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Electrical Characterization of Self-Assembled Monolayers

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Abstract

Electrical characterization of alkanethiol self-assembled monolayers (SAMs) has been performed using a nanometer-scale device structure. Temperature-variable current-voltage measurement is carried out to distinguish between different conduction mechanisms and temperature-independent transport characteristics are observed, revealing that tunneling is the dominant conduction mechanism of alkanethiols. Electronic transport through alkanethiol SAMs is further investigated with the technique of inelastic electron tunneling spectroscopy (IETS). The obtained IETS spectra exhibit characteristic vibrational signatures of the alkane molecules used, presenting direct evidence of the presence of molecular species in the device structure. Further investigation on the modulation broadening and thermal broadening of the spectral peaks yields intrinsic linewidths of different vibrational modes, which may give insight into molecular conformation and prove to be a powerful tool in future molecular transport characterization.

1.1 Introduction

The research field of nanoscale science and technology has made tremendous progress in the past decades, ranging from the experimental manipulations of single atoms and single molecules to the synthesis and possible applications of carbon nanotubes and semiconductor nanowires [1–3]. As the enormous literature has shown, nanometer scale device structures provide suitable testbeds for the investigations of novel physics in a new regime, especially at the quantum level, such as single electron tunneling or quantum confinement effect [4,5]. On the other hand, as the semiconductor device feature size keeps decreasing, the traditional top-down microfabrications will soon enter the nanometer range, and further continuous downscaling will become scientifically and economically challenging [6]. This will motivate researchers around the world to find alternative ways to meet future increasing computing demands.

With a goal of examining individual molecules as self-contained functioning electronic components, molecular transport characterization is an active part of the research field of nanotechnology [2,3]. In 1974, a theoretical model of a unimolecular rectifier was proposed, according to which a single molecule consisting of an electron donor region and an electron acceptor region separated by a σ bridge would behave as a unimolecular p-n junction [7]. However, an experimental realization of such a unimolecular device was hampered by the difficulties of both the chemical synthesis of this type of molecule and the microfabrication of reliable solid-state test structures. A publication in 1997 reported an observation of such a unimolecular rectification in a device containing Langmuir–Blodgett (L-B) films; however, it is not clear if the observed rectifying behavior had the same mechanism since it was just shown in a single current-voltage $I(V)$ measurement [8]. In the meantime, instead of using L-B films, others proposed to exploit self-assembled conjugated oligomers as the active electronic components [9,10] and started the electrical characterization of monolayers formed by the molecular self-assembly technique [2].

Molecular self-assembly is an experimental approach to spontaneously forming highly ordered monolayers on various substrate surfaces [11,12]. Earlier research in this area includes the pioneering study of alkyl disulfide monolayers formed on gold surfaces [13]. This research field has grown enormously in the past two decades and self-assembled monolayers (SAMs) have found their modern-day applications in various areas, such as nanoelectronics, surface engineering, biosensing, etc. [11].

Various test structures have been developed in order to carry out characterizations of self-assembled molecules, and numerous reports have been published in the past several years on the transport characteristics [2,3,14,15]. Nevertheless, many of them have drawn conclusions on transport mechanisms without performing detailed temperature-dependent studies [14,15], and some of the molecular effects were shown to be due to filamentary conduction in further investigations [16–21], highlighting the need to institute reliable controls and methods to validate true molecular transport [22]. A related problem is the characterization of molecules in the active device structure, including their configuration, bonding, and even their very presence.

In this research work, we conduct electrical characterization of molecular assemblies that exhibit understood classical transport behavior and can be used as a control for eliminating or understanding fabrication variables. A molecular system whose structure and configuration are well-characterized such that it can serve as a standard is the extensively studied alkanethiol $[\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}]$ self-assembled monolayer [11,22–25]. This system forms a single van der Waals crystal on the Au(111) surface [26] and presents a simple classical metal–insulator–metal (MIM) tunnel junction when fabricated between metallic contacts because of the large HOMO–LUMO gap (HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital) of approximately 8 eV [27]. Utilizing a nanometer scale device structure that incorporates alkanethiol SAMs, we demonstrate devices that allow temperature-dependent $I(V)$ [$I(V,T)$] and structure-dependent measurements [24]. The obtained characteristics are further compared with calculations from accepted theoretical models of MIM tunneling, and important transport parameters are derived [24,28].

Electronic transport through alkanethiol SAM is further investigated with the technique of inelastic electron tunneling spectroscopy (IETS) [25,29]. IETS was developed in the 1960s as a powerful spectroscopic tool to study the vibrational spectra of organic molecules confined inside metal–oxide–metal

tunnel junctions [29–31]. In our study, IETS is utilized for the purpose of molecule identification, and the investigation of chemical bonding and the conduction mechanism of the “control” SAM. The exclusive presence of well-known characteristic vibrational modes of the alkane molecules used is direct evidence of the molecules in the device structure, which is the first unambiguous proof of such an occurrence. The 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 [22,25].

1.2 Theoretical Background of Tunneling

1.2.1 Electron Tunneling

Tunneling is a purely quantum mechanical behavior [32,33]. During the tunneling process, a particle can penetrate through a barrier—a classically forbidden region corresponding to negative kinetic energy—and transfer from one classically allowed region to another. This happens because the particle also has wave characteristics. Since the development of quantum mechanics, tunneling phenomena have been studied by both theorists and experimentalists on many different systems [34,35].

One of the extensively studied tunneling structures is the metal–insulator–metal tunnel junction. If two metal electrodes are separated by an insulating film, and the film is sufficiently thin, current can flow between the two electrodes by means of tunneling [34,35]. The purpose of this insulating film is to introduce a potential barrier between the metal electrodes. The tunneling current density for a rectangular barrier can be expressed as [34–36]:

$$J = \left(\frac{e}{4\pi^2 \hbar d^2} \right) \left\{ \left(\Phi_B - \frac{eV}{2} \right) \exp \left[-\frac{2(2m)^{1/2}}{\hbar} \left(\Phi_B - \frac{eV}{2} \right)^{1/2} d \right] - \left(\Phi_B + \frac{eV}{2} \right) \exp \left[-\frac{2(2m)^{1/2}}{\hbar} \left(\Phi_B + \frac{eV}{2} \right)^{1/2} d \right] \right\} \quad (1.1)$$

where m is electron mass, d is barrier width, Φ_B is barrier height, $\hbar (= 2\pi\hbar)$ is Planck's constant, and V is applied bias. In the low bias range, Equation (1.1) can be approximated as [36]:

$$J \approx \left(\frac{e^2 (2m\Phi_B)^{1/2}}{h^2 d} \right) V \exp \left[-\frac{2}{\hbar} (2m\Phi_B)^{1/2} d \right] \quad (1.2)$$

which indicates that the tunneling current increases linearly with the applied bias. It also shows that the current depends on the barrier width exponentially as $J \propto \exp(-\beta_0 d)$. The decay coefficient β_0 can be expressed as:

$$\beta_0 = \frac{2(2m)^{1/2}}{\hbar} (\Phi_B)^{1/2} \quad (1.3)$$

An empirical model related to the complex band theory is the so-called Franz two-band model proposed for an MIM junction in the 1950s [37–41]. Unlike the Simmons model, the Franz model considered the contributions from both the conduction band and valence band of the insulating film by taking into account the energy bandgap of E_g [37]. Instead of giving a tunneling current expression, it empirically predicted a non-parabolic energy-momentum dispersion relationship inside the bandgap [37]:

$$k^2 = \frac{2m^*}{\hbar^2} E \left(1 + \frac{E}{E_g} \right) \quad (1.4)$$

where m^* is the electron's effective mass, and E is referenced relative to the conduction band.

The Franz model is useful for finding the effective mass of the tunneling electron inside the band gap [38–41]. From the non-parabolic $E(k)$ relationship of Equation (1.4), the effective mass can be deduced by knowing the barrier height of the MIM tunnel junction [41]. But when the Fermi level of the metal

electrodes is aligned close to one energy band, the effect of the other distant band on the tunneling transport is negligible, and the Simmons model is a good approximation of the Franz model, as shown in the previous analysis [37,42].

1.2.2 Inelastic Electron Tunneling

Inelastic electron tunneling due to localized molecular vibrational modes was discovered by Jaklevic and Lambe in 1966 when they studied the tunneling effect of metal–oxide–metal junctions [29]. Instead of finding band structure effects due to metal electrodes as they initially hoped, they observed structures in the d^2I/dV^2 characteristics which were related to vibrational excitations of molecular impurities contained in the insulator [29,43]. IETS has since been developed into a powerful spectroscopic tool for various applications such as chemical identification, bonding investigation, trace substance detection, and so on [30,31].

Figure 1.1 shows the energy band diagrams of a tunnel junction and the corresponding $I(V)$ plot. When a negative bias is applied to the left metal electrode, the left Fermi level is lifted. An electron from an occupied state on the left side tunnels into an empty state on the right side, and its energy is conserved (process a). This is the elastic process discussed in section 2.1. During this process, the current increases linearly with the applied small bias [Figure 1.1(b)]. However, if there is a vibrational mode with a frequency of ν localized inside this barrier, then when the applied bias is large enough such that $eV \geq h\nu$, the electron can lose a quantum of energy of $h\nu$ to excite the vibration mode and tunnel into another empty state (process b) [44,45]. This opens an inelastic tunneling channel for the electron and its overall tunneling probability is increased. Thus, the total tunneling current has a kink as a function of the applied bias [Figure 1.1(b)]. This kink becomes a step in the differential conductance (dI/dV) plot, and turns into a peak in the d^2I/dV^2 plot. However, since only a small fraction of electrons tunnel inelastically, the conductance step is too small to be conveniently detected. In practice, people use a phase-sensitive detector (“lock-in”) second harmonic detection technique to directly measure the peaks of the second derivative of $I(V)$ [44].

After an IETS spectrum is obtained, the positions, widths, and intensities of the spectral peaks need to be comprehended. The peak position and width can be predicted on very general grounds, independent

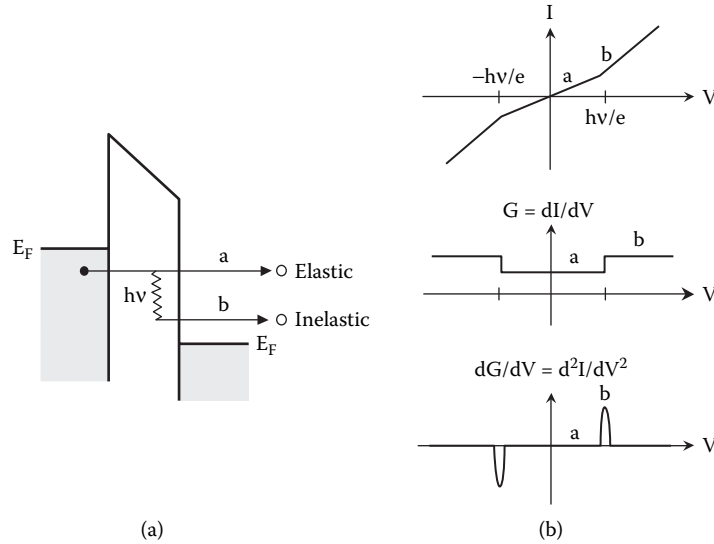


FIGURE 1.1 (a) Energy band diagram of a tunnel junction with a vibrational mode of frequency ν localized inside. a is the elastic tunneling process, while b is the inelastic tunneling process. (b) Corresponding $I(V)$, dI/dV , and d^2I/dV^2 characteristics.

of the electron–molecule interaction details. However, the peak intensity is more difficult to be calculated since it depends on the detailed aspects of the electron-molecule couplings [44].

1.2.2.1 Peak Identification

As discussed earlier, an inelastic process can only start to occur when the applied bias reaches $V_i = \hbar\nu_i/e$ [29]. Therefore, a peak at a position of bias V_i corresponds directly to a molecular vibrational mode of energy $\hbar\nu_i$. This conclusion is based on energy conservation and is independent of the mechanism for the electron–molecule coupling. By referring to the huge amount of assigned spectra obtained by other techniques such as infrared (IR), Raman, and high-resolution electron energy loss spectroscopy (HREELS), the IETS peaks can be identified individually [43–45].

1.2.2.2 Peak Width

According to IETS theoretical studies, the width of a spectral peak includes a natural intrinsic linewidth and two width broadening effects: thermal broadening that is due to the Fermi level smearing effect, and modulation broadening that is due to the dynamic detection technique used to obtain the second harmonic signals [44].

The thermal broadening effect was first studied by Lambe and Jaklevic [43,46]. Assuming that the voltage dependence of the tunneling current is only contained in the Fermi functions of the metal electrodes, and the energy dependence of the effective tunneling density of states is negligible, the predicted thermal linewidth broadening at half maximum is $5.4 kT/e$ [43,46]. This broadening prediction has been confirmed by experimental studies [47].

The broadening effect due to the finite modulation technique was first discussed by Klein *et al.* [46]. Assuming a modulation voltage of V_ω at a frequency of ω is applied to the tunnel junction, the full width at half maximum for the modulation broadening is $1.2 V_\omega$, or $1.7 V_{rms}$, the rms value of the modulation voltage, which is usually measured directly [44,46].

Of these two broadening contributions, the modulation broadening is more dominant [45]. By lowering the measurement temperature, the thermal broadening effect can be reduced—for example, at liquid helium temperature it gives a resolution of 2 meV. In order to make the modulation broadening comparable to the thermal effect, the modulation voltage should be less than 1.18 mV. However, since the second harmonic signal is proportional to the square of the modulation voltage and the signal-to-noise improvements varies with the square root of the averaging time, at such a small modulation the measurement time would be impractically extended. Therefore, little is gained by further lowering measurement temperature since the modulation broadening is more dominant [45].

The experimentally obtained spectral peak linewidth, W_{exp} , consists of three parts: the natural intrinsic linewidth, $W_{intrinsic}$; the thermal broadening $W_{thermal}$ that is proportional to $5.4 kT$; and the modulation broadening $W_{modulation}$ that is proportional to $1.7 V_{rms}$. These three contributions add as squares [43,48]:

$$W_{exp} = \sqrt{W_{intrinsic}^2 + W_{thermal}^2 + W_{modulation}^2} \quad (1.5)$$

1.2.2.3 Peak Intensity

After the experimental discovery of inelastic electron tunneling due to molecular vibrations, several theoretical models were proposed for the purpose of quantitative analysis of the IETS spectra. The first theory was developed by Scalapino and Marcus in order to understand the interaction mechanism [49]. They treated the electron–molecule coupling as a Coulomb interaction between the electron and the molecular dipole moment and considered the case where the molecule of dipole moment is located very close to one of the electrodes so that the image dipole must be included. The interaction potential was treated as a perturbation on the barrier potential that was assumed to be rectangular. Using the WKB approximation, they could estimate the ratio of the inelastic conductance to the elastic one and predict that the intensities in a tunneling spectrum should be the same as in an infrared spectrum. However, it is found experimentally

that although large peaks in IR spectra usually correspond to large peaks in tunneling spectra, the proportionality is not exact. Furthermore, peaks that are completely absent in IR spectra also appear in tunneling spectra [44].

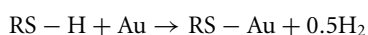
Lambe and Jaklevic studied other mechanisms for electron–molecule interactions and generalized the preceding treatment to include the Raman type of interaction, where the electron induces a dipole moment in the molecule and interacts with this induced dipole [43]. Their calculation showed that the Raman-type interaction produces inelastic conductance changes of nearly the same order of magnitude as the IR-type electron–dipole interaction.

The preceding dipole approximations provided clear physical pictures of the interaction mechanisms of the tunneling electron and the localized molecular vibration; however, the calculations were oversimplified. Using the transfer Hamiltonian formalism [50,51], Kirtley *et al.* developed another theory for the intensity of vibrational spectra in IETS [44,52,53]. Rather than making the dipole approximation, they assumed that the charge distribution within the molecule can be broken up into partial charges, with each partial charge localized on a particular atom. These partial charges arise from an uneven sharing of the electrons involved in the bonding. The interaction potential between the tunneling electron and the vibrating molecule is thus a sum of Coulomb potentials with each element in the sum corresponding to a partial charge. This partial charge treatment allows one to describe the interaction at distances comparable to interatomic length. The inelastic tunneling matrix element, which corresponds to the tunneling transmission coefficient, can be calculated considering the WKB wave functions and the partial charge interaction potential [52]. The calculation results show that molecular vibrations with net dipole moments normal to the junction interface have larger inelastic cross sections than vibrations with net dipole moments parallel to the interface for dipoles close to one electrode. This is because when this close to a metal surface the image dipole adds to the potential of a dipole normal to the interface but tends to cancel out the potential of a dipole parallel to the interface. However, the case is different for vibrational modes localized deep inside the tunnel junction, where dipoles oriented parallel to the junction interface are favored, although at a lower scattering amplitude [44,52,53].

1.3 Experimental Methods

1.3.1 Self-Assembled Monolayers of Alkanethiols

Molecular self-assembly is a chemical technique to form highly ordered, closely packed monolayers on various substrates via a spontaneous chemisorption process at the interface [11]. Alkanethiol is a thiol-terminated *n*-alkyl chain molecular system $[\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}]$ [11]. As an example, Figure 1.2(a) shows the chemical structure of octanethiol, one of the alkanethiol molecules. It is well known that when self-assembled on Au(111), surface alkanethiol forms a densely packed, crystalline-like structure with the alkyl chain in an all-trans conformation [13]. The SAM deposition process is shown in Figure 1.2(b), where a clean gold substrate is immersed into an alkanethiol solution and, after time, a monolayer is formed spontaneously on the gold surface via the following chemical reaction [11,12,54]:



where R is the backbone of the molecule. This chemisorption process has been observed to undergo two steps: a rapid process that takes minutes (depending on the thiol concentration) and gives $\sim 90\%$ of the film thickness, followed by a second, much slower process that lasts hours and reaches the final thickness and contact angles [11,12]. Research has shown that the second process is governed by a transition from a SAM lying-down phase into an ordered standing-up phase, and it is also accompanied or followed by a crystallization of the alkyl chains associated with molecular reorganization [11,55–57]. Three forces likely determine this SAM formation process and the final monolayer structure: the interaction between the thiol head group and gold lattice, the dispersion force between alkyl chains (the van der Waals force, etc.), and the interaction between the end groups [11,12].

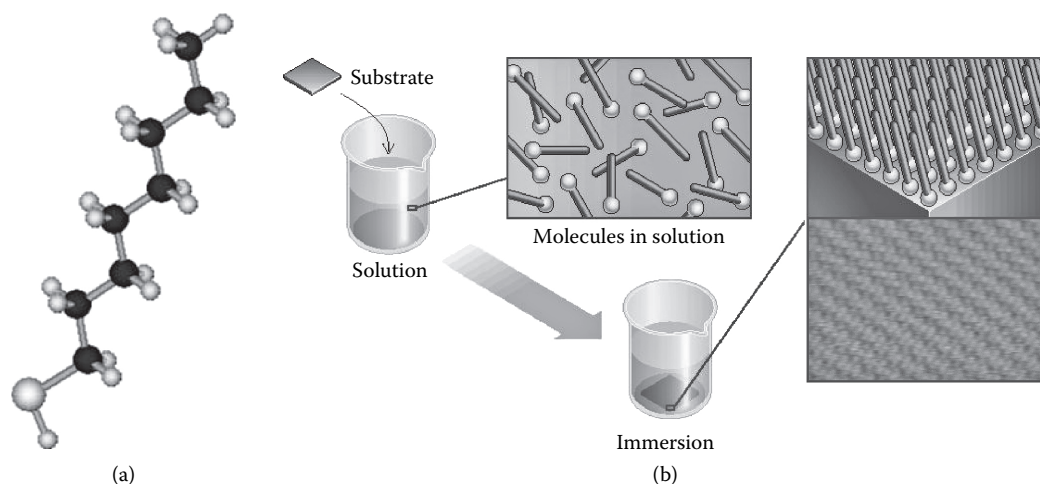


FIGURE 1.2 (a) Chemical structure of an octanethiol molecule. (b) Schematic of the SAM deposition process, after Ref. 54 and 61. It also shows an STM image of the SAM [see Figure 1.3].

Various surface analytical tools have been utilized to investigate the surface and bulk properties of alkanethiol SAMs, such as infrared (IR) and Fourier transform infrared (FTIR) spectroscopy [13,58], x-ray photoelectron spectroscopy (XPS) [59], Raman spectroscopy [60], scanning tunneling microscopy (STM) [23,61], etc. As an example, Figure 1.3(a) shows a constant current STM image of a dodecanethiol SAM formed on an Au(111) surface (adapted from Reference 61). Figure 1.3(b) is the schematic of the commensurate crystalline structure that alkanethiol SAM adopts, which is characterized by a $c(4 \times 2)$ superlattice of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice [23,62]. In Figure 1.3(b), the large circular symbols represent the alkanethiol molecules and the small circular symbols represent the underlying gold atoms, and a and b are lattice vectors of the molecular rectangular unit cell with dimensions of 0.8 and 1.0 nm, respectively [61]. Investigations have also shown that the standing-up alkyl chains of alkanethiol SAMs on the Au(111)

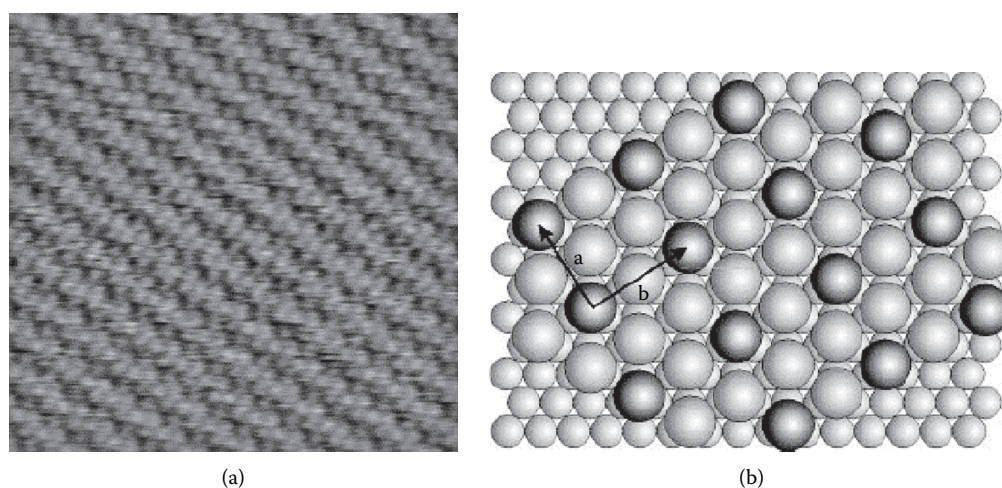


FIGURE 1.3 (a) STM image of a dodecanethiol SAM formed on Au(111) surface. The image size is $13 \times 13 \text{ nm}^2$. (b) Schematic of the alkanethiol SAM commensurate crystalline structure. Large circular symbols represent the alkanethiol molecules, and small circular symbols represent the underlying gold atoms. a and b are lattice vectors of a rectangular unit cell with dimensions of 0.8 and 1.0 nm, respectively. After Ref. 61.

surface are tilted $\sim 30^\circ$ from the surface normal [62] and the bonding energy between the thiolate head group and the gold lattice is ~ 40 kcal/mol (~ 1.7 eV) [11].

Studies have revealed that defects, such as pinholes or grain boundaries, exist in the self-assembled monolayers, and the domain size of an alkanethiol SAM usually is on the order of several hundred Ångströms [11,23]. In addition to the irregularities introduced during the self-assembly process, another source of the defects is the roughness of the substrate surface. For example, although frequently called “flat” gold, grain boundaries exist on the Au surface layer, which introduce defects into the assembled monolayer [23]. However, surface migration of thiolate–Au molecules, the so-called SAM annealing process, is found to be helpful for healing some of the defects [11,23].

Alkanethiols are large HOMO–LUMO gap (~ 8 eV [27,63–66]) molecules with short molecular lengths ($\sim$ several nanometers), therefore the electronic transport mechanism is expected to be tunneling. Electrical characterizations have been performed on alkanethiol SAMs and will be discussed in the next section.

1.3.2 Methods of Molecular Transport Characterization

A correct understanding of the electronic transport properties through self-assembled molecules requires fabrication methods that can separate the effects of contacts from the intrinsic properties of the molecular layer. However, such transport measurements are experimentally challenging due to the difficulties of making repeatable and reliable electrical contacts to a nanometer-scale layer. A number of experimental characterization methods have been developed to achieve this goal, and in the following we briefly review some of the major techniques.

Various scanning probe–related techniques have been utilized for the study of molecular electronic structures, which include STM and atomic force microscopy (C-AFM). STM has been used widely at the early stage of molecular characterization due to its capability to image, probe, and manipulate single atoms or molecules [67–69]. Transport measurement on a single molecule contacted by STM has also been reported [70–73]. However, for such a measurement, the close proximity between the probe tip and the sample surface could modify what is being measured by tip-induced modification of the local surface electronic structure. The presence of a vacuum gap between the tip and the molecule also complicates the analysis [74]. Besides, contamination could occur if the measurement is taken in ambient conditions; therefore, inert gas (nitrogen or argon) filled or vacuum STM chamber is preferred [75,76].

The C-AFM technique also has been employed recently for the purpose of electrical characterizations of SAMs [77–80]. For example, Wold *et al.* reported C-AFM measurements on alkanethiol molecules [77]; Cui *et al.* bound gold nanoparticles to alkanedithiol in a monothiol matrix and measured its conductance [78]. However, in this technique the C-AFM tip might penetrate and/or deform the molecular layer as well as create a force-dependent contact junction area. Adhesion force analysis (to rule out deformation or penetration) and a complimentary temperature-dependent characterization need to be performed to make C-AFM measurements a broadly applicable method for determining molecular conductivity [28].

Another important characterization method is the mechanically controllable break junction technique [81–84]. It can create a configuration of a SAM sandwiched between two stable metallic contacts, and two-terminal $I(V)$ characterizations can be performed on the scale of single molecules [81]. In the fabrication process, a metallic wire with a notch is mounted onto an elastic bending beam and a piezo electric element is used to bend the beam and thus break the wire. The wire breaking is carried out in the molecular solution and after the breaking the solvent is allowed to evaporate, then the two electrodes are brought back together to form the desired molecular junction [84]. A lithographically fabricated version of the break junction uses e-beam lithography and the lift-off process to write a gold wire on top of an insulating layer of polyimide on a metallic substrate. The polyimide is then partially etched away and a free standing gold bridge is left on the substrate. The suspended gold bridge is then bent and broken mechanically using a similar technique to form a nanometer scale junction [83]. Using the break junction method, Reed *et al.* measured the charge transport through a benzene-1,4-dithiol molecule at room temperature [81]. Using a similar technique, Kergueris *et al.* [82] and Reichert *et al.* [83] performed conductance measurements on SAMs and concluded that $I(V)$ characterizations of a few or individual molecules were achieved.

Recently, another type of break junction that utilizes the electromigration properties of metal atoms has been developed [85–87]. For this testbed, a thin gold wire with a width of several hundred nanometers is created via e-beam lithography and angle evaporation [85]. Bias is then applied and a large current passing through this nanoscale wire causes the gold atoms to migrate, thus creating a small gap a few nanometers wide. Molecules are deposited on the wire at room temperature before electro-breaking at cryogenic temperatures [86]. The advantage of this technique is that a third gating electrode can be introduced; therefore, three-terminal characterizations can be achieved. Using this electromigration break junction technique, Park *et al.* measured two types of molecules at cryogenic temperatures and observed Coulomb blockade behavior and the Kondo effect [86]. Similar Kondo resonances in a single molecular transistor were also observed by Liang *et al.* using the same test structure on a different molecular system [87]. However, in these measurements the molecules just serve as impurity sites [87], and the intrinsic molecular properties have yet to be characterized.

The cross-wire tunnel junction is a test structure reported in 1990 in an attempt to create an oxide-free tunnel junction for IETS studies [88]. It is formed by mounting two wires in such a manner that the wires are in a crossed geometry with one wire perpendicular to the applied magnetic field. The junction separation is then controlled by deflecting this wire with the Lorentz force generated from a direct current [88]. Using this method, Kushmerick *et al.* recently studied various molecules and observed conductance differences due to molecular conjugation and molecular length differences [89,90]. The drawback of this method is that it is very difficult to control the junction gap distance: the top wire might not touch the other end of the molecules or it might penetrate into the monolayer. Furthermore, temperature-variable measurement has not been reported using this test structure.

Other experimental techniques utilized in molecular transport studies include the mercury-drop junction [91,92] and the nanorod [93], among many others. For example, the mercury-drop junction consists of a drop of liquid Hg, supporting an alkanethiol SAM, in contact with the surface of another SAM supported by a second Hg drop [91,92]. This junction has been used to study the transport through alkanethiol SAMs, but the measurement can only be performed at room temperature [91].

For the research conducted in this work, we mainly use the so-called nanopore technique [24,94,95]. Using the nanopore method, we can directly characterize a small number of self-assembled molecules ($\sim$ several thousand) sandwiched between two metallic contacts. The contact area is around 30 to 50 nm in diameter, which is close to the domain size of the SAM [11]. Thus, the adsorbed monolayer is highly ordered and mostly defect free. This technique guarantees good control over the device area and intrinsic contact stability and can produce a large number of devices with acceptable yield so that statistically significant results can be achieved. Fabricated devices can be easily loaded into cryogenic or magnetic environments; therefore, critical tests of transport mechanisms can be carried out.

1.3.3 Device Fabrication

Figure 1.4 shows the process flow diagram of the nanopore fabrication. The fabrication starts with double-side polished 3-inch (100) silicon wafers with a high resistivity ($\rho > 10 \Omega \cdot \text{cm}$). The thickness of the substrate is 250 μm . Using the low pressure chemical vapor deposition (LPCVD) method, a low stress Si_3N_4 film of 50 nm thick is deposited on both sides of the wafer. A low stress film is required in order to make the subsequent membrane less sensitive to mechanical shocks. Next, a 400 $\mu\text{m} \times 400 \mu\text{m}$ window is opened on the backside of the substrate via standard photolithography processing and reactive ion etching (RIE). Before the photolithography step, the topside of the substrate is coated with FSC (front side coating) to protect the nitride film. This FSC is removed after RIE by first soaking in acetone and then isopropanol alcohol. The exposed silicon is then etched through by anisotropic wet etching with the bottom nitride as the etch mask. The etchant is an 85% KOH solution heated to 85 to 90°C, and during the etching a magnetic stirrer is used to help the gas byproducts escape. At the end of the KOH etching, an optically transparent membrane of 40 $\mu\text{m} \times 40 \mu\text{m}$ is left suspended on the topside of the wafer. Figure 1.5(a) is an optical image of the suspended transparent membrane.

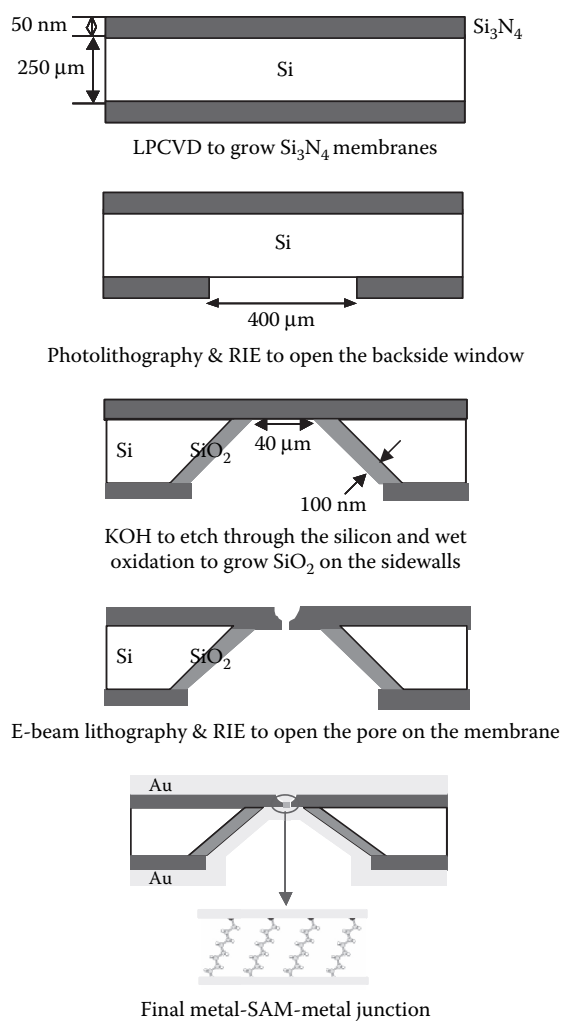


FIGURE 1.4 Schematics of the nanopore fabrication process.

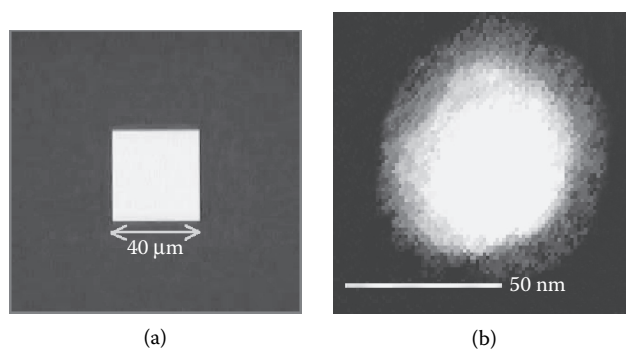


FIGURE 1.5 (a) Optical image of the membrane (topside view). (b) TEM image of an etched-through nanopore.

The wafer is carefully rinsed in water and then immersed in an isotropic silicon etchant ($\text{HNO}_3\text{:H}_2\text{O:HF} = 300\text{:}150\text{:}2$) for 5 minutes to remove any remaining silicon nodules on the membrane and to round out the sharp edges. The wafer is subsequently cleaned with the standard RCA cleaning process to remove any organic and metallic contaminations and then loaded into a wet oxidation furnace to oxidize the exposed silicon sidewalls for the purpose of preventing future electrical leakage current through the substrate. In order to reduce the thermal stress to the membrane caused by this high-temperature process, the wafer is loaded very slowly in and out of the furnace. A wet oxidation processing at 850°C for 60 minutes grows $\sim 1000\text{ \AA}$ SiO_2 on the sidewalls, which is enough to provide a good electrical insulation.

The last, and most critical, steps are the electron beam (e-beam) lithography and subsequent RIE etching to open a nanometer scale pore on the membrane. For the e-beam patterning, the PMMA thickness is 200 nm (4% 495K in anisole spun at 3500 rpm) and the e-beam dosage is between 40 to 300 mC/cm^2 . After the exposure, the wafer is developed in MIBK:IPA of 1:1 for 60 seconds and then loaded into an RIE chamber to transfer the developed patterns. A CHF_3/O_2 plasma is used to etch the hole in the membrane and the etching time is varied from 2 to 6 minutes for a 50-nm thick nitride film. The RIE chamber has to be cleaned thoroughly by an O_2 plasma before the etching and every 2 minutes during the etching to remove the hydrocarbon residues deposited in the chamber. The etching is severely impeded deep in the pore due to the redeposition of hydrocarbon on the sidewalls; therefore, the opening at the far side is much smaller than that actually patterned, rendering a bowl-shaped cross section. After the etching is completed, the PMMA residue is stripped off in the O_2 plasma.

SEM and TEM (Transmission Electron Microscope) examination and metallization have been used to determine if a pore is etched through. If not, further etching is performed until the hole is completely open. As an example, a TEM picture of an etched nanopore is shown in Figure 1.5(b). The size of the hole is roughly 50 nm in diameter, small enough to be within the domain size of both the evaporated gold film and the SAM layer. However, SEM and TEM examination is very time consuming and a more practical way to verify whether the pore is etched open is to deposit metal contacts on both sides of the membrane and measure the junction resistance. For a completely etched pore, $I(V)$ measurement on a regular probe station usually shows a good ohmic short with a resistance of several ohms. For a non-etched-through device, $I(V)$ measurement shows an open-circuit characteristic with a current level of $\sim \text{pA}$ at 1.0 Volt.

After the nanofabrication, 150 nm of gold is thermally evaporated onto the topside of the membrane to fill the pore and form one of the metallic contacts. The device is then transferred into a molecular solution to deposit the SAM. This deposition is done for 24 hours inside a nitrogen filled glove box with an oxygen level of less than 100 ppm. The sample is then rinsed with the deposition solvent and quickly loaded in ambient conditions into an evaporator with a cooling stage to deposit the opposing Au contact. A challenging step in fabricating molecular junctions is to make the top electrical contact. During the fabrication of metal–SAM–metal junctions, metallic materials deposited on the top of molecules often either penetrate through the thin molecular layer or contact directly with the substrate via defect sites (such as grain boundaries) in the monolayer, causing shorted circuit problems. Examination showed that $\sim 90\%$ of the devices were shorted with ambient temperature evaporation [74]; therefore, a low-temperature deposition technique is adopted [24,95]. During the thermal evaporation under the pressure of $\sim 10^{-8}$ Torr, liquid nitrogen is kept flowing through the cooling stage to minimize the thermal damage to the molecular layer. This technique reduces the kinetic energy of evaporated Au atoms at the surface of the monolayer, thus preventing Au atoms from punching through the SAM. For the same reason, the evaporation rate is kept very low. For the first 10 nm of gold evaporated, the rate is less than $0.1\text{ \AA/s}$. Then the rate is increased slowly to $0.5\text{ \AA/s}$ for the remainder of the evaporation, and a total of 200 nm of gold is deposited to form the contact.

Preliminary $I(V)$ measurements are carried out on a probe station at room temperature to screen out the functioning devices from those exhibiting either short circuit (top and bottom electrodes are shorted together) or open circuit (the nitride membrane is not etched through). The wafer is then diced into individual chips and the working devices are bonded onto a 16-pin packaging socket for further electrical characterizations.

1.3.4 Lock-in Measurement for IETS Characterizations

The IETS signal, which is proportional to the second derivative of $I(V)$, is usually measured by an AC modulation method, the so-called lock-in technique [29,31]. Theoretically, the signal can also be determined by the mathematical differential approach that computes the numerical derivatives of the directly measured $I(V)$ characteristics [96]. But this is generally not feasible in practice. On the contrary, the lock-in second harmonic detection technique measures a quantity directly proportional to d^2I/dV^2 [30,31]. During the lock-in measurement, a small sinusoidal signal is applied to modulate the voltage across the device, and the response of the current through the device to this modulation is studied. The detection of the first (ω) and second (2ω) harmonic signals give the scaled values of the first and second derivatives of $I(V)$, respectively.

Experimentally, this modulation detection is realized by a lock-in amplifier. In our experiment, a typical DC source is used as the DC voltage provider, and a synthesized function generator is used as the AC modulation source, as well as to provide the reference signal to the lock-in amplifier. The DC bias and AC modulation are attenuated and mixed together by a custom-built voltage adder and then applied to the device under test (DUT). If a higher bias range is desired, a voltage shifter is included in the measurement setup before the DUT to increase the DC base voltage. An I-V converter is used if the voltage input of the lock-in amplifier is chosen for the measurement. The output of the lock-in amplifier is read by a digital multimeter.

1.4 Electronic Conduction Mechanisms in Self-Assembled Alkanethiol Monolayers

1.4.1 Conduction Mechanisms of Metal-SAM-Metal Junctions

In a metal-SAM-metal system, just as in a metal-semiconductor-metal junction, the Fermi level alignment is critical in determining the charge transport mechanism [97]. Created by the overlap of the atomic orbitals of a molecule's constituents, two molecular orbitals, lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), play similar roles as conduction band and valence band in a semiconductor, respectively. The energy difference between them, the HOMO–LUMO gap, is typically of the order of several electron volts [2,3]. In general, the Fermi level of the metallic contacts does not energetically align with either the HOMO or the LUMO of the molecule, but instead lies close to the center of the gap [98]. This energy level mismatch gives rise to a contact barrier, and depending on the height and thickness of this barrier and the presence of defects, charge transport in such a metal-SAM-metal system exhibits a variety of behaviors. Table 1.1 gives a summary of possible conduction mechanisms with their characteristic behavior, temperature dependence, and voltage dependence [22,24,99–101].

Based on whether thermal activation is involved, the conduction mechanisms fall into two distinct categories: (1.1) thermionic or hopping conduction which has temperature-dependent $I(V)$ behavior, and (1.2) direct tunneling or Fowler–Nordheim tunneling which does not have temperature-dependent $I(V)$ behavior. Thermionic emission is a process in which carriers overcome the metal-dielectric barrier by thermal agitation, and the current has a strong dependence on temperature. The extra voltage term in

TABLE 1.1 Possible Conduction Mechanisms. J is the Current Density, d is the Barrier Width, T is the Temperature, V is the Applied Bias, and Φ is the Barrier Height. After Ref. 99

Conduction Mechanism	Characteristics Behavior	Temperature Dependence	Voltage Dependence
Direct Tunneling	$J \sim V \exp(-\frac{2d}{h} \sqrt{2m\Phi})$	None	$J \sim V$
Fowler-Nordheim Tunneling	$J \sim V^2 \exp(-\frac{4d\sqrt{2m\Phi^{3/2}}}{3qhV})$	None	$\ln(\frac{J}{V^2}) \sim \frac{1}{V}$
Thermionic Emission	$J \sim T^2 \exp(-\frac{\Phi - q\sqrt{qV/4\pi\epsilon d}}{kT})$	$\ln(\frac{J}{T^2}) \sim \frac{1}{T}$	$\ln(J) \sim V^{\frac{1}{2}}$
Hopping Conduction	$J \sim V \exp(-\frac{\Phi}{kT})$	$\ln(\frac{J}{V}) \sim \frac{1}{T}$	$J \sim V$

the exponential is due to image-force correction and it lowers the barrier height at the metal–insulator interface. Hopping conduction usually is defect-mediated, and in a hopping process the thermally activated electrons hop from one isolated state to another, and the conductance also depends strongly on temperature. However, unlike thermionic emission, there is no barrier-lowering effect in hopping transport. Tunneling processes (both direct and Fowler–Nordheim tunnelings) do not depend on temperature (to first order), but strongly depend on film thickness and voltage [99–101]. After a bias is applied, the barrier shape of a rectangular barrier is changed to a trapezoidal form. Tunneling through a trapezoidal barrier is called direct tunneling because the charge carriers are injected directly into the electrode. However, if the applied bias becomes larger than the initial barrier height, the barrier shape is further changed from trapezoidal to a triangular barrier. Tunneling through a triangular barrier, where the carriers tunnel into the conduction band of the dielectric, is called Fowler–Nordheim tunneling or field emission [99,100].

For a given metal–insulator–metal system, certain conduction mechanism(s) may dominate in certain voltage and temperature regimes. For example, thermionic emission usually plays an important role for high temperatures and low barrier heights. Hopping conduction is more likely to happen at low applied bias and high temperature if the insulator has a low density of thermally generated free carriers in the conduction band. Tunneling transport will occur if the barrier height is large and the barrier width is thin.

Temperature-variable $I(V)$ characterization is an important experimental technique to elucidate the dominant transport mechanism and to obtain key conduction parameters such as effective barrier height. This is especially crucial in molecular transport measurements where defect-mediated conduction often complicates the analysis. For example, previous work on self-assembled thiol-terminated oligomers illustrated that one can deduce the basic transport mechanisms by measuring the $I(V,T)$ characteristics [95]. It has been found that the physisorbed aryl–Ti interface gave a thermionic emission barrier of approximately 0.25 eV [95]. Another study on Au–isocyanide SAM–Au junctions showed both thermionic and hopping conduction with barriers of 0.38 and 0.30 eV, respectively [74].

In this research work, we investigate the charge transport mechanism of self-assembled alkanethiol monolayers. $I(V,T)$ characterizations are performed on certain alkanethiols to distinguish between different conduction mechanisms. Electrical measurements are also carried out on alkanethiols with different molecular length to further examine length-dependent transport behavior.

1.4.2 Previous Research on Alkanethiol SAMs

Alkanethiol SAM $[\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}]$ is a molecular system whose structure and configuration are sufficiently well-characterized such that it can serve as a test standard [11]. This system is useful as a control since properly prepared alkanethiol SAM forms a single van der Waals crystal [11,23]. This system also presents a simple classical MIM tunnel junction when fabricated between two metallic contacts due to its large HOMO–LUMO gap of ~ 8 eV [27,63–66].

Electronic transport through alkanethiol SAMs have been characterized by STM [70,73], conducting atomic force microscopy [77–80], mercury-drop junctions [91,92,102,103], cross-wire junctions [89], and electrochemical methods [104–106]. However, due to the physical configurations of these test structures it is very hard, if not impossible, to perform temperature-variable measurements on the assembled molecular layers; therefore, these investigations were done exclusively at ambient temperature, which is insufficient for an unambiguous claim that the transport mechanism is tunneling (which is expected, assuming that the Fermi level of the contacts lies within the large HOMO–LUMO gap). In the absence of $I(V,T)$ characteristics, other transport mechanisms such as thermionic, hopping, or filamentary conduction can contribute and complicate the analysis. Previous $I(V)$ measurements performed at room and liquid nitrogen temperatures on Langmuir–Blodgett alkane monolayers exhibited a large impurity-dominated transport component [107,108], further emphasizing the need and significance of $I(V,T)$ measurement in SAM characterizations.

Using the nanopore test structure that contains alkanethiol SAMs, we demonstrate devices that allow $I(V,T)$ and length-dependent measurements [24,25], and show that the experimental results can be compared with theoretical calculations from accepted models of MIM tunneling.

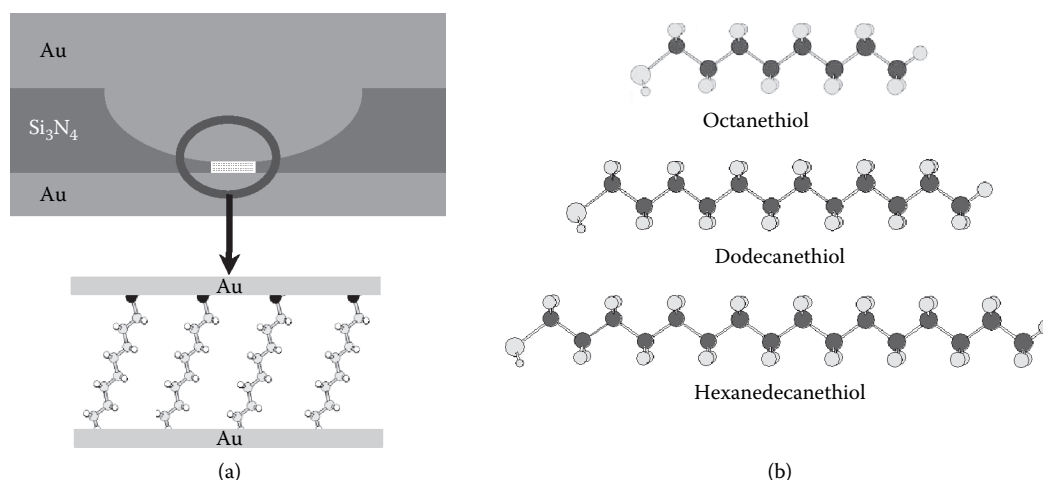


FIGURE 1.6 (a) Schematic of the nanopore structure used in this study. (b) Chemical structures of octanethiol, dodecanethiol, and hexadecanethiol.

1.4.3 Sample Preparation

Electronic transport measurement on alkanethiol SAMs is performed using the nanopore testbed [Figure 1.6(a)]. After 150 nm of gold is thermally evaporated onto the topside of the wafer, the sample is transferred into a molecular solution to deposit the SAM layer. For our experiments, a ~ 5 mM alkanethiol solution is prepared by adding ~ 10 μL of alkanethiols into 10 mL of ethanol. The deposition is done in solution for 24 hours inside a nitrogen-filled glove box with an oxygen level of less than 100 ppm. Three alkanethiol molecules of different molecular lengths—octanethiol [$\text{CH}_3(\text{CH}_2)_7\text{SH}$; denoted as C8, for the number of alkyl units]; dodecanethiol [$\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, denoted as C12]; and hexadecanethiol [$\text{CH}_3(\text{CH}_2)_{15}\text{SH}$, denoted as C16]—were used to form the active molecular components. The chemical structures of these molecules are shown in Figure 1.6(b). The sample is then rinsed with ethanol and transferred to the evaporator for the deposition of 200 nm of gold onto the bottom side. Next, it is packaged and loaded into a low-temperature cryostat for electrical characterizations.

In order to statistically determine the pore size, test patterns (arrays of pores) were created under the same fabrication conditions (e-beam dose and etching time) as the real devices. Figure 1.7 shows a scanning electron microscope image of one such test pattern array. This indirect method for the measurement of device size is adopted because SEM examination of the actual device can cause hydrocarbon contamination of the device and subsequent contamination of the monolayer. Using SEM, the diameters have been examined for 112 pores fabricated with an e-beam dose of $100 \text{ mC}/\text{cm}^2$ and an etching time of 4.5 minutes, 106 pores fabricated with an e-beam dose of $100 \text{ mC}/\text{cm}^2$ and an etching time of 7 minutes, 130 pores fabricated with an e-beam dose of $200 \text{ mC}/\text{cm}^2$ and etching time of 6 minutes, and 248 pores fabricated with an e-beam dose of $300 \text{ mC}/\text{cm}^2$ and an etching time of 6 minutes. These acquired diameters were used as the raw data input file for the statistics software Minitab. Using Minitab, a regression analysis has been conducted on the device size as a function of e-beam dose and etching time, and a general size relation is obtained:

$$\text{Size(in nm)} = 35.0 + 0.027 \times \text{dose(in mC/cm}^2\text{)} + 1.63 \times \text{time(in min)}$$

Using the same software, a device size under particular fabrication conditions can be predicted via entering the fabrication dose and etching time. The error range of the size is determined by specifying a certain confidence interval. For example, the fabrication conditions for the C8, C12, and C16 devices that are used in the length dependence study are an e-beam dose of $100 \text{ mC}/\text{cm}^2$ and an etching time of

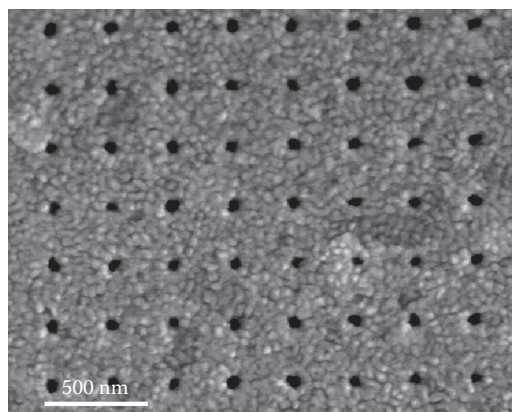


FIGURE 1.7 A representative scanning electron microscope image of an array of pores used to calibrate device size. The scale bar is 500 nm.

7 minutes, 88 mC/cm^2 and 4.5 minutes, and 85 mC/cm^2 and 5 minutes, respectively. From the regression analysis, the device sizes of the C8, C12, and C16 samples are predicted as 50 ± 8 , 45 ± 2 , and 45 ± 2 nm in diameters with a 99% confidence interval, respectively. We will use these device sizes 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 it would be a constant systematic error.

1.4.4 Tunneling Characteristics of Alkanethiol SAMs

1.4.4.1 $I(V,T)$ Characterization of Alkane SAMs

In order to determine the conduction mechanism of self-assembled alkanethiol molecular systems, $I(V,T)$ measurements in a sufficiently wide temperature range (300 to 80 K) and resolution (10 K) on dodecanethiol (C12) were performed. Figure 1.8 shows representative $I(V,T)$ characteristics measured with the device structure shown in Figure 1.6(a). Positive bias in this measurement corresponds to electrons injected from the physisorbed Au contact [the bottom contact in Figure 1.6(a)] into the molecules. By using the contact area of 45 ± 2 nm in diameter determined from the SEM study, a current density of

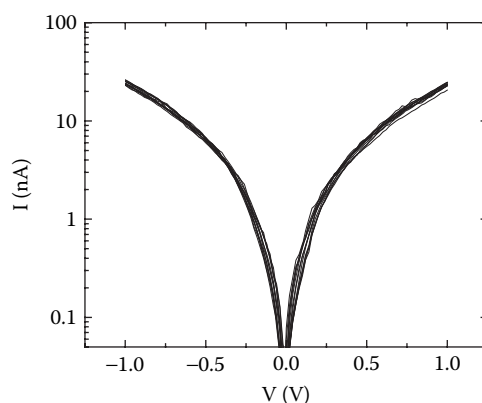


FIGURE 1.8 Temperature-dependent $I(V)$ characteristics of dodecanethiol. $I(V)$ data at temperatures from 300 to 80 K with 20 K steps are plotted on a log scale.

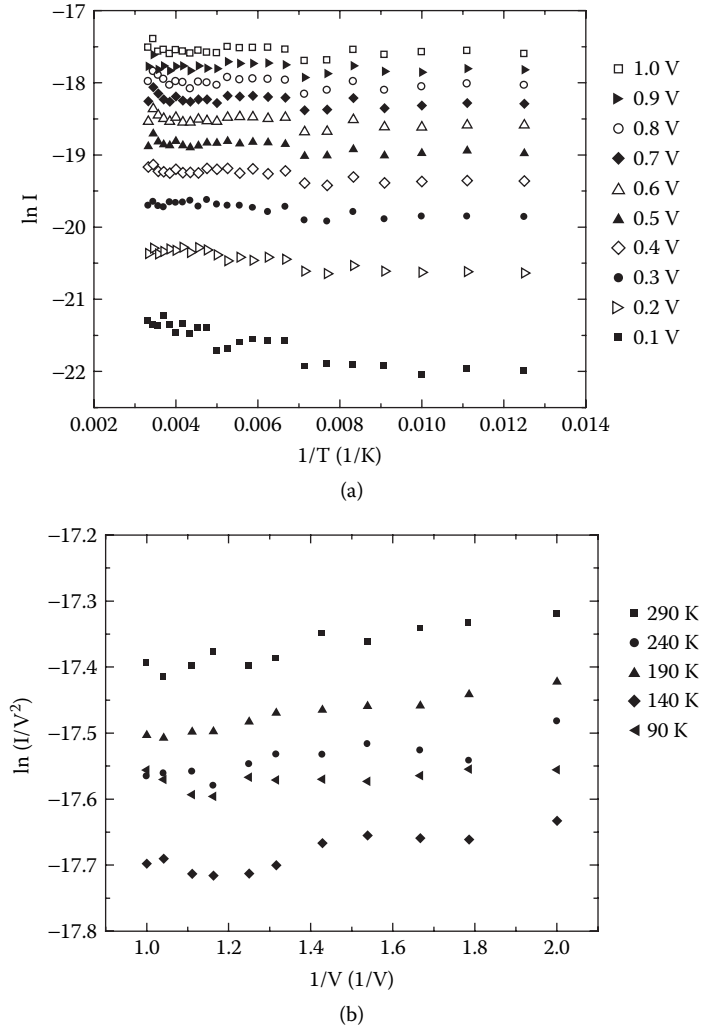


FIGURE 1.9 (a) Arrhenius plot generated from the $I(V,T)$ data in Figure 1.8 at voltages from 0.1 to 1.0 Volt with 0.1 Volt steps. (b) Plot of $\ln(I/V^2)$ versus $1/V$ at selected temperatures to examine the Fowler–Nordheim tunneling.

$1500 \pm 200 \text{ A/cm}^2$ at 1.0 Volt is obtained. No significant temperature dependence of the characteristics from $V = 0$ to 1.0 Volt is observed over the temperature range from 300 to 80 K. An Arrhenius plot ($\ln I$ versus $1/T$) is shown in Figure 1.9(a), exhibiting little temperature dependence in the slopes of $\ln I$ versus $1/T$ at different biases, and thus indicating the absence of thermal activation. Therefore, we conclude that the conduction mechanism through alkanethiol is tunneling contingent on demonstrating correct molecular length dependence.

Based on the applied bias as compared with the barrier height (Φ_B), 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 by their distinct voltage dependencies (see Table 1.1). Analysis of $\ln(I/V^2)$ versus $1/V$ [in Figure 1.9(b)] of the C12 $I(V,T)$ data shows no significant voltage dependence, indicating no obvious Fowler–Nordheim transport behavior in the bias range of 0 to 1.0 Volt and thus determining that the barrier height is larger than the applied bias, i.e., $\Phi_B > 1.0 \text{ eV}$. This study is restricted to applied biases ≤ 1.0 Volt and the transition from direct to Fowler–Nordheim tunneling requires higher bias.

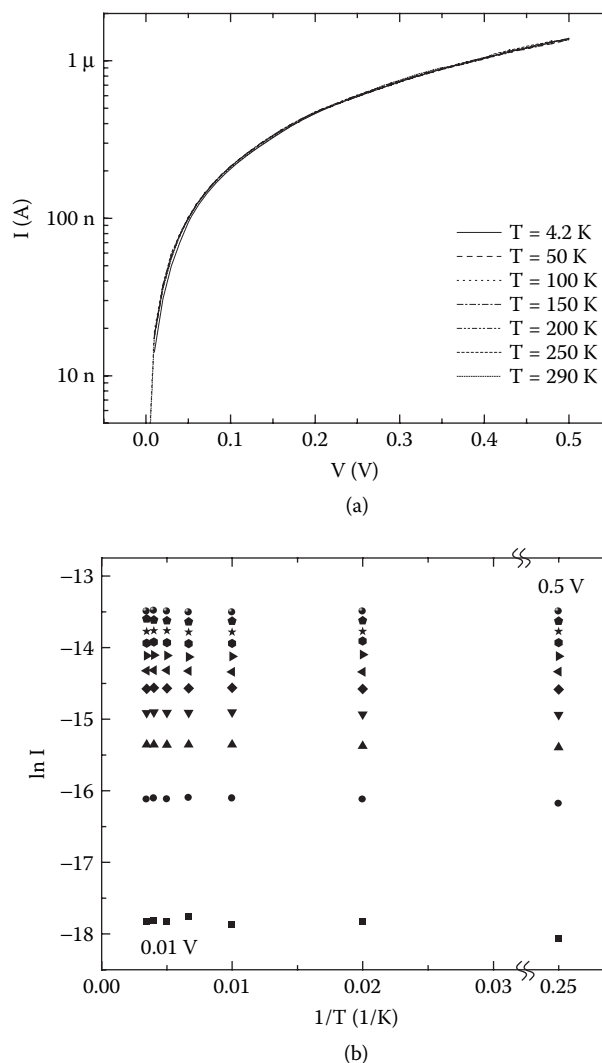


FIGURE 1.10 (a) $I(V,T)$ characteristics of an octanedithiol device measured from room temperature to 4.2 K (plotted on a log scale). (b) Arrhenius plot generated from the $I(V,T)$ data in (a) at voltages from 0.1 to 0.5 Volt with 0.05 Volt steps.

$I(V,T)$ characterizations have also been done on other alkane molecules. As an example, Figure 1.10(a) shows the $I(V,T)$ measurement of an octanedithiol device from 290 to 4.2 K. As the corresponding Arrhenius plot [Figure 1.10(b)] exhibits, there is no thermal activation involved, confirming that the conduction through alkane SAMs is tunneling.

As discussed in the previous section, temperature-variable $I(V)$ measurement is a very important experimental method in molecular transport characterizations. This importance is demonstrated by Figure 1.11. Figure 1.11(a) shows a room-temperature $I(V)$ characteristic of a device containing C8 molecules. The shape of this $I(V)$ looks very similar to that of a direct tunneling device. Indeed, it can be fit using the Simmons model (see the next subsection), which gives a barrier height of 1.27 eV and an α of 0.96 (though a larger value; see the next section). However, further $I(V,T)$ measurements display an obvious temperature dependence [Figure 1.11(b)], which can be fit well to a hopping conduction model (Table 1.1) with a well-defined activation energy of 190 meV, as illustrated by Figure 1.11(c). Another example is shown in

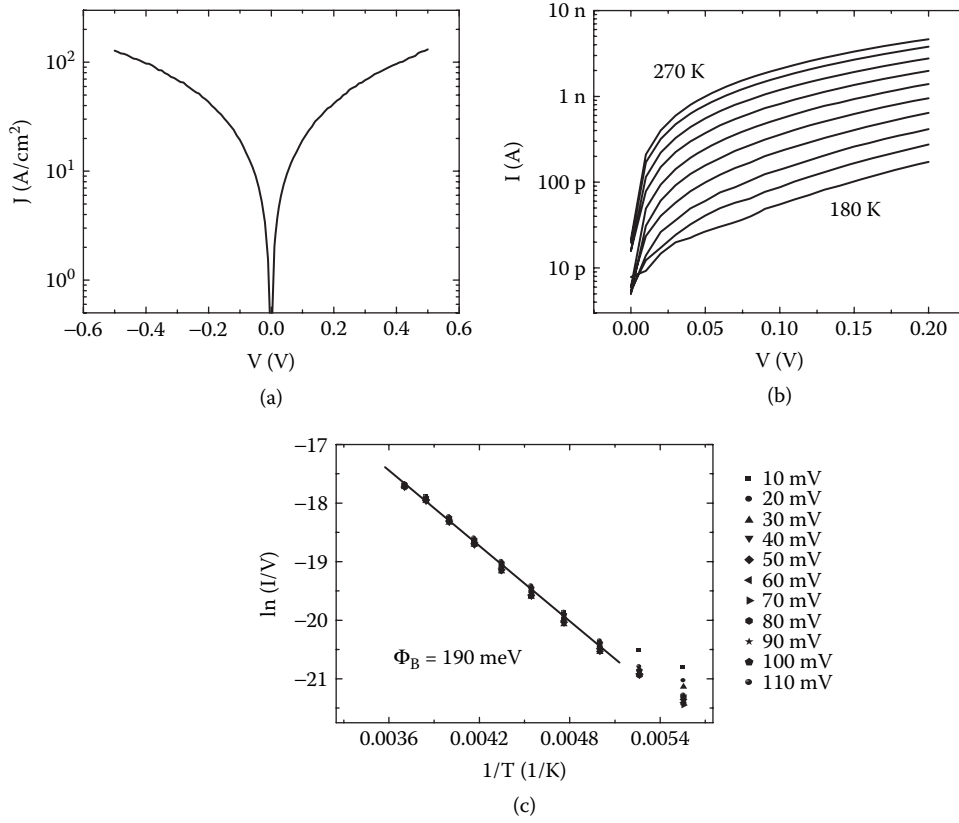


FIGURE 1.11 (a) $I(V)$ characteristic of a C8 device at 270 K. (b) Temperature dependence of the same device from 270 to 180 K (in 10-K increments). (c) Plot of $\ln(I/V)$ versus $1/T$ at various voltages. The line is the linear fitting, and a hopping barrier of 190 meV is determined from this fitting.

Figure 1.12: Figure 1.12(a) shows the $I(V)$ for a C12 device measured at 4.2 K, while Figure 1.12(b) is the corresponding numerical differential conductance. Instead of displaying a direct tunneling conduction, this device exhibits a Coulomb blockade behavior with an energy gap of ~ 60 meV, which corresponds to a device capacitance of 3×10^{-18} F. These impurity-mediated transport phenomena are indicative of the unintentional incorporation of a trap or defect level in the devices and $I(V,T)$, and subsequent IETS characterizations are needed to discover the correct conduction mechanism.

1.4.4.2 $I(V)$ Fitting Using the Simmons Model

Having established tunneling as the main conduction mechanism of alkanethiols, we can now obtain the transport parameters, such as the effective barrier height, by comparing our experimental $I(V)$ data with theoretical calculations from a tunneling model.

The current density (J) expression in the direct tunneling regime ($V < \Phi_B/e$) from the Simmons model is expressed as [Equation (1.1); 36,91]:

$$J = \left(\frac{e}{4\pi^2 \hbar d^2} \right) \left\{ \left(\Phi_B - \frac{eV}{2} \right) \exp \left[-\frac{2(2m)^{1/2}}{\hbar} \alpha \left(\Phi_B - \frac{eV}{2} \right)^{1/2} d \right] - \left(\Phi_B + \frac{eV}{2} \right) \exp \left[-\frac{2(2m)^{1/2}}{\hbar} \alpha \left(\Phi_B + \frac{eV}{2} \right)^{1/2} d \right] \right\} \quad (1.6)$$

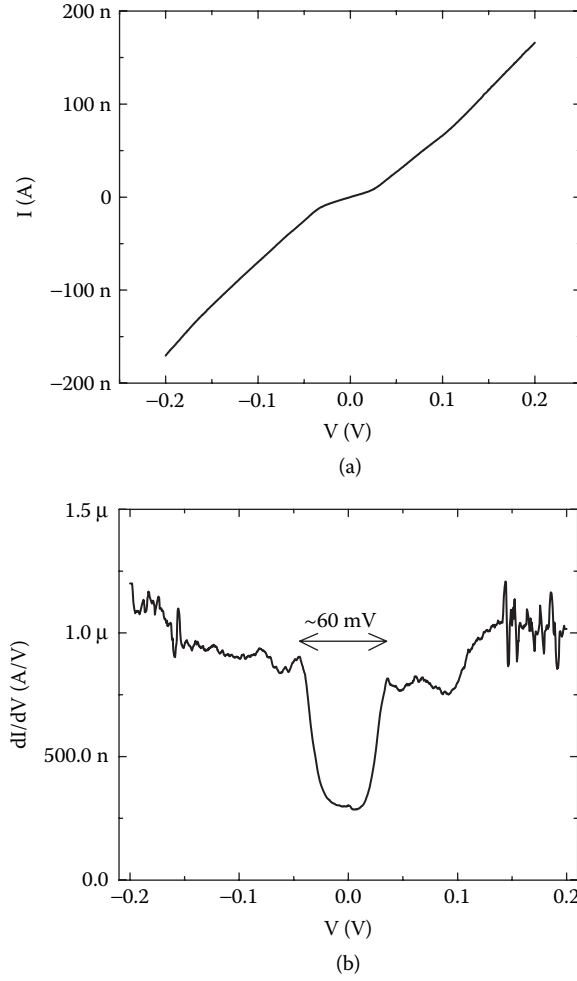


FIGURE 1.12 (a) $I(V)$ characteristic of a C12 device at 4.2 K. (b) Numerical derivative of the $I(V)$ in (a) exhibits a gap due to the Coulomb blockade effect.

For molecular systems, the Simmons model has been modified with a unitless adjustable parameter α [36,78,91]. α is introduced to account for the effective mass (m^*) of the tunneling electrons through a molecular wire. $\alpha = 1$ corresponds to the case of a bare electron, which previously has been shown not to fit $I(V)$ data well for some alkanethiol measurements at fixed temperature (300 K) [91]. By fitting individual $I(V)$ data using Equation (1.6), Φ_B and α can be found.

Equation (1.6) can be approximated in two limits: low bias and high bias, as compared with the barrier height Φ_B . In the low bias range, Equation (1.6) can be approximated as:

$$J \approx \left(\frac{(2m\Phi_B)^{1/2} e^2 \alpha}{h^2 d} \right) V \exp \left[-\frac{2(2m)^{1/2}}{\hbar} \alpha (\Phi_B)^{1/2} d \right]. \quad (1.7)$$

To determine the high bias limit, we compare the relative magnitudes of the first and second exponential terms in Equation (1.6). At high bias, the first term is dominant and thus the current density can be

approximated as

$$J \approx \left(\frac{e}{4\pi^2 \hbar d^2} \right) \left(\Phi_B - \frac{eV}{2} \right) \exp \left[-\frac{2(2m)^{1/2}}{\hbar} \alpha \left(\Phi_B - \frac{eV}{2} \right)^{1/2} d \right] \quad (1.8)$$

The tunneling currents in both bias regimes have exponential dependence on the barrier width d . In the low bias regime, the tunneling current density is $J \propto \frac{1}{d} \exp(-\beta_0 d)$, where β_0 is a bias-independent decay coefficient:

$$\beta_0 = \frac{2(2m)^{1/2}}{\hbar} \alpha (\Phi_B)^{1/2} \quad (1.9)$$

While in the high bias regime $J \propto \frac{1}{d^2} \exp(-\beta_V d)$, where β_V is a bias-dependent decay coefficient:

$$\beta_V = \frac{2(2m)^{1/2}}{\hbar} \alpha \left(\Phi_B - \frac{eV}{2} \right)^{1/2} = \beta_0 \left(1 - \frac{eV}{2\Phi_B} \right)^{1/2} \quad (1.10)$$

At high bias, β_V decreases as bias increases, which results from a barrier lowering effect due to the applied bias.

The preceding distinction between low and high bias in the direct tunneling regime may seem unnecessary at first. However, it is needed to clarify the confusion and misleading conclusions present in current literature and to deduce the decay coefficient expressions from a solid tunneling model. For example, in previous publications [78,80], the expression of the decay coefficient β_V [Equation (1.10)] has been postulated and applied in the entire bias range from 0 to 1 [78] and 3 Volts [80], which are incorrect according to Equation (1.6) since over these bias ranges there is no simple exponential dependence of $J \propto \exp(-\beta_V d)$. In another published report [92], the correct Simmons equation [Equation (1.6)] has been utilized to fit the measured $I(V)$ data, but again the β_V expression is used for the whole bias range. Some groups [27,77–80,91] used the general quantum mechanical exponential law

$$G = G_0 \exp(-\beta d) \quad (1.11)$$

to analyze the length dependence behavior of the tunneling current, but this equation is incapable of explaining the observed bias dependence of the decay coefficient β . On the contrary, in our study the Simmons equation (1.6) is used to fit the $I(V)$ data in the direct tunneling regime and is reduced to Equation (1.7) in the low bias range to yield a similar bias-independent decay coefficient as Equation (1.11). While in the high bias range, the exponential term of $e^{-C\sqrt{\Phi_B - \frac{eV}{2}}}$ in Equation (1.6) dominates, and thus Equation (1.6) is approximated by Equation (1.8), giving a bias-dependent coefficient β_V . This distinction between the low and high biases will be seen to explain the experimental data very well in a later subsection.

Using the modified Simmons Equation (1.6), by adjusting two parameters Φ_B and α a nonlinear least squares fitting has been performed on the measured C12 $I(V)$ data. The tunneling gap distance is the length of the adsorbed alkanethiol molecule, which is determined by adding an Au-thiol bonding length of 2.3 Å to the length of the free molecule [77]. For C12, the length (therefore the gap distance) is calculated as 18.2 Å. By using a device size of 45 nm in diameter, the best fitting parameters (minimizing χ^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 Φ_B and α are dominated by potential device size fluctuations of 2 nm. Figure 1.13(a) shows this best-fitting result (solid curve) as well as the original $I(V)$ data (circular symbol) on a linear scale. A calculated $I(V)$ for $\alpha = 1$ and $\Phi_B = 0.65$ 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 a limited region of the $I(V)$ curve can be fit (specifically here, for $|V| < 0.3$ Volt). The same plots are shown on a log scale in Figure 1.13(b). The value of the fitting parameter α obtained earlier, corresponds to an effective mass m^* ($= \alpha^2 m$) of 0.42 m .

Likewise, $I(V)$ measurements have also been performed on octanethiol (C8) and hexadecanethiol (C16) SAMs. The Simmons fitting on C8 with an adsorbed molecular length of 13.3 Å (tunneling gap distance)

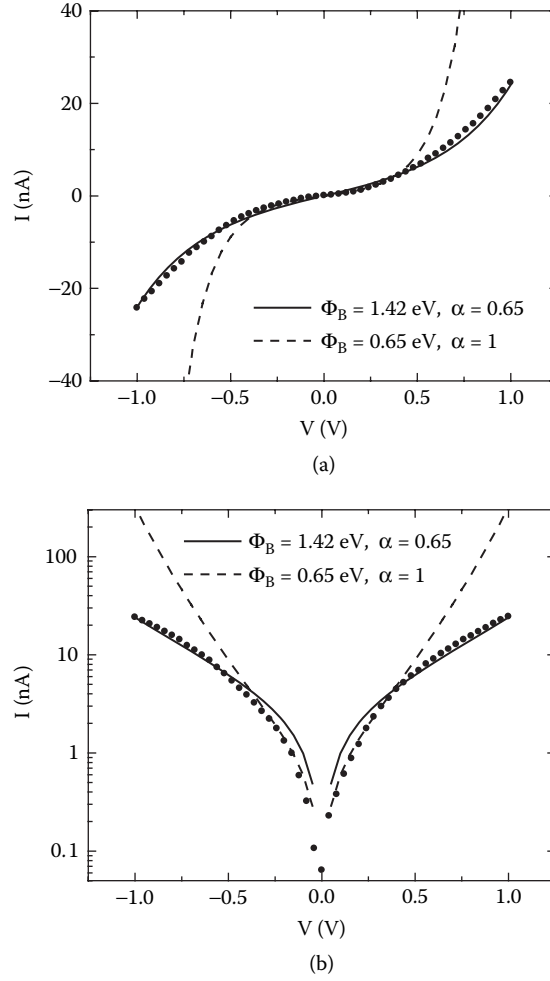


FIGURE 1.13 Measured C12 $I(V)$ data (circular symbol) is compared with calculation (solid curve) using the optimum fitting parameters of $\Phi_B = 1.42$ eV and $\alpha = 0.65$. The calculated $I(V)$ from a simple rectangular model ($\alpha = 1$) with $\Phi_B = 0.65$ eV is also shown as the dashed curve. Current is plotted on (a) linear scale and (b) log scale.

and a device diameter of 50 ± 8 nm yields values of $\{\Phi_B = 1.83 \pm 0.10$ eV and $\alpha = 0.61 \pm 0.01\}$. Same fitting on C16 with a length of 23.2 Å and a device diameter of 45 ± 2 nm gives a data set of $\{\Phi_B = 1.40 \pm 0.03$ eV, $\alpha = 0.68 \pm 0.01\}$. The $I(V)$ data and fitting results are shown in Figure 1.14(a) and (b) for C8 and C16, respectively.

Nonlinear least square fittings on C12 $I(V)$ data at different measurement temperatures allow us to determine $\{\Phi_B, \alpha\}$ over the entire temperature range (300 to 80 K) and the fitting results show that Φ_B and α values are temperature-independent. From these fittings, average values of $\Phi_B = 1.45 \pm 0.02$ eV and $\alpha = 0.64 \pm 0.01$ are obtained [$1\sigma_M$ (standard error)].

In order to investigate the dependence of the Simmons model fitting on Φ_B and α , a fitting minimization analysis is undertaken on the individual Φ_B and α values, as well as their product form of $\alpha\Phi_B^{1/2}$ in Equation (1.9). $\Delta(\Phi_B, \alpha) = (\sum |I_{exp,V} - I_{cal,V}|^2)^{1/2}$ is calculated and plotted, where $I_{exp,V}$ is the experimental current value and $I_{cal,V}$ is the calculated one from Equation (1.6). A total of 7500 different $\{\Phi_B, \alpha\}$ pairs are used in the analysis with Φ_B , ranging from 1.0 to 2.5 eV (0.01 eV increment) and α from 0.5 to 1.0 (0.01 increment). Figure 1.15(a) is a representative contour plot of $\Delta(\Phi_B, \alpha)$ versus Φ_B and α generated for the C12 $I(V)$

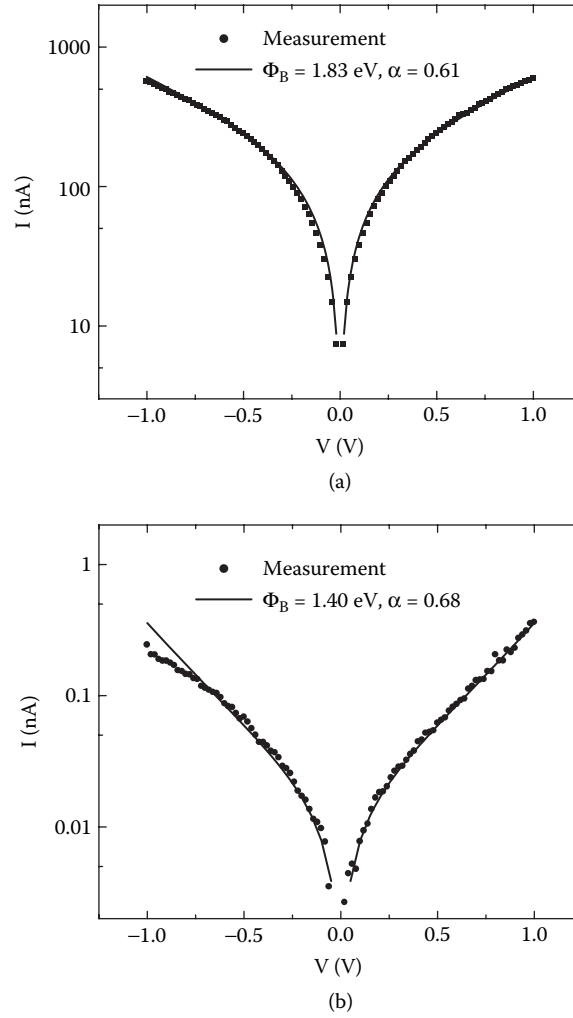


FIGURE 1.14 (a) Measured C8 $I(V)$ data (symbol) are compared with calculations (the solid curve) using the optimum fitting parameters of $\Phi_B = 1.83$ eV and $\alpha = 0.61$. (b) Measured C16 $I(V)$ data (symbol) are compared with calculations (the solid curve) using the optimum fitting parameters of $\Phi_B = 1.40$ eV and $\alpha = 0.68$.

data where darker regions represent smaller $\Delta(\Phi_B, \alpha)$, and various shades correspond to $\Delta(\Phi_B, \alpha)$ with half order-of-magnitude steps. The darker regions also represent better fits of Equation (1.6) to the measured $I(V)$ data. In the inset in Figure 1.15(a), one can see there is a range of possible Φ_B and α values yielding good fittings. Although the tunneling parameters determined from the previous Simmons fitting $\{\Phi_B = 1.42$ eV and $\alpha = 0.65\}$ lie within this region, there is also a distribution of other possible values.

A plot of $\Delta(\Phi_B, \alpha)$ versus $\alpha\Phi_B^{1/2}$ is shown in Figure 1.15(b). As it exhibits, except for the minimum point of $\Delta(\Phi_B, \alpha)$, different Φ_B and α pairs could give the same $\Delta(\Phi_B, \alpha)$ value. For this plot, the $\Delta(\Phi_B, \alpha)$ is minimized at $\alpha\Phi_B^{1/2}$ of 0.77 (eV) $^{1/2}$, which yields a β_0 value of $0.79 \text{ \AA}^{-1}$ from Equation (1.9). The C8 and C16 devices show similar results, confirming that the Simmons fitting has a strong $\alpha\Phi_B^{1/2}$ dependence. For the C8 device, although Φ_B obtained from the fitting is a little larger, combined α and Φ_B give a similar β_0 value within the error range as the C12 and C16 devices. The values of Φ_B and α for C8, C12, and C16 devices are summarized in Table 1.2, as well as the β_0 values calculated from Equation (1.9).

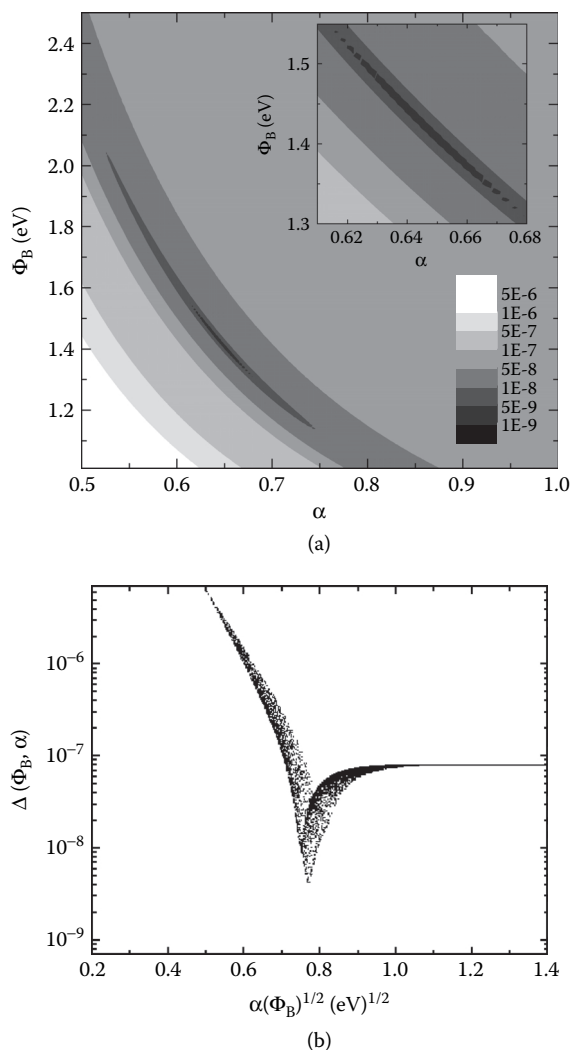


FIGURE 1.15 (a) Contour plot of $\Delta(\Phi_B, \alpha)$ values for C12 device as a function of Φ_B and α , where the darker region corresponds to a better fitting. Inset shows detailed minimization fitting regions. (b) Plot of $\Delta(\Phi_B, \alpha)$ as a function of $\alpha\Phi_B^{1/2}$.

1.4.4.3 Length Dependence of the Tunneling Current through Alkanethiols

As discussed in subsection 4.4.2 [Equations (1.7) and (1.8)], the tunneling currents in the low and high bias ranges have an exponential dependence on the molecular length as $J \propto \frac{1}{d} \exp(-\beta_0 d)$ and $J \propto \frac{1}{d^2} \exp(-\beta_V d)$, respectively, where β_0 and β_V are the decay coefficients. In order to study this length-dependent tunneling behavior, $I(V)$ characterizations are performed on three alkanethiols of different

TABLE 1.2 Summary of Alkanethiol Tunneling Parameters Obtained Using the Simmons Model

Molecules	J at 1 V (A/cm ²)	Φ_B (eV)	α	m^* (m)	β_0 (Å ⁻¹)
C8	$31,000 \pm 10,000$	1.83 ± 0.10	0.61 ± 0.01	0.37	0.85 ± 0.04
C12	$1,500 \pm 200$	1.42 ± 0.04	0.65 ± 0.01	0.42	0.79 ± 0.02
C16	23 ± 2	1.40 ± 0.03	0.68 ± 0.01	0.46	0.82 ± 0.02

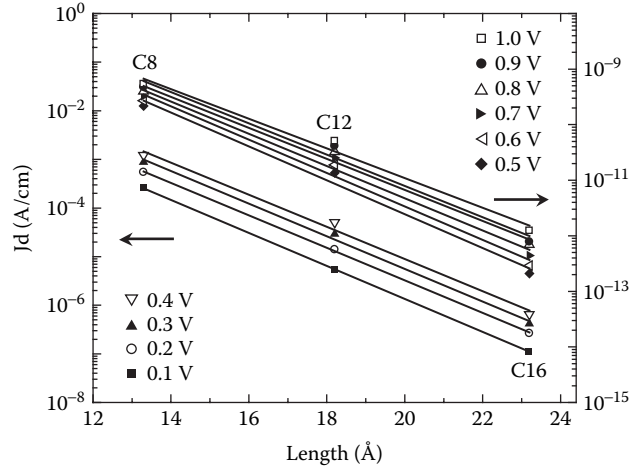


FIGURE 1.16 Log plot of tunneling current densities (symbols) multiplied by molecular length d at low bias and by d^2 at high bias versus molecular length. The lines through the data points are linear fittings.

molecular length: C8, C12, and C16 [Figure 1.6(b)]. The adsorbed molecular length of C8, C12, and C16 are 13.3, 18.2, and 23.2 Å, respectively, as used in the Simmons fitting. To define the boundary of the high and low bias ranges, the relative magnitudes of the first and second exponential terms in Equation (1.6) are evaluated. 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 0.5 Volt, which is chosen as the bias boundary.

Figure 1.16 is a semi-log plot of the tunneling current density multiplied by molecular length— Jd at low bias and Jd^2 at high bias—as a function of the molecular length for these alkanethiols. As seen in this figure, the tunneling currents (symbols) show exponential dependence on molecular lengths. The decay coefficient β can be determined from the slopes of the linear fittings (lines in Figure 1.16) on the measured data. The obtained β values at each bias are plotted in Figure 1.17(a) and the error bar of an individual β value in this plot is determined by considering both the device size uncertainties and the linear fitting errors.

As Figure 1.17(a) shows, in the low bias range ($V < 0.5$ V) the β values are almost independent of bias, while in the high bias range ($V > 0.5$ V) β has bias dependence: β decreases as bias increases due to the barrier lowering effect. From Figure 1.17(a), an average β_w of $0.77 \pm 0.06 \text{ Å}^{-1}$ can be calculated in the low bias region. According to Equation (1.10), β_V^2 depends on bias V linearly in the high bias range. Figure 1.17(b) is a plot of β_V^2 versus V in this range (0.5 to 1.0 Volt) and a linear fitting of the data. $\Phi_B = 1.35 \pm .20$ eV and $\alpha = 0.66 \pm 0.04$ are obtained from the intercept and slope of this fitting, respectively, which are consistent with the values acquired from the nonlinear least squares fitting on the $I(V)$ data in the previous subsection.

Table 1.3 is a summary of previously reported alkanethiol transport parameters obtained by different techniques [28]. The current densities (J) listed in Table 1.3 are for C12 monothiol or dithiol devices at 1 V, which are extrapolated for some techniques from published results of other length alkane molecules using the exponential law of Equation (1.11). The large variation of J among reports can be attributed to the uncertainties in device contact geometry and junction area, as well as complicating inelastic or defect contributions. The β_o value ($0.77 \pm 0.06 \text{ Å}^{-1} \approx 0.96 \pm 0.08$ per methylene) for alkanethiols obtained in our study using the Simmons model is comparable to previously reported values as summarized in Table 1.3.

Length-dependent analysis using the exponential equation (1.11) in the entire applied bias range (0 to 1.0 V) has also been performed in order to compare with these reported β values. This gives

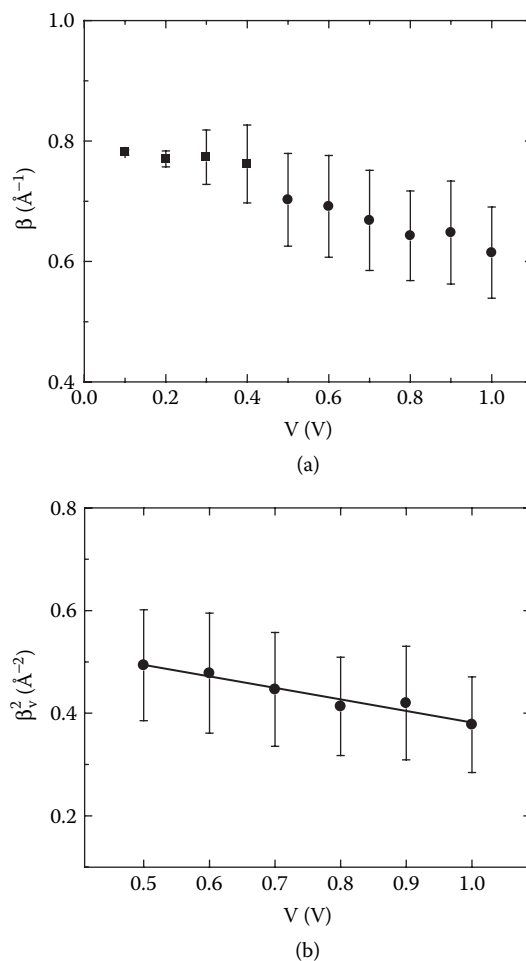


FIGURE 1.17 (a) Plot of β versus bias in the low bias range (square symbol) and high bias range (circular symbol). (b) β_V^2 versus bias plot (symbol) with a linear fitting (solid curve).

β values from 0.84 to $0.73 \text{ \AA}^{-1}$ in the bias range from 0.1 to 1.0 Volt, which are similar to the reported values. For example, Holmlin *et al.* reported a β value of $0.87 \text{ \AA}^{-1}$ by mercury-drop experiments [91], Wold *et al.* have reported β of $0.94 \text{ \AA}^{-1}$, and Cui *et al.* reported β of $0.64 \text{ \AA}^{-1}$ for various alkanethiols by using a conducting atomic force microscope technique [79,80]. However, these reported β were treated as bias-independent quantities, contrary to the results from our study and those observed in a slightly different alkane system (ligand-encapsulated nanoparticle/alkane-dithiol molecules) [78]. Since all of these experiments were performed at room temperature, the reported parameters have not been checked with a temperature-dependent analysis and non-tunneling components can dramatically affect the derived values.

1.4.4.4 $I(V)$ Fitting Using the Franz Model

We can also analyze our experimental data using the Franz two-band model [37–42]. By considering the contributions from both the conduction band and valence band, the Franz model empirically predicted a non-parabolic $E(k)$ relationship inside the bandgap, as expressed by Equation (1.4). By using this equation, the effective mass of the tunneling electron can be deduced by knowing the barrier height of the tunnel junction [41,109]. However, since there is no reliable experimental data on the Fermi level alignment in the

TABLE 1.3 Summary of Alkanethiol Tunneling Parameters Obtained by Different Test Structures

Junction	β ($\text{\AA}^{-1}$)	J (A/cm^2) at 1 V	Φ_B (eV)	Technique	Ref
(bilayer) monothiol	0.87 ± 0.1	25–200 ^{a)}	2.1 ^{e)}	Hg-junction	91
(bilayer) monothiol	0.71 ± 0.08	0.7–3.5 ^{a)}		Hg-junction	102
monothiol	0.79 ± 0.01	1500 ± 200 ^{b)}	1.4 ^{e)}	Solid M-I-M	24
monothiol	1.2			STM	70
dithiol	0.8 ± 0.08	$3.5\text{--}5 \times 10^5$ ^{c)}	5 ± 2 ^{f)}	STM	73
monothiol	0.73–0.95	1100–1900 ^{d)}	2.2 ^{e)}	CAFM	77
monothiol	0.64–0.8	10–50 ^{d)}	2.3 ^{e)}	CAFM	78
dithiol	0.46 ± 0.02	$3\text{--}6 \times 10^5$ ^{c)}	1.3–1.5 ^{e)}	CAFM	80
monothiol	1.37 ± 0.03		1.8 ^{f)}	Tuning fork AFM	141
monothiol	0.97 ± 0.04			Electrochemical	104
monothiol	0.85			Electrochemical	105
monothiol	0.91 ± 0.08			Electrochemical	106
monothiol	0.76	2×10^4 (at 0.1 V)	1.3–3.4 ^{g)}	Theory	122
monothiol	0.76			Theory	142
monothiol	0.79			Theory	143

Note:

- (1) Some decay coefficient β are converted into the unit of $\text{\AA}^{-1}$ from the unit of per methylene.
- (2) The junction areas are estimated by an optical microscope^{a)}, SEM^{b)}, assuming a single molecule^{c)}, and Hertzian contact theory^{d)}.
- (3) Current densities (J) for C12 monothiol or dithiol at 1 V are extrapolated from published results of other length molecules using the exponential law of $G \propto \exp(-\beta b)$.
- (4) Barrier height values are obtained from Simmons equation^{e)}, bias-dependence of β ^{f)}, and theoretical calculation^{g)}.

Au-alkanethiol SAM-Au system, Φ_B is unknown and is thus treated as an adjustable parameter together with m^* in our analysis. The imaginary k value is related to the decay coefficient β [$k^2 = -(\beta/2)^2$] obtained from the length-dependent study. Using an alkanethiol HOMO–LUMO gap of 8 eV, a least squares fitting has been performed on the experimental data, and Figure 1.18 shows the resultant $E(k)$ relationship and the corresponding energy band diagrams. The zero of energy in this plot is chosen as the LUMO energy.

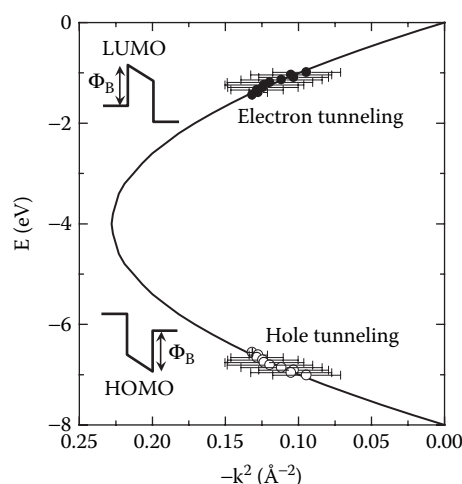


FIGURE 1.18 $E(k)$ relationship generated from the length-dependent measurement data of alkanethiols. Solid and open symbols correspond to electron and hole conduction, respectively. The solid curve is the Franz two-band $E(k)$ plot for $m^* = 0.43 m$ and $E_g = 8$ eV. The insets show the corresponding energy band diagrams.

The best fitting parameters obtained by minimizing χ^2 are $\Phi_B = 1.49 \pm 0.51$ eV and $m^* = 0.43 \pm 0.15$ m, where the error ranges of Φ_B and m^* are dominated by the error fluctuations of β . Both electron tunneling near the LUMO, and hole tunneling near the HOMO can be described by these parameters. $\Phi_B = 1.49$ eV indicates that the Fermi level is aligned close to one energy level in either case. The Φ_B and m^* values obtained here are in reasonable agreement with previous results deduced from the Simmons model.

1.5 Inelastic Electron Tunneling Spectroscopy of Alkanethiol SAMs

1.5.1 A Brief Review of IETS

As discussed previously, IETS was discovered by Jaklevic and Lambe in 1966 when they studied tunnel junctions containing organic molecules and the vibrational modes of the molecules were detected by electrons that tunneled inelastically through the barrier [29,43]. In the earlier stage of IETS, the tunnel barrier was usually made of a metal oxide, therefore the choice of the metallic material was crucial since it must be capable of forming a coherent and stable oxide layer with a thickness of several nanometers [30,31,44]. For this purpose, aluminum was often utilized because of its good oxide quality. The molecular species were then introduced by either vapor phase exposure or liquid solution deposition on the surface of the barrier. Care also needed to be taken for top electrode deposition since high temperature evaporation may destroy the adsorbed molecular layer [44]. IETS has been mostly used in the spectra range of 0 to 500 meV (0 to 4000 cm^{-1}), which covers almost all molecular vibrational modes [30,31,44].

In the 1990s, another type of tunneling barrier was reported for IETS measurements [88]. This so-called cross-wire structure replaces the metal oxide barrier with an inert gas film. In order to form the tunnel junction, molecular species are mixed with the inert gas at a predetermined composition, and then are introduced into the vacuum chamber, where they then condense on the wire surfaces [88,110]. Recently, this test structure has been used again for the investigation of vibronic contributions to charge transport across molecular junctions [111]. However, due to the difficulties in controlling the exact position of the top wire, the top wire might not touch the other end of the molecules to form a perfect metal–SAM–metal junction, or it might penetrate into the monolayer. Besides, no temperature-dependent measurement has been reported using this structure.

Another important advance in this field is the realization of single molecular vibrational spectroscopy by STM-IETS [112]. The possibility of performing IETS studies utilizing STM was discussed soon after its invention [67]. However, due to the difficulties in achieving the extreme mechanical stability that is necessary to observe small changes in tunneling conductance, this technique has only been realized recently [112]. In the STM implementation of IETS, the metal–oxide–metal tunnel junction is replaced by an STM junction consisting of a sharp metallic tip, a vacuum gap, and a surface with the adsorbed molecules. Using STM-IETS, imaging and probing can be performed at the same time, and vibrational spectroscopy studies on a single molecule can be achieved [112].

The advantage of inelastic tunneling spectroscopy over conventional optical vibrational spectroscopy such as IR and Raman is its sensitivity [30,31]. IR spectroscopy is a well-developed technology and has been used widely for studies of adsorbed species. It does not require cryogenic temperature measurement and can be applied to a variety of substrates [30]. Raman spectroscopy is used when IR is difficult or impossible to perform, such as for seeing vibrations of molecules in solvents that are infrared opaque or for vibrations that are not infrared active [30]. Both IR and Raman have lower sensitivities compared with IETS: they require 10^3 or more molecules to provide a spectrum. Since the interaction of electrons with molecular vibrations is much stronger than that of photons, as small as one monolayer of molecules is enough to produce good IETS spectra [44,45]. Additionally, IETS is not subject to the selection rules of infrared or Raman spectroscopy. It has an orientational preference, as discussed earlier, but there are no rigorous selection rules. Both IR and Raman active vibrational modes appear in IETS spectra with comparable magnitudes [44,45].

After its discovery, IETS found many applications in different areas such as surface chemistry, radiation damage, and trace substance detection, among many others [30,31]. It is a powerful spectroscopic tool for

chemical identification purposes: the vibrational spectra can be used as fingerprints to identify the molecular species confined inside a tunnel junction. It can also be used for chemical bonding investigations—in a solid state junction, the breaking of various bonds can be monitored by the decrease in intensities of the corresponding vibrational peaks, and the formation of new bonds can be monitored by the growth of new vibrational peaks [30,31]. The application of IETS has branched out to the modern silicon industry as well, where it is utilized to study phonons in silicon, the nature of the SiO₂ tunneling barrier, interface states in metal-oxide-semiconductor (MOS) systems, and high-k dielectrics [113,114].

In our study, IETS is utilized to identify the molecular species confined inside a solid state junction [25]. The measurement is performed using the nanopore test structure. Unlike earlier tunnel junctions, the nanopore uses the self-assembled molecules themselves as the tunnel barrier; thus, it creates oxide-free junctions, and intrinsic molecular properties can be investigated. Because the tunneling current depends exponentially on the barrier width, in the cross-wire and STM tunnel junctions a small change in the tunneling gap distance caused by vibration of the top electrode can produce a large change in the junction conductance, which can mask the conductance change associated with the inelastic channels. Compared to these systems, the nanopore structure has direct metal-molecule contacts and a fixed top electrode, and both ensures intrinsic contact stability and eliminates the preceding problems. The molecular species used are the “control” molecules—alkane SAMs—which have been shown to form good insulating layers and present well-defined tunnel barriers in previous studies.

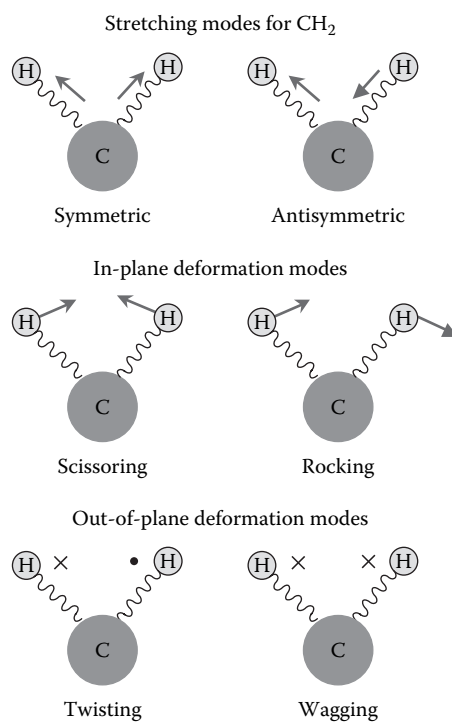
1.5.2 Alkanethiol Vibrational Modes

Various spectroscopic techniques have been developed to help chemists investigate the chemical structures of molecules and to study their interactions. These include mass spectrometry, nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, ultraviolet (UV) spectroscopy, Raman spectroscopy, and high-resolution electron energy loss spectroscopy (HREELS) [115–119]. The majority of these spectroscopic tools analyze molecules based on differences in how they absorb electromagnetic radiation [116]. A very important concept in molecular spectroscopies is the so-called group frequency. A molecule usually consists of many atoms, and even though these atoms will move during a normal mode of vibration, most of the motion can be localized within a certain molecular fragment that vibrates with a characteristic frequency. Thus, the existence of a functional group can be inferred by the appearance of an absorption band in a particular frequency range. In other words, we can detect the presence of a specific functional group in a molecule by identifying its characteristic frequency [116,117]. By identifying individual functional groups in a molecule, we can determine the molecule's chemical composition.

As for the case of alkanethiol molecules, the important vibrational modes include the stretching modes of C-C and C-S groups and various vibrations of the CH₂ group. Figure 1.19 illustrates the available CH₂ group vibrational modes, which include the symmetric and antisymmetric stretching modes, in-plane scissoring and rocking modes, and out-of-plane wagging and twisting modes [25,116]. Each of the different vibrational modes gives rise to a characteristic frequency in a spectroscopic spectrum.

Vibrational structures of self-assembled alkanethiols on Au(111) surface have been investigated by spectroscopic tools such as IR, Raman, and HREELS, and a large literature exists on the subject. References 118–121 are representative publications in this field. For example, IR measurement was conducted at the earlier stage to characterize the packing and orientation of the alkanethiol SAMs formed on the Au(111) surface. The results suggest they are densely packed in a crystalline arrangement [26, 62]. It has also been used by Castiglioni *et al.* to study the CH₂ rocking and wagging vibrations and to obtain related characteristic group frequencies [120]. Using Raman spectroscopy, Bryant *et al.* have investigated the C-C stretching bands of alkanethiols on Au surfaces since these bands are weak in the IR spectra. They have also characterized other vibrational features such as the C-S, S-H, and C-H stretching modes [121]. Duwez *et al.* and Kato *et al.* utilized HREELS to study various vibrational structures of alkanethiol SAMs and the Au-S bonding [118,119].

Table 1.4 is a summary of the alkanethiol vibrational modes obtained using the aforementioned spectroscopic methods [25,118–121]. In this table, the symbols of $\delta_{s,r}$ and $\gamma_{w,t}$ denote in-plane scissoring (s)

**FIGURE 1.19** CH₂ vibrational modes. After Ref. 115.**TABLE 1.4** Summary of Alkanethiol Vibrational Modes Obtained from IR, Raman, and HREELS. After Ref. 118–121

Modes	Methods	Wavenumber (cm ⁻¹)	(meV)
$\nu(\text{Au-S})$	HREELS	225	28
$\nu(\text{C-S})$	Raman	641	79
	Raman	706	88
$\delta_r(\text{CH}_2)$	HREELS	715	89
	IR	720	89
	IR	766	95
	IR	925	115
$\nu(\text{C-C})$	HREELS	1050	130
	Raman	1064	132
	Raman	1120	139
$\gamma_{w,t}(\text{CH}_2)$	IR	1230	152
	HREELS	1265	157
	IR	1283	159
	IR	1330	165
$\delta_s(\text{CH}_2)$	HREELS	1455	180
$\nu(\text{S-H})$	Raman	2575	319
$\nu_s(\text{CH}_2)$	Raman	2854	354
	HREELS	2860	355
$\nu_{as}(\text{CH}_2)$	Raman	2880	357
	Raman	2907	360
	HREELS	2925	363

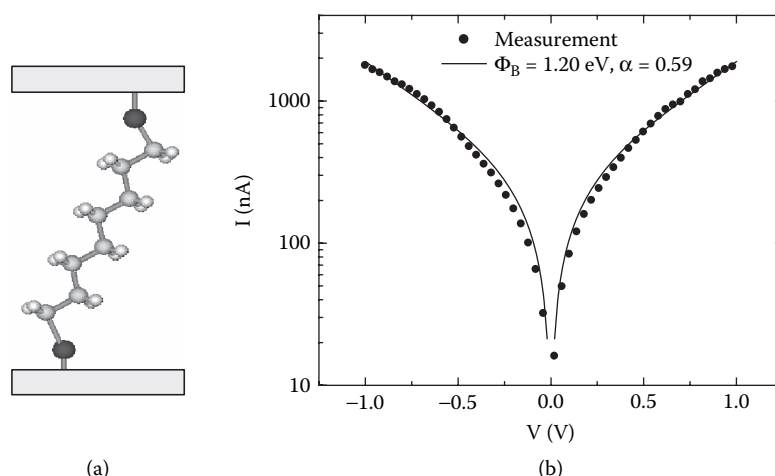


FIGURE 1.20 (a) Schematic of an octanedithiol device. (b) $I(V)$ measurement data at room temperature (circular symbol) and the fitting from Simmons equation (solid curve).

and rocking (r) and out-of-plane wagging (w) and twisting (t) modes, respectively. ν and $\nu_{s,as}$ denote stretching and CH_2 group symmetrical (s) and antisymmetrical (as) stretching modes, respectively. These characteristic group frequencies will be compared to the signal peaks in our acquired IETS spectra to identify the molecular species confined in the device junction.

1.5.3 IETS of Octanedithiol SAM

Electrical measurements on octanedithiol SAM are performed with the nanopore structure discussed earlier. The molecular solution is prepared by adding $\sim 10 \mu\text{L}$ octanedithiol to 10 mL ethanol. SAM formation is carried out for 24 hours inside a nitrogen-filled glove box with an oxygen level of less than 5 ppm. Figure 1.20(a) shows the schematic of the device configuration. $I(V,T)$ measurement from 4.2 to 290 K shows a tunneling transport behavior (see Figure 1.10). Figure 1.20(b) is the room temperature $I(V)$ measurement result with the fitting from the Simmons equation. Using a junction area of $51 \pm 5 \text{ nm}$ in diameter obtained from statistical studies of the nanopore size with SEM, a current density of $(9.3 \pm 1.8) \times 10^4 \text{ A/cm}^2$ at 1.0 Volt is calculated. Using the modified Simmons model [Equation (1.6)], the transport parameters of $\Phi_B = 1.20 \pm 0.03 \text{ eV}$ and $\alpha = 0.59 \pm 0.01$ ($m^* = 0.34 m$) are obtained for this C8 dithiol device. As a comparison, the C8 monothiol device used in the length-dependent study has a current density of $(3.1 \pm 1.0) \times 10^4 \text{ A/cm}^2$ at 1.0 Volt, a barrier height of $1.83 \pm 0.10 \text{ eV}$, and an α of 0.61 ± 0.01 ($m^* = 0.37 m$). That the observed current density of the C8 dithiol device is approximately three times larger than that of monothiol is consistent with previously published theoretical calculations and experimental data [122]. For example, Kaun *et al.* performed first-principle calculations on alkane molecules in a metal–SAM–metal configuration using nonequilibrium Green's functions combined with density functional theory [122]. They found that in an Au–alkanedithiol–Au device, although both Au leads are contacted by a sulfur atom, the transport behavior is essentially the same as that of an alkanemonothiol device where only one Au lead is contacted by sulfur. However, the current through alkanedithiols is found to be approximately ten times larger than that through alkanemonothiols, which, they suggest, indicates that the extra sulfur atom provides a better coupling between the molecule and the lead [122]. Experimental measurement on alkanedithiol molecules has also been performed by Cui *et al.* using the conducting AFM technique, and the result shows that alkanedithiol has ~ 100 times larger current than alkanemonothiol has [78,80].

IETS measurements are performed on the molecular devices using the lock-in technique. The second harmonic signal (proportional to d^2I/dV^2) is directly measured with a lock-in amplifier, which has also

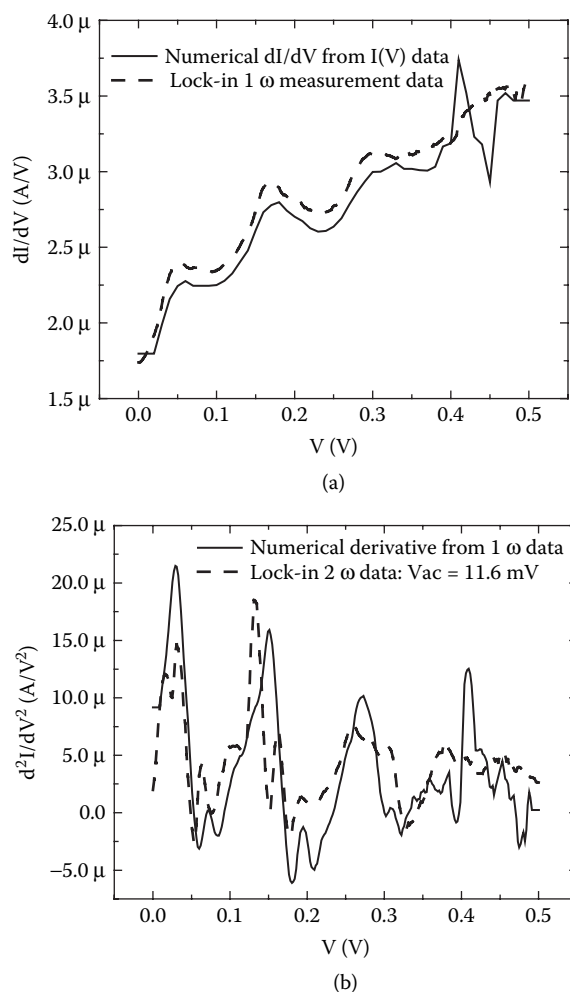


FIGURE 1.21 (a) Lock-in 1ω data and the numerical dI/dV obtained from $I(V)$ measurement data. (b) Lock-in 2ω data and the numerical derivative of the lock-in 1ω data in (a). All measurement data are taken at 4.2 K.

been checked to be consistent with the numerical derivative of the first harmonic signal. As an example, Figure 1.21(a) shows the lock-in first harmonic measurement data compared with the numerical derivative of the $I(V)$ of the C8 dithiol device, while Figure 1.21(b) is the 2nd harmonic measurement result checked with the numerical derivative of the first harmonic signal (all of the data are taken at 4.2 K). As Figure 1.21(b) demonstrates, the IETS spectrum calculated from the numerical differential method is compatible with that obtained from the lock-in 2nd harmonic measurement; however, the lock-in measurement yields a much more resolved spectrum.

Figure 1.22 shows the inelastic electron tunneling 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 is 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 to 200 mV region at 33, 133, and 158 mV. From comparison with previously reported IR, Raman, and HREEL spectra of alkanethiol SAMs on Au(111) surfaces (Table 1.4) [118–121], these three peaks are assigned to Au-S stretching, C-C stretching, and CH_2 wagging modes of a surface bound alkanethiolate. The absence of a strong S-H stretching signal at ~ 329 mV suggests that most of the thiol groups have reacted with the gold bottom

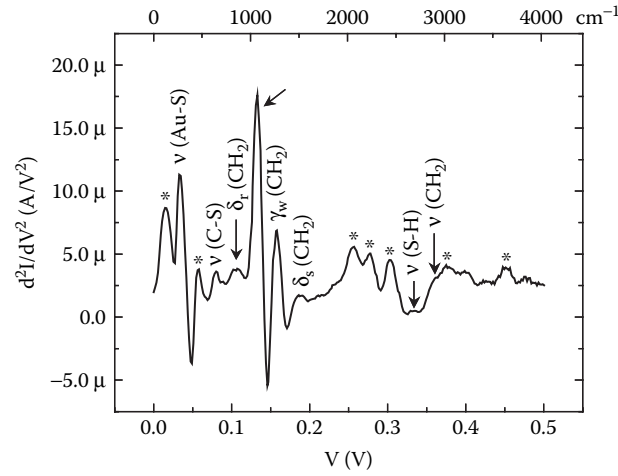


FIGURE 1.22 Inelastic electron tunneling spectrum of a C8 dithiol SAM obtained from lock-in second harmonic measurement with an AC modulation of 8.7 mV (rms value) at a frequency of 503 Hz ($T = 4.2$ K). Peaks labeled * are most probably background due to the encasing Si_3N_4 .

and top contacts. Peaks are also reproducibly observed at 80, 107, and 186 mV. They correspond to C-S stretching, CH_2 rocking, and CH_2 scissoring modes. The stretching mode of the CH_2 groups appears as a shoulder at 357 meV. The peak at 15 mV is due to vibrations from either Si, Au, or $\delta(\text{C-C-C})$ since all three materials have characteristic frequencies in this energy range [123,125]. We note that all alkanethiol peaks without exception or omission occur in the spectra. Peaks at 58, 257, 277, and 302, as well as above 375 mV are likely to originate from Si-H and N-H vibrations related to the silicon nitride membrane [123,126,127], which forms the SAM encasement. Measurement of the background spectrum from Si_3N_4 of an “empty” nanopore device with only gold contacts is hampered by either too low (open circuit) or too high (short circuit) currents in such a device.

According to the IETS theory [128], molecular vibrations with net dipole moments perpendicular to the tunneling junction interface have stronger peak intensities than vibrations with net dipole moments parallel to the interface. In our device configuration [Figure 1.20(a)], the vibrational modes of Au-S, C-S, and C-C stretching and CH_2 wagging are perpendicular to the junction interface, while the vibrations of the CH_2 group rocking, scissoring, and stretching modes are parallel to the interface. In the obtained IETS spectrum (Figure 1.22), the vibrations perpendicular to the junction interface produce peaks of stronger intensities, while those vibrations parallel to the interface generate less dominant peaks. This experimental observation of the relative IETS peak intensities is in good agreement with the theory.

1.5.4 Spectra Linewidth Study

In order to verify that the obtained spectra are indeed valid IETS data, the peak width broadening effect is examined as a function of temperature and applied modulation voltage. IETS measurements have been performed with different AC modulations at a fixed temperature, and at different temperatures with a fixed AC modulation. Figure 1.23 shows the modulation dependence of the IETS spectra obtained at $T = 4.2$ K, and the modulation voltages used are 11.6, 10.2, 8.7, 7.3, 5.8, 2.9, and 1.2 mV (rms values). According to theoretical analysis, AC modulation will bring in a linewidth broadening of $1.7 V_{rms}$ for the full width at half maximum (FWHM) [46]. Besides, the Fermi level smearing effect at finite temperature will also produce a thermal broadening of $5.4 kT$ [43], and these two broadening effects add as squares [43,48]. In order to determine the experimental FWHMs, a Gaussian distribution function is utilized to fit the spectra peaks [48,129] and an individual peak is defined by its left and right minima. Figure 1.24 shows the modulation broadening analysis of the C-C stretching mode at $T = 4.2$ K. The circular symbols are FWHMs of the

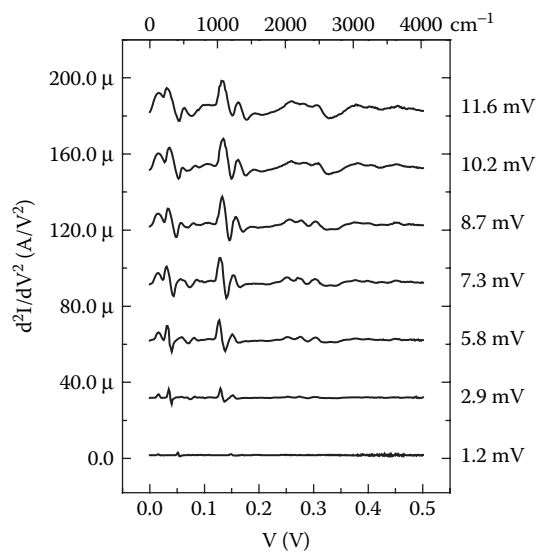


FIGURE 1.23 Modulation dependence of IETS spectra obtained at 4.2 K.

experimental peaks obtained from the Gaussian fitting, and the square symbols are calculated values. The error range of the experimental data is also determined by the Gaussian fitting. As shown in Figure 1.24, the agreement is excellent over most of the modulation range; however, the saturation of the experimental linewidth at low modulation bias indicates the existence of a non-negligible intrinsic linewidth.

Taking into account the known thermal and modulation broadenings, and including the intrinsic linewidth (W_I), the measured experimental peak width (W_{exp}) is given by Equation (1.5):

$$W_{exp} = \sqrt{W_I^2 + W_{thermal}^2 + W_{modulation}^2}$$

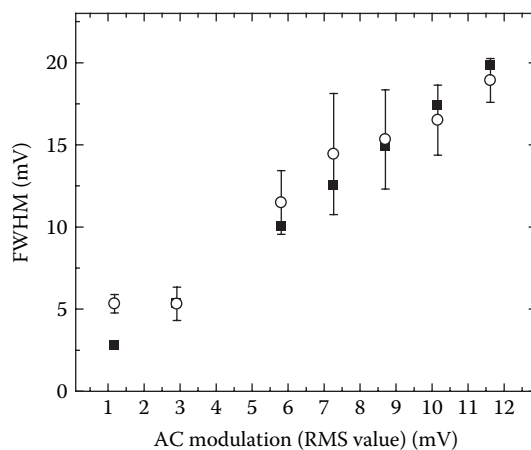


FIGURE 1.24 Line broadening of the C-C stretching mode as a function of AC modulation. The circular symbols are experimental FWHMs and the square symbols are theoretical calculations including both thermal and modulation broadenings.

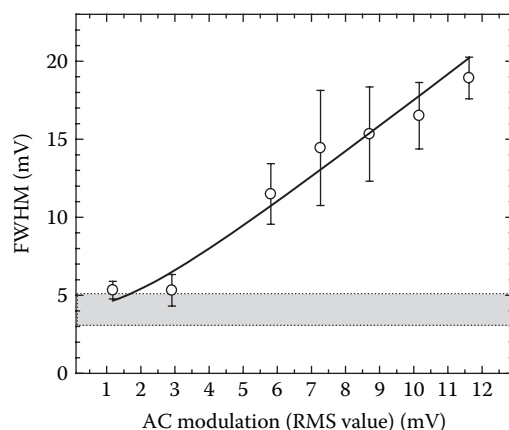


FIGURE 1.25 Nonlinear least squares fitting (solid line) on the modulation broadening data (circular symbol) to determine the intrinsic linewidth of the C-C stretching mode. The shaded bar indicates the expected saturation due to this intrinsic linewidth and the thermal contribution at 4.2 K.

By treating W_I as a fitting parameter, a nonlinear least squares fitting using Equation (1.5) on the AC modulation data can be performed. Figure 1.25 shows the fitting result, and from this fitting an intrinsic linewidth of 3.73 ± 0.98 meV can be obtained for the C-C stretching mode (the error range is determined by the NLS fitting). The shaded bar in Figure 1.25 denotes the expected saturation due to this derived intrinsic linewidth (including a 5.4 kT thermal contribution).

The broadening of the linewidth due to thermal effect can also be independently checked at a fixed modulation voltage. Figure 1.26 shows the temperature dependence of the IETS spectra obtained with an AC modulation of 8.7 mV (rms value) at temperatures of 4.2, 20, 35, 50, 65, and 80 K. Figure 1.27 shows the thermal broadening analysis of the same C-C stretching mode. The circular symbols (and corresponding error bars) are experimental FWHM values determined by the Gaussian fitting (and error of the fitting) to

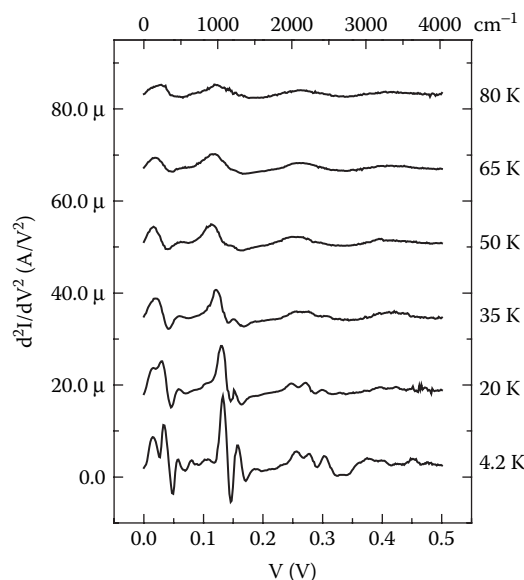


FIGURE 1.26 Temperature dependence of the IETS spectra obtained at a fixed modulation of 8.7 mV.

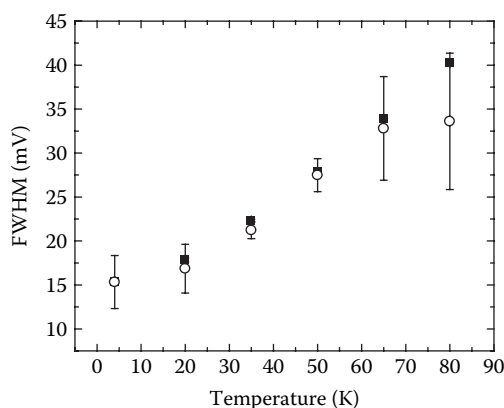


FIGURE 1.27 Line broadening of the C-C stretching mode as a function of temperature. The circular symbols are experimental FWHMs and the square symbols are calculations including thermal and modulation broadenings and the intrinsic linewidth.

the experimental lineshapes. The square symbols are calculations included from thermal broadening, modulation broadening, and the intrinsic linewidth of 3.73 meV determined from the modulation broadening analysis. 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 ($\times 0.5$) to above ($\times 10$) the thermally broadened intrinsic linewidth.

Similar linewidth investigation has also been carried out on other vibrational modes. For example, Figure 1.28 shows the modulation broadening analysis on the Au-S stretching mode at 33 meV and the CH_2 wagging mode at 158 meV. For the Au-S stretching mode, the deviation of experimental data from calculated values 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 fitting using Equation (1.5) [the solid curve in Figure 1.28(b)] gives an intrinsic linewidth of 13.5 ± 2.4 meV. For other vibrational modes (because of the weak spectral peaks), the obtained FWHMs from the lineshape fitting have large error ranges; thus, the intrinsic linewidths cannot be well resolved.

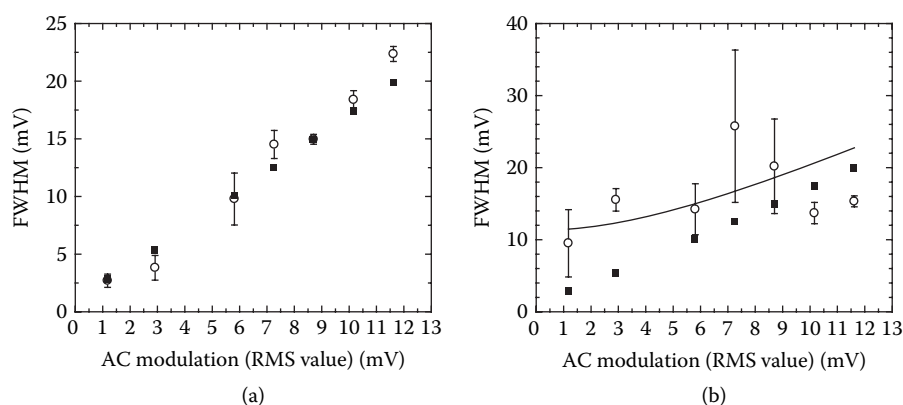


FIGURE 1.28 Line broadenings as a function of AC modulation obtained at 4.2 K for (a) the Au-S stretching mode and (b) the CH_2 wagging mode. The circular symbols are experimental FWHMs and the square symbols are calculations including both modulation and thermal contributions. A nonlinear least squares fitting using Equation (1.5) to determine the intrinsic linewidth is shown as the solid curve in (b).

The inspection of intrinsic linewidth was not generally considered in the classical IETS literatures [30,31]. Linewidth broadening effects due to thermal and modulation contributions have been explored; however, the intrinsic linewidth was usually treated as negligible [44]. A recent report of the IETS intrinsic linewidth comes from the STM-IETS study on the C-H stretching peak of a single HCCH molecule adsorbed on the Cu(001) surface [48]. The reported value of 4 ± 2 meV is found to be consistent with the value of 6 ± 2 meV estimated for the hindered rotation of CO on Cu(001) from similar STM-IETS studies of the same research group [48,129]. Nevertheless, by comparing to the intrinsic linewidth value of ~ 6 cm⁻¹ (~ 0.75 meV) obtained from an IR study on the same type of molecules [130], the authors argue that the natural linewidth is negligible and that this intrinsic linewidth may be dominated by instrumental broadening originating from control electronics or the environment [48].

The preceding STM-IETS study reported only one intrinsic linewidth from the obtained spectrum [48]. Our nanopore-based IETS characterization produces a spectrum with multiple peaks originated from different vibrational modes. The obtained intrinsic linewidths are different for different peaks; therefore, they cannot be attributed to one systematic broadening effect, but rather are due to intrinsic molecular device properties. Furthermore, analysis on Raman or IR spectra of alkanethiols on gold shows that the spectral linewidths could be much larger than 1 meV, and different spectral peaks could have similar linewidths. For example, linewidth fittings using both Lorentzian and Gaussian distribution functions on a Raman spectrum [131] containing both Au-S stretching and CH₂ wagging peaks yield linewidths of ~ 6 meV and ~ 5 meV, respectively. Therefore, such comparison provides little help in the understanding of the origin of the intrinsic linewidths in our case.

A recent theoretical study by Galperin *et al.* on the linewidths of vibrational features in inelastic electron tunneling spectroscopy proposes that the intrinsic IETS linewidths are actually dominated by the couplings of molecular vibrations to electron-hole pair excitations in the metallic electrodes [132]. Using a nonequilibrium Green's function (NEGF) approach, the authors have investigated a junction consisting of two electrical leads bridged by a single molecule. After self-consistently solving the related Green's functions and self-energies, important junction characteristics such as the total tunneling current and intrinsic linewidth of the vibrational feature can be estimated. It is found that the interaction of the bridge phonon and the thermal environment contributes little (less than 0.1 meV) to the linewidth, and the dominant part of the intrinsic linewidth comes from the coupling between the bridge phonon and the electronic states of the electrodes [132]. Calculations show that the dominant part of the intrinsic linewidth has a dependence on the bridge-electrode electrical couplings. For coupling parameters corresponding to the nanopore structure, the calculated linewidth value exceeds 1 meV, which has the same order of magnitude as that obtained from the experiment [132].

One might assume that an inhomogeneous contribution would be a dominant part of the measured intrinsic linewidths because the nanopore junction contains several thousand molecules; however, it is very unlikely such a contribution based on the number of molecules would give different linewidths for different vibrational modes. Furthermore, the characterized linewidths from the nanopore method have a similar order of magnitude to the STM-IETS measurement results, where only a single molecule is examined [48,129].

The asymmetric line shapes and negative values of our IETS spectra such as those at 33 mV (Au-S stretching) and 133 mV (C-C stretching) can also be explained by the same theoretical model [132–137]. Asymmetric features in IETS spectra have been observed in several cases in an aluminum oxide tunnel junction and STM-IETS studies [138–140]. Theoretical investigations based on the same molecule-induced resonance model found that the inelastic channel always gives positive contribution to the tunneling conductance, while depending on the junction energetic parameters the contribution from the elastic channel could be negative and, furthermore, could possibly overweight the positive contribution from the inelastic channel and result in a negative peak in the IETS spectra [132,134,135]. The source of the negative contribution of the elastic channel, which only happens at the threshold voltage of $V = \hbar\omega/e$, is the interference between the purely elastic current amplitude that does not involve electron-phonon interaction and the elastic amplitude associated with the excitation and reabsorption of virtual molecular

vibrations. By setting certain values of the couplings of the bridging molecular state with the electrodes in the previously discussed model, numerical calculations have been performed to examine the change of the IETS spectrum as a function of the molecular energy level [132,135]. However, an analytical expression is needed from theoretical studies in order to fit the experimental data reported here and better understand such features.

The experimental study presented in this work has also stimulated theoretical investigations, especially first-principle simulations, of the alkanethiol IETS spectra in order to, for instance, understand the effect of the molecule-metal contact geometry change on the tunneling spectra or to provide further details in the peak assignments [144,145]. For example, Solomon *et al.* have used the Green's function density-functional tight-binding ("gDFTB") method to exam an octanedithiol molecule sandwiched between two gold electrodes [145]. As Figure 1.29 shows, the reported calculation result showed good agreement with the experimental data [25, 145]. Based on the theoretical calculations, the authors proposed that some experimental spectra peaks in the low bias region, which has previously been attributed to the Si_3N_4 matrix [25], could actually have molecular origins such as from the C-C-C scissoring vibrations [145]. By comparing the calculated IETS spectra of different molecular binding configurations, the authors have also studied the effect of the contact geometry on the intensities of the peaks and showed that the IETS spectra should have considerable variations with subtle changes of the binding sites [145].

In summary, our observed intrinsic linewidths of spectral peaks of different vibrational modes are dominated by intrinsic molecular properties. Theoretical inspections using nonequilibrium Green's function formalism on a simplified metal-single bridge molecule-metal model suggests that the coupling of the molecular vibrational modes to the electronic continua of the electrodes makes a substantial contribution to the spectral line shape and linewidth. The observed intrinsic linewidth differences can be qualitatively explained by the linewidth dependence on the threshold voltage. By choosing appropriate junction parameters, a quantitative comparison between theory and experiment is expected.

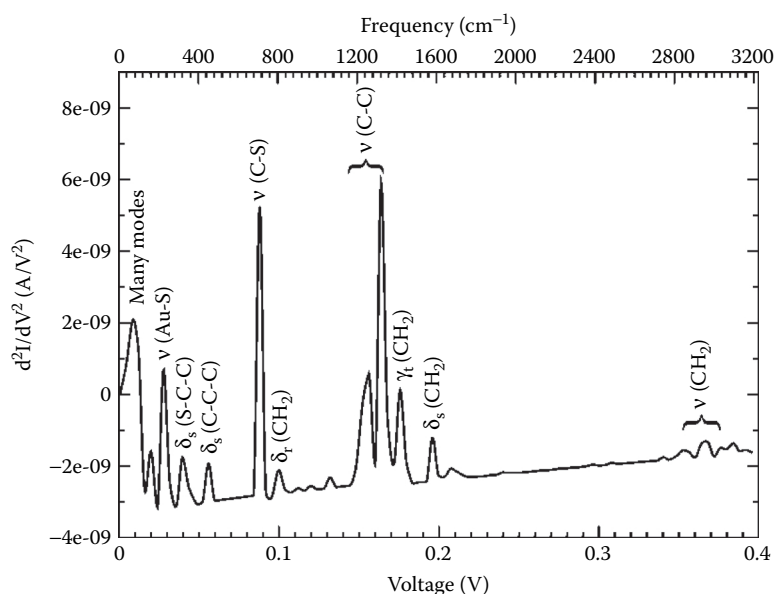


FIGURE 1.29 The calculated IETS spectrum for octanedithiol between two gold electrodes, which suggests that some experimental peaks in the low bias region that have previously been attributed to the Si_3N_4 matrix could actually be from molecular vibrations such as the C-C-C scissoring vibrations. After Ref. 145.

1.6 Conclusion

Using a nanometer-scale device structure, we have performed temperature-dependent $I(V)$ characterization for the first time on alkanethiol SAMs, and demonstrated unambiguously that tunneling is the dominant conduction mechanism. Comparing to a standard model of metal–insulator–metal tunneling, important transport parameters such as the barrier height have been derived, which qualitatively described the tunneling process. In addition, the inelastic electron tunneling spectroscopy technique has been applied to the study of molecular transport. This technique is used to fingerprint the chemical species inside the molecular junction. The obtained spectra exhibit characteristic vibrational signatures of the confined molecular species, presenting direct evidence of the presence of molecules in a molecular transport device for the first time.

The field of “molecular electronics” is rich in proposals and promises of plentiful device concepts, but unfortunately has a dearth of reliable data and characterization techniques upon which to test these ideas. As our results have shown, a well-prepared self-assembled alkanethiol monolayer behaves as a good, thin insulating film and shows understood “canonical” tunneling transport behavior. This molecular system should be used as a standard control structure for future molecular transport characterizations. The IETS technique has been proven to be a dependable tool for the identification of chemical species. It has especially indispensable applications in solid state molecular devices, where other spectroscopic tools such as IR or Raman are hard, if not impossible, to employ. The spectroscopic study conducted in this research verified the characterization of intrinsic molecular properties; therefore, it should be generally utilized for any future molecular transport investigations. Understanding the fundamental charge transport processes in self-assembled monolayers is a challenging task. However, the model control system and the reliable characterization methods presented in this research work should assist in guiding future research work toward more interesting and novel molecular transport systems.

References

- [1] Timp, G., Ed., *Nanotechnology*, Springer-Verlag, Berlin, Germany, 1999.
- [2] Aviram, A. and Ratner, M.A., Eds., *Molecular Electronics: Science and Technology*, The Annals of the New York Academy of Sciences, 852, The New York Academy of Sciences, New York, 1998.
- [3] Reed, M.A. and Lee, T., Eds., *Molecular Nanoelectronics*, American Scientific Publishers, 2003.
- [4] Grabert, H. and Devoret, M.H., Eds., *Single Charge Tunneling*, Plenum, New York, 1991.
- [5] Reed, M.A. and Seabaugh, A.C., Prospect for semiconductor quantum devices, in *Molecular and Biomolecular Electronics*, Birge, R.R., ed., American Chemical Society, Washington, 1994.
- [6] International Technology Roadmap for Semiconductors; <http://public.itrs.net/>.
- [7] Aviram, A. and Ratner, M.A., *Chem. Phys. Lett.*, 29, 277, 1974.
- [8] Metzger, R.M. et al., *J. Am. Chem. Soc.*, 119, 10455, 1997.
- [9] Reed, M.A., U.S. Patent No. 5,475,341, 1995.
- [10] ———, U.S. Patent No. 5,589,629, 1996.
- [11] Ulman, A., *An Introduction to Ultrathin Organic Films from Langmuir–Blodgett to Self-Assembly*, Academic Press, Boston 1991.
- [12] ———, *Chem. Rev.*, 96, 1533, 1996.
- [13] Nuzzo, R.G., and Allara, D. L., *J. Am. Chem. Soc.*, 105, 4481, 1983.
- [14] Aviram, A. et al., Eds., *Molecular Electronics II*, The Annals of the New York Academy of Sciences, 960, The New York Academy of Sciences, New York, 2002.
- [15] Reimers, J. et. al., Eds., *Molecular Electronics III*, The Annals of the New York Academy of Sciences, 1006, The New York Academy of Sciences, New York, 2003.
- [16] Chen, Y. et al., *Nanotechnology*, 14, 462, 2003.
- [17] Beyond Silicon: Breakthroughs in Molecular Electronics, <http://www.hpl.hp.com/research/qs/> (Hewlett-Packard Quantum Science Research).
- [18] Luo, Y. et al., *Chem. Phys. Chem.*, 3, 519, 2002.

- [19] Collier, C.P. et al., *Science*, 289, 1172, 2000.
- [20] Stewart, D.R. et al., *Nano Lett.*, 4, 133, 2004.
- [21] Lau, C.N. et al., *Nano Lett.*, 4, 569, 2004.
- [22] Wang, W., Lee, T., and Reed, M.A., *Rep. Prog. Phys.*, 68, 523, 2005.
- [23] Poirier, G.E., *Chem. Rev.*, 97, 1117, 1997.
- [24] Wang, W., Lee, T., and Reed, M.A., *Phys. Rev. B.*, 68, 035416, 2003.
- [25] Wang, W. et al., *Nano Lett.*, 4, 643, 2004.
- [26] Nuzzo, R.G., Dubois, L.H., and Allara, D.L., *J. Am. Chem. Soc.*, 112, 558, 1990.
- [27] Ratner, M.A. et al., in *Molecular Electronics: Science and Technology*, The Annals of the New York Academy of Sciences, 852, Aviram, A. and Ratner, M. Eds., The New York Academy of Sciences, New York, 1998.
- [28] Lee, T. et al., *J. Phys. Chem. B.*, 108, 8742, 2004.
- [29] Jaklevic, R.C. and Lambe, J., *Phys. Rev. Lett.*, 17, 1139, 1966.
- [30] Wolfram, T., Ed., *Inelastic Electron Tunneling Spectroscopy*, Springer, New York, 1978.
- [31] Hansma, P.K., Ed., *Tunneling Spectroscopy: Capabilities, Applications, and New Techniques*, Plenum, New York, 1982.
- [32] Bohm, D., *Quantum Theory*, Prentice-Hall, Inc., New York, 1951.
- [33] Landau, L.D. and Lifshitz, E.M., *Quantum Mechanics (Non-relativistic Theory)*, 3rd ed., Pergamon Press, New York, 1977.
- [34] Burstein, E. and Lundqvist, S., Eds., *Tunneling Phenomena in Solids*, Plenum Press, New York, 1969.
- [35] Duke, C.B., *Tunneling in Solids*, Academic Press, New York, 1969.
- [36] Simmons, J.G., *J. Appl. Phys.*, 34, 1793, 1963.
- [37] Franz, W., in *Handbuch der Physik*, 17, 155, Flugge, S., Ed., Springer-Verlag, Berlin, Germany, 1956.
- [38] Lewicki, G. and Mead, C.A., *Phys. Rev. Lett.*, 16, 939, 1966.
- [39] Stratton, R. et al., *J. Phys. Chem. Solids.*, 27, 1599, 1966.
- [40] Parker, G.H. and Mead, C.A., *Phys. Rev. Lett.*, 21, 605, 1968.
- [41] Brar, B. et al., *Appl. Phys. Lett.*, 69, 2728, 1996.
- [42] Maserjian, J. and Petersson, G.P., *Appl. Phys. Lett.*, 25, 50, 1974.
- [43] Lambe, J. and Jaklevic, R.C., *Phys. Rev.*, 165, 821, 1968.
- [44] Hansma, P.K., *Phys. Reports (Sec. C of Phys. Lett.)*, 30, 145, 1977.
- [45] Adkins, C.J. and Phillips, W.A., *J. Phys. C.*, 18, 1313, 1985.
- [46] Klein, J. et al., *Phys. Rev. B.*, 7, 2336, 1973.
- [47] Jennings, R.J. and Merrifi, J.R., *J. Phys. Chem. Solids*, 33, 1261, 1972.
- [48] Lauhon, L.J. and Ho, W., *Rev. Sci. Instrum.*, 72, 216, 2001.
- [49] Scalapino D.J. and Marcus, S.M., *Phys. Rev. Lett.*, 18, 459, 1967.
- [50] Bardeen, J., *Phys. Rev. Lett.*, 6, 57, 1961.
- [51] Harrison, W.A., *Phys. Rev.*, 123, 85, 1961.
- [52] Kirtley, J. et al., *Phys. Rev. B.*, 14, 3177, 1976.
- [53] Kirtley, J. and Hall, J.T., *Phys. Rev. B.*, 22, 848, 1980.
- [54] Reed, M. A. and Tour, J.M., *Scientific American*, 282, 86, 2000.
- [55] Bain, C.D. et al., *J. Am. Chem. Soc.*, 111, 321, 1989.
- [56] Grunze, M., *Phys. Scr.*, T49B, 711, 1993.
- [57] Noh, J. and Hara, M., *Langmuir*, 18, 1953, 2002.
- [58] Nuzzo, R.G. et al., *J. Am. Chem. Soc.*, 109, 733, 1987.
- [59] Walczak, M.W. et al., *J. Am. Chem. Soc.*, 113, 2370, 1991.
- [60] Widrig, C.A. et al., *J. Electroanal. Chem.*, 310, 335, 1991.
- [61] Schäfer, A.H. et al., *Adv. Mater.*, 10, 839, 1998.
- [62] Porter, M.D. et al., *J. Am. Chem. Soc.*, 109, 3559, 1987.
- [63] Although the HOMO–LUMO gap of alkyl chain type molecules has been reported, there is no experimental data on the HOMO–LUMO gap for the Au/alkanethiol SAM/Au system. 8 eV is commonly used as the HOMO–LUMO gap of alkanethiol.

- [64] Boulas, C. et al., *Phys. Rev. Lett.*, 76, 4797, 1996.
- [65] Fujihira, M. and Inokuchi, H., *Chem. Phys. Lett.*, 17, 554, 1972.
- [66] Lias, S.G. et al., Gas-phase ion and neutral thermochemistry, *J. Phys. Chem.*, Ref. Data, 17, 1, 1988.
- [67] Binnig, G. et al., *Phys. Rev. Lett.*, 49, 57, 1982.
- [68] Eigler, D.M. and Schweizer, E. K., *Nature*, 344, 524, 1990.
- [69] Lee, H.J. and Ho, W., *Science*, 286, 1719, 1999.
- [70] Bumm, L.A. et al, *Science*, 271, 1705, 1996.
- [71] Donhauser, Z.J. et al., *Science*, 292, 2303, 2001.
- [72] Dorogi, M. et al., *Phys. Rev. B.*, 52, 9071, 1995.
- [73] Xu, B. and Tao, N., *Science*, 301, 1221, 2003.
- [74] Chen, J., Molecular wires, switches, and memories, Ph.D. thesis, Yale University, 2000.
- [75] Onipko, A.I. et al., *Phys. Rev. B.*, 61, 11118, 2000.
- [76] Cygan, M. T. et al., *J. Am. Chem. Soc.*, 120, 2721, 1998.
- [77] Wold, D.J. et al., *J. Phys. Chem. B.*, 106, 2813, 2002.
- [78] Cui, X.D. et al., *Science*, 294, 571, 2001.
- [79] Wold, D.J. and Frisbie, C.D., *J. Am. Chem. Soc.*, 122, 2970, 2000.
- [80] Cui, X.D. et al., *Nanotechnology*, 13, 5, 2002.
- [81] Reed, M.A. et al., *Science*, 278, 252, 1997.
- [82] Kergueris, C. et al., *Phys. Rev. B.*, 59, 12505, 1999.
- [83] Reichert, J. et al., *Phys. Rev. Lett.*, 88, 176804, 2002.
- [84] Zhou, C., Atomic and molecular wires, Ph.D. thesis, Yale University, 1999.
- [85] Park, H. et al., *Appl. Phys. Lett.*, 75, 301, 1999.
- [86] Park, J. et al., *Nature*, 417, 722, 2002.
- [87] Liang, M.P. et al., *Nature*, 417, 725, 2002.
- [88] Gregory, S., *Phys. Rev. Lett.*, 64, 689, 1990.
- [89] Kushmerick, J.G. et al., *J. Am. Chem. Soc.*, 124, 10654, 2002.
- [90] Kushmerick, J.G. et al., *Phys. Rev. Lett.*, 89, 086802, 2002.
- [91] Holmlin, R. et al., *J. Am. Chem. Soc.*, 123, 5075, 2001.
- [92] Rampi, M. A. and Whitesides, G. M., *Chem. Phys.*, 281, 373, 2002.
- [93] Mbindyo, J.K.N. et al., *J. Am. Chem. Soc.*, 124, 4020, 2002.
- [94] Ralls, K.S. et al., *Appl. Phys. Lett.*, 55, 2459, 1989.
- [95] Zhou, C. et al., *Appl. Phys. Lett.*, 71, 611, 1997.
- [96] Horiuchi, T. et al., *Rev. Sci. Instrum.*, 60, 994, 1989.
- [97] Datta, S. et al., *Phys. Rev. Lett.*, 79, 2530, 1997.
- [98] Xue, Y. et al., *J. Chem. Phys.*, 115, 9, 4292, 2001.
- [99] Sze, S.M., *Physics of Semiconductor Devices*, Wiley, New York, 1981.
- [100] Lamb, D.R., *Electrical Conduction Mechanisms in Thin Insulating Films*, Methue, London, 1967.
- [101] Rhoderick, E.H. and Williams, R.H., *Metal-Semiconductor Contact*, Clarendon Press, Oxford, UK, 1988.
- [102] Slowinski, K. et al., *J. Am. Chem. Soc.*, 121, 7257, 1999.
- [103] York, R.L. et al., *J. Am. Chem. Soc.*, 125, 5948, 2003.
- [104] Smalley, J.F. et al., *J. Phys. Chem.*, 99, 13141, 1995.
- [105] Weber, K. et al., *J. Phys. Chem. B.*, 101, 8286, 1997.
- [106] Slowinski, K. et al., *J. Am. Chem. Soc.*, 119, 11910, 1997.
- [107] Mann, B. and Kuhn, H., *J. Appl. Phys.*, 42, 4398, 1971.
- [108] Polymeropoulos, E. E. and Sagiv, J., *J. Chem. Phys.*, 69, 1836, 1978.
- [109] Joachim, C. and Magoga, M., *Chem. Phys.*, 281, 347, 2002.
- [110] Zimmerman, D.T. et al., *Appl. Phys. Lett.*, 75, 2500, 1999.
- [111] Kushmerick, J.G. et al., *Nano Lett.*, 4, 639, 2004.
- [112] Stipe, B.C. et al., *Science*, 280, 1732, 1998.

- [113] Bencuya, I., Electron tunneling in metal/tunnel-oxide/degenerate silicon junctions, Ph.D. thesis, Yale University, 1984.
- [114] Lye, W-K., Inelastic electron tunneling spectroscopy of the silicon metal-oxide-semiconductor system, Ph.D. thesis, Yale University, 1998.
- [115] Vollhardt, K.P. and Schore, N.E., *Organic Chemistry: Structure and Function*, 3rd ed., W.H. Freeman and Company, New York, 1999.
- [116] Kemp, W., *Organic Spectroscopy*, John Wiley and Sons, New York, 1975.
- [117] Cooper, J.W., *Spectroscopic Techniques for Organic Chemists*, John Wiley and Sons, New York, 1980.
- [118] Duwez, A.-S. et al., *Langmuir*, 16, 6569, 2000.
- [119] Kato, H. S. et al., *J. Phys. Chem. B.*, 106, 9655, 2002.
- [120] For sample IR data, see Castiglioni, C. et al., *Chem. Phys.*, 95, 7144, 1991.
- [121] For sample Raman data, see Bryant, M.A. and Pemberton, J.E., *J. Am. Chem. Soc.*, 113, 8284, 1991.
- [122] Kaun, C-C. and Guo, H., *Nano Lett.*, 3, 1521, 2003.
- [123] Molinary, M. et al., *Mat. Sci. Eng. B.*, 101, 186, 2003.
- [124] Bogdanoff, P.D. et al., *Phys. Rev. B.*, 60, 3976, 1999.
- [125] Mazur, U. and Hipps, K.W., *J. Phys. Chem.*, 86, 2854, 1982.
- [126] ———, *J. Phys. Chem.*, 85, 2244, 1981.
- [127] Kurata, H. et al., *Jap. J. Appl. Phys.*, 20, L811, 1981.
- [128] Kirtley, J., *The Interaction of Tunneling Electrons with Molecular Vibrations in Tunneling Spectroscopy*, P.K. Hansma, Ed., Plenum, New York, 1982.
- [129] Lauhon, I.J. and Ho, W., *Phys. Rev. B.*, 60, R8525, 1999.
- [130] Hirschmugl, C.J. et al., *Phys. Rev. Lett.*, 65, 480, 1990.
- [131] Joo, S.W. et al., *J. Phys. Chem. B.*, 104, 6218, 2000.
- [132] Galperin, M. et al., *Nano Lett.*, 4 1605, 2004.
- [133] Persson, B.N.J. and Baratoff, A., *Phys. Rev. Lett.*, 59, 339, 1987.
- [134] Persson, B.N.J., *Phys. Scr.*, 38, 282, 1987.
- [135] Mii, T. et al., *Phys. Rev. B.*, 68, 205406, 2003.
- [136] ———, *Surface Science*, 502–503, 26, 2002.
- [137] Tikhodeev, S.G. et al., *Surface Science*, 493, 63, 2001.
- [138] Bayman, A. et al., *Phys. Rev. B.*, 24, 2449, 1981.
- [139] Hahn, J.R. et al., *Phys. Rev. Lett.*, 85, 1914, 2000.
- [140] Pascual, J.I. et al., *Phys. Rev. Lett.*, 86, 1050, 2001.
- [141] Fan, F.F. et al., *J. Am. Chem. Soc.*, 124, 5550, 2002.
- [142] Piccinin, S. et al., *Chem. Phys.*, 119, 6729, 2003.
- [143] Tomfohr, J.K. et al., *Phys. Rev. B.*, 65, 245105, 2002.
- [144] Jiang, J. et al., *Nano Lett.*, 5 1551, 2005.
- [145] Solomon, G.C. et al., *J. Chem. Phys.*, 124, 094704, 2006.

