Electronic Transport in Molecular Self-Assembled Monolayer Devices

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Invited Paper

A review on the mechanisms and characterization methods of electronic transport through self-assembled monolayers (SAMs) is presented. Using SAMs of alkanethiols in a nanometer-scale-device structure, tunneling is unambiguously demonstrated as the main intrinsic conduction mechanism for defect-free large bandgap SAMs, exhibiting well-known temperature and length dependencies. Inelastic electron tunneling spectroscopy exhibits clear vibrational modes of the molecules in the device, presenting direct evidence of the presence of molecules in the device.

Keywords—Molecular electronics, spectroscopy, tunneling.

I. INTRODUCTION

The suggestion [1] and demonstration [2] of utilizing molecules as the active region of electronic devices has recently generated considerable interest in both the basic transport physics and potential technological applications of “molecular electronics” [3], [4], [71]. However, some reports of molecular mechanisms in electronic devices [5], [6], [72], [73] have been shown to be premature and due to filamentary conduction, [7], [74] 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 structure, including their configuration, bonding, and indeed even their very presence. 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 first unambiguous evidence of the presence of molecules in the junction and further confirm the charge transport mechanism obtained by standard current–voltage characterizations.

A molecular system whose structure and configuration are sufficiently well characterized such that it can serve as a standard is the alkanethiol \( \text{CH}_2(\text{CH}_2)_{n-1}\text{SH} \) self-assembled monolayer (SAM) [9]. This system is useful as a control, since properly prepared SAMs form single van der Waals crystals, [9], [10] and presents a simple classical metal–insulator–metal (MIM) tunnel junction when fabricated between metallic contacts due to the large HOMO–LUMO gap (HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital) of approximately 8 eV [11], [12], [75]–[77].

Various surface analytical tools have been utilized to investigate the surface and bulk properties of the alkanethiol SAMs, such as X-ray photoelectron spectroscopy, [13] Fourier transform infrared spectroscopy (FTIR), [14] Raman spectroscopy, [15] scanning tunneling microscopy (STM) [10] etc. For example, studies have shown that the bonding of the thiolate group to the gold surface is strong with a bonding energy of \( \sim 1.7 \) eV [9]. STM topography examinations revealed that alkanethiols adopt the commensurate crystalline lattice characterized by a \( \alpha(4 \times 2) \)

1Although the HOMO–LUMO gap of alkyl chain type molecules has been reported (see ref [12]), there is no experimental data on the HOMO–LUMO gap for the Au/alkanethiol SAM/Au system. Eight electronvolts is commonly used as the HOMO–LUMO gap of alkanethiol.

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superlattice of a \((\sqrt{3} \times \sqrt{3})R30^\circ\) [10], [16]. FTIR investigations showed that the orientation of the alkane thiol SAMs on Au(111) surfaces are tilted \(\sim 30^\circ\) from the surface normal [17].

Electronic transport through alkanethiol SAMs have also been characterized by STM [18], [19], conducting atomic force microscopy [20]–[23], mercury-drop junctions [24]–[27], cross-wire junctions [28], and electrochemical methods [29]–[31]. 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 (such as thermionic, hopping, or filamentary conduction) cannot be excluded completely [AU: Please clarify] the analysis, and thus such a claim is premature.

Utilizing a nanometer-scale-device structure that incorporates alkanethiol SAMs, we demonstrate devices that allow \(I(V,T)\) and structure-dependent measurements [32], [33] with results that can be compared with accepted theoretical models of MIM 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) [33]. 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 [34]–[38]. 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 are 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 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.

II. EXPERIMENT

Electronic transport measurements on alkanethiol SAMs were performed using a device structure similar to one reported previously [32], [33], [39]–[41], [78]. In this device, a number of molecules (\(\sim\) 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 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 of \(40 \mu m \times 40 \mu m\) and thickness of \(\sim 70 nm\)) 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 of 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 \(\sim 5 mM\) alkanethiol solution is prepared by adding \(\sim 10 \mu L\) alkanethiols into 10 mL ethanol.\(^2\) The deposition is done in solution for 24 h inside a nitrogen-filled glove box with an oxygen level of less than 100 ppm. Three alkanethiol molecules of different molecular lengths–octanethiol (CH\(_3(CH_2)_7SH\); denoted as C8, for the number of alkyl units); dodecanethiol (CH\(_3(CH_2)_{11}SH\), denoted as C12), and hexadecanethiol (CH\(_3(CH_2)_{15}SH\), denoted as C16) and one alkanedithiol molecule, octanedithiol (HS(CH\(_2)_8SH\), denoted as C8-dithiol) were used to form the active molecular components.\(^3\)

In order to statistically determine the pore size, test patterns (arrays of pores) were created under similar fabrication conditions. This indirect measurement of device size is done because scanning electron microscope (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 diameter, respectively. A more ideal (less parasitic) C8 sample supersedes that of previous reports [32] 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 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 sample is then transferred in ambient conditions to an evaporator that has a cooling stage to deposit the opposing Au contact. During the thermal evaporation (under the pressure of \(\sim 10^{-8}\) torr), liquid nitrogen is kept flowing through the cooling stage in order to avoid thermal damage to the molecular layer [32], [42]. 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 10 nm of gold evaporated, the rate is less than 0.1 Å/s. Then the rate is increased slowly to 0.5

\(^2\)Ethanol and alkane molecules were purchased from Sigma-Aldrich.

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Å/s for the rest of the evaporation and a total of 200 nm of 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 K to 4.2 K 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 semiconductor parameter analyzer. Inelastic electron tunneling spectra are obtained via a standard lock-in second harmonic measurement technique [34], [35]. A synthesized function generator is used to provide both the modulation and the lock-in reference signal. The second harmonic signal (proportional to $d^2I/dV^2$) 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 ac modulation is added to a dc bias using operational amplifier-based custom circuitry [43].

III. THEORY

Possible conduction mechanisms are elucidated by determining characteristic current, temperature and voltage dependencies [44] (we do not discuss filamentary tunneling mechanisms, which are easier to categorize [45], [79], [80]). 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-thioacetyl-biphenyl SAMs [39] and 1,4-phenylene diisocyanide SAMs [78]. 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 [11], [12][75]–[77]. Previous work on Langmuir–Blodgett alkane monolayers [46], [81] exhibited a significant impurity-dominated transport component, complicating the analysis. $I(V)$ measurements on self-assembled alkanethiol monolayers have also been reported [18]–[28], [47]; however, all of these measurements were performed at a fixed temperature (300 K) which is insufficient to prove tunneling as the dominant mechanism.

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 [48]–[51], [82], [83]. This model provides a non-parabolic energy-momentum $E(k)$ dispersion relationship by considering the contributions of both the HOMO and LUMO energy levels [48]

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

(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 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 [52] is an excellent approximation [53], [84]. Simmons model expressed the tunneling current density through a barrier in the tunneling regime of $V < \Phi_B/e$ as [24], [52]

$$J = \frac{e}{4\pi^2\hbar d} \times \left\{ \left( \frac{\Phi_B - eV}{2} \right) \exp \left[ -\frac{2(2m)^{2/3} \alpha (\Phi_B - eV/2)}{\hbar} d \right] - \left( \frac{\Phi_B + eV}{2} \right) \exp \left[ -\frac{2(2m)^{2/3} \alpha (\Phi_B + eV/2)}{\hbar} d \right] \right\}$$

(2)

where $m$ is the electron mass, $d$ is the barrier width, $\Phi_B$ is the barrier height, and $V$ is the applied bias. For molecular systems, the Simmons model has been modified with a parameter $\alpha$ [24], [32], $\alpha$ 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 [24], or an adjustment to account for the effective mass ($m^*$) of the tunneling electrons through a rectangular barrier [24], [32], [51], [54], or both. $\alpha = 1$ corresponds to the case for a rectangular barrier and bare electron mass. By fitting individual $I(V)$ data using (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, (2) can be approximated as [52]

$$J \approx \left( \frac{(2m\Phi_B)^{2/3} e^{2}\alpha}{h^2d} \right) \times \left[ \frac{2(2m)^{2/3} \alpha (\Phi_B)}{\hbar} d \right].$$

(3a)

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

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

(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 \(J \propto (1/d) \exp(-\beta_0 d)\), where \(\beta_0\) is bias-independent decay coefficient

\[
\beta_0 = \frac{2(2m)^{\frac{1}{2}}}{\hbar} \alpha (\Phi_B)^{\frac{1}{2}}
\]

(4a)

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

\[
\beta_\nu = \frac{2(2m)^{\frac{1}{2}}}{\hbar} \alpha \left( \Phi_B - \frac{eV}{2} \right)^{\frac{1}{2}} = \beta_0 \left( 1 - \frac{eV}{2\Phi_B} \right)^{\frac{1}{2}}
\]

(4b)

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

IV. RESULTS

A. Tunneling Current–Voltage Characteristics

In order to determine the conduction mechanism of self-assembled alkanethiol molecular systems, \(I(V)\) measurements in a sufficiently wide temperature range (300 K–80 K) and resolution (10 K) were performed. Fig. 1(a) shows a representative \(I(V, T)\) characteristic of dodecanethiol (C12). Positive bias corresponds to electrons injected from the physiosorbed Au contact 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 \(V = 0\) to 1.0 V) is observed over the range from 300 K to 80 K. An Arrhenius plot (\(\ln(I)\) versus 1/\(T\)) of this is shown in Fig. 1(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, i.e., along the tilted molecular chains between the metal contacts [21], [22], [31], [55], [85]. Based on the applied bias as compared with the barrier height (\(\Phi_B\)), the tunneling through a SAM layer can be categorized into either direct

\(V < \Phi_B/e\) or Fowler–Nordheim (\(V > \Phi_B/e\)) tunneling. These two tunneling mechanisms can be distinguished due to their distinct voltage dependencies. Analysis of \(\ln(I/V^2)\) versus 1/\(V\) [in Fig. 1(c)] shows no significant voltage dependence, indicating no obvious Fowler–Nordheim transport behavior in this bias range (0–1.0 V) and thus determining that the barrier height is larger than the applied bias, i.e., \(\Phi_B > 1.0\) eV. This study is restricted to applied biases \(\leq 1.0\) V and the transition from direct to Fowler–Nordheim tunneling requires higher bias.
Hopping conduction and other similar impurity-mediated transport phenomena (such as Coulomb blockade) are observed in a subset of devices, revealed by temperature-dependent studies, and is indicative of the unintentional incorporation of a trap or defect level in those devices. This study instead focuses on devices which 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. From the modified Simmons model (2) by adjusting two parameters $\Phi_B$ and $\alpha$, a non-linear least squares fitting can be performed to fit the measured C12 $I(V)$ data [calculation assuming $\alpha = 1$ has been previously shown to fit $I(V)$ data well for some alkanethiol measurements at fixed temperature (300 K)] [24]. 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 $\Phi_B = 1.42 \pm 0.04$ 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 $\{\Phi_B = 1.83 \pm 0.10$ eV and $\alpha = 0.61 \pm 0.01\}$ and $\{\Phi_B = 1.40 \pm 0.03$ eV, $\alpha = 0.68 \pm 0.01\}$, respectively. For the case of a rectangular barrier, the $\alpha$ parameter fit presented above corresponds to an effective mass $m^*(=\alpha^2m)$ of 0.42 m.

In order to investigate the dependency 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 (4a). $\Delta(\Phi_B, \alpha) = (\Sigma I_{\text{exp}}V^2 - I_{\text{calc}}V^2)^{1/2}$ was calculated and plotted where $I_{\text{exp}}V$ is the experimental current-voltage values and $I_{\text{calc}}V$ is calculated using (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). Fig. 2 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 (2) to the measured $I(V)$ data. In the inset, 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.

Three alkanethiols of different molecular length, C8, C12, and C16, were investigated to study length-dependent tunneling behavior. Fig. 3 is a semilog 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 [21]. Note that these lengths assume through-bond tunneling [21], [22], [31], [55], [85]. The high- and low-bias regimes are defined 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 squares fitting of the C12 $I(V)$ 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 Fig. 3, the tunneling current shows exponential dependence on molecular length, which is consistent with the Simmons tunneling model (3). The $\beta$ values can be determined from the slope at each bias and are plotted in Fig. 4. 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. The determined $\beta$ values are almost independent of bias in the low-bias range.
This gives a $\beta$ value from 0.84 to 0.73 $\text{Å}^{-1}$ in the bias range from 0.1 to 1.0 V, which is comparable to results reported previously. For example, Holmlin et al. reported a $\beta$ value of 0.87 $\text{Å}^{-1}$ by mercury drop experiments [24]; and Wold et al. have reported $\beta$ of 0.94 $\text{Å}^{-1}$ and Cui et al. reported $\beta$ of 0.64 $\text{Å}^{-1}$ for various alkanethiols by using a conducting atomic force microscope technique [20], [22]. These reported $\beta$ were treated as bias-independent quantities, contrary to the results that are reported here and that were observed [AU: OK as edited?] in a slightly different alkane system (ligand-encapsulated nanoparticle/alkane-dithiol molecules) [23]. We also caution against the use of parameters that have not been checked with a temperature-dependent analysis, since small non-tunneling components can dramatically affect derived values of $\beta$.

We have analyzed our experimental data using a Franz two-band model [48]–[51], [82], [83]. 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 nonparabolic $E(k)$ relationship [(1)] using an alkanethiol HOMO–LUMO gap of 8 eV [12], [75]–[77]. The best fitting parameters obtained by minimizing $\chi^2$ were $\Phi_B = 1.49 \pm 0.51 \text{eV}$ and $m^* = 0.43 \pm 0.15 \text{m}$, where the error ranges of $\Phi_B$ and $m^*$ are dominated by the error fluctuations of $\langle k^2 \rangle$ [22].

Both electron tunneling near the LUMO and hole tunneling near the HOMO can be described by these parameters. $\Phi_B = 1.49 \text{eV}$ indicates that the Fermi level is aligned close to one energy level in either case; therefore, the Simmons model is a valid approximation. The $\Phi_B$ and $m^*$ values obtained here are in reasonable agreement with the previous results obtained from the Simmons model.

### B. Inelastic Electron Tunneling Spectroscopy

Electronic transport through alkanethiol SAMs is further investigated with the technique of inelastic electron tunneling spectroscopy [33], such as the works of 1966 by Jaklevic and Lambe, who studied the conductance of a tunnel junctions with encased organic molecules [34]. Since then it has become a powerful spectroscopic tool for chemical identification, chemical bonding investigation, and surface chemistry and physics studies [37]. 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 [36]. 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 $eV$

$$G = G_0 \exp(-\beta d).$$

Although the HOMO–LUMO gap of alkyl chain type molecules has been reported (see ref [12]), there is no experimental data on the HOMO–LUMO gap for the Au/alkanethiol SAM/Au system. Eight electronvolts is commonly used as the HOMO–LUMO gap of alkanethiol.
a phase-sensitive detector that yields the characteristic frequencies of the corresponding vibrational modes as well as other information [35]–[37].

$I(V,T)$ measurements and additional IETS studies have been performed on an octanedithiol (C8-dithiol) SAM using the aforementioned device structure [33]. The $I(V,T)$ data for this device was obtained from 300 K to 4.2 K. An Arrhenius plot shown in Figure [AU: Please specify figure] exhibits no 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. 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 (2), the transport parameters of $\Phi_B = 1.20 \pm 0.03$ eV and $\alpha = 0.50 \pm 0.01$ ($m^* = 0.34$ m) were obtained for C8-dithiol SAM.

Figure 11[AU: Please provide correct figure reference] shows the IETS spectrum of the same C8-dithiol SAM device obtained at $T = 4.2$ K. An ac modulation of 8.7 mV (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 range at 33, 133, and 158 mV. From comparison with previously reported IR, Raman, and high resolution electron energy loss (HREEL) spectra of SAM-covered gold surfaces, these three peaks are assigned to $\nu$(Au–S), $\nu$(C–C), and $\gamma$(CH$_2$) modes of a surface-bound alkanethiolate [58]–[60]. 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 $\delta$(C–S), $\delta$(CH$_2$), and $\delta$(CH$_3$) 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) [61], [86], [87]. 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 [61], [62], [88], which forms the SAM encasement. 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$_3$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 [63].

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 [64], 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, i.e., $\nu$(Au–S), $\nu$(C–S), $\nu$(C–C), and $\gamma$(CH$_2$), dominate the IETS spectrum, while modes parallel to the interface, i.e., $\delta$(CH$_2$) and $\nu$(CH$_2$), are weak, as shown in Fig. 4.

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. Fig. 5(a) shows the modulation dependence of the IETS spectra obtained at 4.2 K, and Fig. 5(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 a FWHM and the error range [65]. The square symbols are calculated FWHM values ($W_{\text{theoretical}}$) taking into account both a finite temperature effect ($W_{\text{thermal}} \sim 5.4$ kBT) [35] and a finite voltage modulation effect ($W_{\text{modulation}} \sim 1.7 V_{\text{rms}}$) [66]. These two broadening contributions add as the squares $W_{\text{total}}^2 = W_{\text{thermal}}^2 + W_{\text{modulation}}^2$. 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 ($W_I$) [67] as a
fitting parameter, the measured peak width \( W_{\text{exp}} \) is given by

\[
W_{\text{exp}} = \sqrt{W_T^2 + W_{\text{thermal}}^2 + W_{\text{modulation}}^2} \quad (6)
\]

\( W_T \) can be determined by using a nonlinear least squares fit to the ac modulation data (Fig. 12) with (6), giving an intrinsic linewidth of 3.73 ± 0.98 meV for this line. This is shown (with the error range) in Fig. 5(b) as a shaded bar, including the thermal contribution.

We can independently check the thermal broadening of the line at fixed modulation. Fig. 6(a) shows the temperature dependence of the IETS spectra obtained with an ac modulation of 8.7 mV (rms value). In Fig. 6(b) the circular symbols (and corresponding error bars) are experimental FWHM values of the C-C stretching mode from Fig. 6(a), determined by a Gaussian fit (and error of the fit) to the experimental lineshape. For simplicity we have only considered Gaussian lineshapes [65] resulting in increased error bars for the lower temperature range due to an asymmetric lineshape. The square symbols are theoretical calculations considering thermal broadening, modulation broadening, and the intrinsic linewidth determined above. The error ranges of the calculation (due to the intrinsic linewidth error) are approximately the size of the data points. The agreement between theory and experiment is very good, spanning a temperature range from below (×0.5) to above (×10) the thermally broadened intrinsic linewidth. This linewidth should be a sensitive test to compare to theoretical models of transmission probabilities [68].
Similar intrinsic linewidths have been determined for the Au–S stretching mode (33 meV) and the CH$_2$ wagging mode (158 meV). For the Au–S stretching mode, the deviation of experimental data from calculated values (thermal and modulation width only) is little, indicating that its intrinsic linewidth is small. A linewidth upper limit of 1.69 meV is determined for this vibrational mode. For the CH$_2$ wagging mode, a nonlinear least squares fit to (6) gave an intrinsic linewidth of 13.5 ± 2.4 meV. The linewidths and their variation throughout the molecule are potentially due to inhomogeneous configuration of the molecular constituents, and a more detailed understanding may give detailed structural information of these device structures.

V. CONCLUSION

We present here a study of electron tunneling through 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 MIM tunneling junctions, as well as presenting a system on which tunneling spectroscopy can be performed.

The field of “molecular electronics” is rich in the proposal and promise of numerous device concepts [69], [70], but unfortunately has an absence of reliable data and characterization techniques upon which to test these ideas. It is incumbent upon the experimentalist to carefully institute controls to carefully 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.

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