designed such that, for example, [Au/Ag] refers to [Au–S–(CH$_2$)$_n$CH$_3$/Ag], that is, the chemisorbed contact to the Au electrode and physisorbed contact to the Ag electrode for alkanemonothiol (Figure 14(a)) or [Au–S–(CH$_2$)$_n$–S–Ag], that is, the chemisorbed contacts to both Au and Ag electrodes for alkanedithiol (Figure 14(b)). And for different metallic junctions (e.g., [Au/Ag], [Ag/Cu], etc.), the average value of the two individual metal work functions was assigned as the work function. As mentioned earlier, the natures of the chemisorbed and physisorbed contacts are quite different. Because the chemisorbed contacts ([metal–S–C]) can form stronger bondings by molecular overlapping than physisorbed contacts (metal/CH$_3$ or metal/H), generally the contact decay coefficient for chemisorbed contacts are smaller than that of physisorbed contacts ($\beta_C < \beta_P$), that is, less tunneling electron decay through chemisorbed contacts. In MBT model, the contact decay coefficients ($\beta_C$, $\beta_P$) in various metallic junctions are dependent on the contact barrier height ($\Phi_C$, $\Phi_P$) and effective mass ($\alpha_C$ and $\alpha_P$), which can be affected by metal work function, as expressed in equation 10. Note that the contact decay coefficient was observed to decrease when metal work function is increased. The $R_C$ values were found to be different for asymmetric metal contacts (e.g., [Ag/Au] and [Au/Ag]) for alkanemonothiol because of the different natures of metal–molecule contacts (physisorbed vs. chemisorbed contact side), as shown in Figure 14(a), whereas $R_C$ values for that of alkanedithiol were found to be same for even asymmetric contacts because of the same nature of metal–molecule contact, as shown in Figure 14(b). As a result, it was determined that when the average metal work function increases, $R_C$ decreases due to a reduction of the contact barrier height (or contact decay coefficients). The $R_C$ values calculated by the MBT model are in good agreement with those obtained from reported literatures [24,64,71a,b], as indicated by the arrows, as shown in Figure 14.

4.16.4.3 Inelastic Tunneling

4.16.4.3.1 Inelastic electron tunneling spectroscopy

Electronic transport through alkanethiol SAMs is further investigated with the technique of inelastic electron tunneling spectroscopy [36], for example, by Jaklevic and Lambe, who studied, in 1966, the conductance of tunnel junctions with encased organic molecules [37]. Since then it has become a powerful spectroscopic tool for chemical identification, chemical bonding investigation, and studies in surface chemistry and physics [40]. In an inelastic tunneling process, the electron loses energy to a localized vibrational mode with a frequency $\nu$ when the applied bias satisfies the condition of $eV = h\nu$. As a result, an additional tunneling channel is opened for
the electron, resulting in an increase in the total current at the applied bias corresponding to the vibrational mode energy [39]. Typically only a small fraction of tunneling electrons are involved in the inelastic tunneling process (determined by the electron–vibronic mode coupling coefficient), resulting in a small conductance change, which is commonly measured in the second harmonics of a phase-sensitive detector that yields the characteristic frequencies of the corresponding vibrational modes as well as other information [38–40].

Measurements of $I(V,T)$ and additional IETS studies have been performed on an octanethiol (C8-dithiol) SAM using the aforementioned device structure shown in Figure 1(a) [36]. Figure 15(a) is the $I(V,T)$ data for this device obtained from 300 to 4.2 K. An Arrhenius plot shown in Figure 15(b) exhibits mild temperature dependence, verifying that tunneling is the main transport mechanism for C8-dithiol SAM. This result is in good agreement with the tunneling transport characteristics observed previously. Figure 15(c) shows the room temperature $I(V)$ measurement result. Using a junction area of $51 \pm 5$ nm in diameter (obtained from statistical studies of the nanopore size with SEM), a current density of $(9.3 \pm 1.8) \times 10^{-4}$ A cm$^{-2}$ at 1.0 V is calculated. As a comparison, the current density of $(3.1 \pm 1.0) \times 10^{-4}$ A cm$^{-2}$ at 1.0 V was observed for C8 monothiol SAM. Using the modified Simmons model (equation 2), the transport parameters of $\Phi_B = 1.20 \pm 0.03$ eV and $\alpha = 0.59 \pm 0.01$ (m$^2$ = 0.34 m) were obtained for this C8-dithiol SAM.

Figure 16 shows the IETS spectrum of the same C8-dithiol SAM device obtained at $T = 4.2$ K. An AC modulation of 8.7 mV (root-mean-square (RMS) value) at a frequency of 503 Hz was applied to the sample to acquire the second-harmonic signals. The spectra are stable and repeatable upon successive bias sweeps. The spectrum at 4.2 K is characterized by three pronounced peaks in the 0–200 mV region at 33, 133, and 158 mV. From a comparison with previously reported infrared (IR), Raman, and high-resolution electron energy loss (HREEL) spectra of SAM covered gold surfaces (Table 6), these three peaks are assigned to $\nu(Au–S)$, $\nu(C–C)$, and $\gamma_w(CH_2)$ modes of a surface bound alkanethiolate [72–75]. The absence of a strong $\nu(S–H)$ signal at $\sim 329$ mV suggests that most of the thiol groups have reacted with the gold bottom and top contacts. Peaks are also reproducibly observed at 80, 107, and 186 mV. They correspond to $\nu(C–S)$, $\delta_\parallel(CH_2)$, and $\delta_\perp(CH_2)$ modes. The stretching mode of the CH$_2$ groups, $\nu(CH_2)$, appears as a shoulder at 357 mV. The peak at 15 mV is due to vibrations from either Si, Au, or $\delta(C–C–C)$ [76]. We note that all alkanethiolate peaks without exception or omission occur in the spectra. Peaks at 58, 257, 277, and 302 mV, as well as above 375 mV are likely to originate from Si–H and N–H vibrations related to the silicon nitride membrane [76a,77a,b], which forms the SAM encaement. To the best of our knowledge, alkanethiols have no vibrational signatures in these regions. Measurement of the background spectrum of an ‘empty’ nanopore device with only gold contacts to obtain background contributions from Si$_2$N$_4$ is hampered by either too low (open circuit) or too high (short circuit) currents in such a device. Similar IETS result has also been obtained using a different test structure recently [78].

Although there are no selection rules in IETS as there are in IR and Raman spectroscopy, certain selection preferences have been established. According to the IETS theory [79], molecular vibrations with net dipole moments perpendicular to the interface of the tunneling junction have stronger peak intensities than vibrations with net dipole moments parallel to the interface (for dipoles close to the electrodes). Thus, vibrations perpendicular to the electrode interface, that is, $\nu(Au–S)$, $\nu(C–S)$, $\nu(C–C)$, and $\gamma_w(CH_2)$, dominate the IETS spectrum, while modes parallel to the interface, that is, $\delta_\parallel(CH_2)$ and $\nu(CH_2)$, are weak, as clearly shown in Figure 16.

### 4.16.4.3.2 Linewidth study

In order to verify that the observed spectra are indeed valid IETS data, the peak width broadening was examined as a function of temperature and modulation voltage. IETS was performed with different AC modulations at a fixed temperature, and at different temperatures with a fixed AC modulation. Figure 17(a) shows the modulation dependence of the IETS spectra obtained at 4.2 K, and Figure 17(b) shows the modulation broadening of the C–C stretching mode at 133 mV. The circular symbols are the full widths at half maximum (FWHMs) of the experimental peak at $T = 4.2$ K with various modulation voltages. A Gaussian distribution function was utilized to obtain an FWHM and the error range [80]. The square symbols are calculated FWHM values ($W_{\text{theoretical}}$) taking into account both a finite-temperature effect ($W_{\text{thermal}} \sim 5.4 k_B T$) [38] and a finite-voltage modulation effect ($W_{\text{modulation}} \sim \frac{1}{2} V_{ac,\text{RMS}}^2$) [81]. These two broadening contributions add as the squares: $W_{\text{theoretical}}^2 = W_{\text{thermal}}^2 + W_{\text{modulation}}^2$.
The agreement is excellent over most of the modulation range, but we note a saturation of the linewidth at low-modulation bias indicating the influence of a non-negligible intrinsic linewidth. Taking into account the known thermal and modulation broadenings, and including the intrinsic linewidth ($W_i$) as a fitting parameter, the measured peak width ($W_{\text{exp}}$) is given by

$$W_{\text{exp}} = W_i.$$
Inelastic electron tunneling spectrum of C8 dithiol SAM obtained from lock-in second-harmonic measurement with an AC modulation of 8.7 mV (RMS value) at a frequency of 503 Hz ($T = 4.2 \text{K}$). Peaks labeled ‘*’ are most probably background due to the encasing Si$_3$N$_4$.

**Table 6** Summary of the major vibrational modes of alkanethiols

<table>
<thead>
<tr>
<th>Modes</th>
<th>Methods</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>(meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(Au–S)</td>
<td>HREELS [61]</td>
<td>225</td>
<td>28</td>
</tr>
<tr>
<td>$\nu$(C–S)</td>
<td>Raman [60a,b]</td>
<td>641</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>Raman [60a,b]</td>
<td>706</td>
<td>88</td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>HREEL [61]</td>
<td>715</td>
<td>89</td>
</tr>
<tr>
<td>IR [62]</td>
<td>720</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>IR [62]</td>
<td>766</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>IR [62]</td>
<td>925</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>$\nu$(C–C)</td>
<td>HREEL [61]</td>
<td>1050</td>
<td>130</td>
</tr>
<tr>
<td>Raman [60a,b]</td>
<td>1064</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td>Raman [60a,b]</td>
<td>1120</td>
<td>139</td>
<td></td>
</tr>
<tr>
<td>IR [62]</td>
<td>1230</td>
<td>152</td>
<td></td>
</tr>
<tr>
<td>HREELS [61]</td>
<td>1265</td>
<td>157</td>
<td></td>
</tr>
<tr>
<td>IR [62]</td>
<td>1283</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td>IR [62]</td>
<td>1330</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>$\delta$(CH$_2$)</td>
<td>HREELS [61]</td>
<td>1455</td>
<td>180</td>
</tr>
<tr>
<td>$\nu$(S–H)</td>
<td>Raman [60a,b]</td>
<td>2575</td>
<td>319</td>
</tr>
<tr>
<td>$\nu$(CH$_2$)</td>
<td>Raman [60a,b]</td>
<td>2854</td>
<td>354</td>
</tr>
<tr>
<td>HREELS [61]</td>
<td>2860</td>
<td>355</td>
<td></td>
</tr>
<tr>
<td>$\nu$(C–S)</td>
<td>Raman [60a,b]</td>
<td>2880</td>
<td>357</td>
</tr>
<tr>
<td>HREELS [61]</td>
<td>2907</td>
<td>360</td>
<td></td>
</tr>
<tr>
<td>HREELS [61]</td>
<td>2925</td>
<td>363</td>
<td></td>
</tr>
</tbody>
</table>

4.16.5 Conclusions

We present here a study of electronic transport properties of alkanethiol SAMs, with the intent that this system can serve as a simple standard for the development of well-characterized molecular junctions. The characteristics are consistent with accepted models of tunneling junctions, as well as presenting a system on which tunneling spectroscopy can be performed. The metal–molecule contact plays a crucial role in the charge transport through the molecular junctions.

The field of ‘molecular electronics’ is rich in the proposal and promise of numerous device concepts [84,85], but unfortunately reliable data and characterization techniques upon which to test these ideas are not available. It is incumbent upon the experimentalists to carefully institute controls to validate claims of intrinsic molecular behavior. Systematic controls, such as the model system presented here, should assist in guiding further work toward a rational development of the fascinating device structures and systems that the field promises.

Acknowledgments

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Gwangju Institute of Science and Technology.

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Electronic Properties of Alkanethiol Molecular Junctions


Ethanol and alkane molecules were purchased from Sigma-Aldrich.


Electronic Properties of Alkanethiol Molecular Junctions


70. All of these lengths were determined by Chem3D software.


75. The symbols, $\delta$, $\gamma$, and $\nu$ denote in-plane rocking (r) and scissoring (s), out-of-plane wagging (w) and twisting (t), and stretching modes, respectively.


