The Importance of Chemical Bonding to the Contact for Tunneling through Alkyl Chains

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The effect of the presence or absence of chemical bonds between alkyl chain monolayers and the contacts in metal/molecule/semiconductor junctions on the current−voltage characteristics was studied. Three types of junctions were used: Hg/alkylthiols/SiO$_2$/p-Si, Hg/alkylthiols/p-Si−H, and Hg/alkylsilanes/SiO$_2$/p-Si. While in the first two junctions current is attenuated exponentially as a function of the length of the alkyl chain, a characteristic behavior of tunneling, the current through the third junction does not reveal such behavior, suggesting that current transport is different in this case. We postulate that this is because in the first two junctions the monolayers are covalently bound to the Hg, while in the third junction, the alkysilanes are anchored to the Si surface only at a few points and are best viewed as not bonded to either side of the junction. The mechanism of current flow through the first two junctions is thought to be through-bond tunneling, and our results indicate that a chemical bond to at least one of the electrode surfaces is essential for this mechanism to operate. Electrostriction causes changes in the current−voltage characteristics of the first two junctions. Evidence is presented suggesting that electrostriction tilts short chains ($\leq$C$_{12}$), resulting in an additional route to charge transport by tunneling through space. In contrast, long chains ($\geq$C$_{14}$) do not tilt under pressure; instead, gauche defects are formed in their initial all-trans configuration decreasing the efficiency of electronic coupling through them. The use of p-type Si in this study ensures that at low bias voltages holes are the dominant charge carriers. Holes are found to tunnel more efficiently than electrons in agreement with theoretical predictions.

Introduction

Electronic transport measurements through molecules require in nearly all cases electrical contacts to the molecules. For solid-state measurements, those are provided by at least two electrodes, made up of solids, with extended (nonmolecular) bonding having delocalized electrons. The molecules need to contact these solids, something that can be done by making actual chemical bonds or by relying on mechanical contact, which means mostly relying on van der Waals interactions and polarization effects. In the quest to understand the nature of electron transport across metal/molecule/metal and metal/molecule/semiconductor junctions, the nature of this contact is turning out to be of critical importance.[1] It is this question that we address here experimentally.

Theoretical treatments of the effect of adsorption chemistry on electrical transport have so far mainly focused on resonant tunneling[2] through conjugated molecules. Several experiments show substantial changes in the conductivity of conjugated "molecular-wire" molecules by changing the type[3] or the geometry[4] of their contacts to surfaces. Whereas foregoing conjugation limits the possibilities for resonant tunneling, nonresonant tunneling through the nonconjugated molecule−electrode interface should still be affected by the electronic structure at that interface on the basis of McConnell's superexchange model.[5] This then suggests studying effects of contacts on charge transport through nonconjugated alkyl chains. Using simple versions of such molecules has an added advantage in that they can be studied as well-characterized monolayers (on the electrode). Using monolayers in this type of work has the enormous advantage of averaging in a single measurement,

something that needs to be done in other approaches (see below) by a large number of repeat experiments. Also, probably more is known in terms of structure and packing about these than about most other types of molecular monolayers.[6]

In the past, studies of nonresonant electron tunneling across monolayers and bilayers of alkane chains have been conducted using (a) electrochemical junctions of the type metal/molecule/redox couple in solution,[7] (b) solid-state devices of the type Hg/molecule/metal,[8] Hg/molecule/molecule/metal,[9] Hg/molecule/molecule/Hg,[10] Hg/molecule/semiconductor,[11] and Hg/molecule/carbon[12] in which Hg was used as a "soft" top contact so as not to damage the molecules, (c) atomic force microscopy (AFM) with a conducting tip, which can sample small numbers of molecules (and, by diluting molecule A in a matrix of B, even single A molecules) and allows one to study changes in conductivity as a function of pressure on the monolayer.[13]

The current measured across all of these types of junctions obeyed the relation $I = I_0\, e^{-\beta d}$ (see eq 3 and discussion following it in Results and Discussion), where d is the distance through which tunneling takes place and β is the structure-dependent attenuation factor for the molecules.[7−13] The value of β from the electrochemical measurements ranged from 0.8 to 1.0 Å^{-1}. The value based on the solid-state devices was found to be 0.87 $\pm$ 0.1 Å^{-1} for electron tunneling and 0.65 $\pm$ 0.08 Å^{-1} for hole tunneling. The agreement among the values of β suggests that the mechanism of electron transport in the solid-state junctions is closely related to that across self-assembled monolayers into molecules in solution.

In contrast to these β values, studies on tunneling across alkylsilane monolayers on oxidized Si revealed different behavior, that is, low β values. Vuillaume et al. reported suppression of tunneling in junctions of the type n-Si/SiO$_x$/alkylsilanes/metal, resulting in very low conductivity that was

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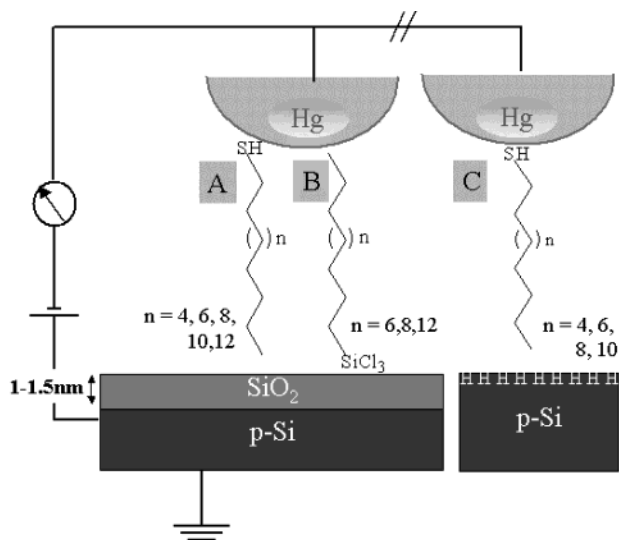*J. Phys. Chem. B, Vol. 106, No. 40, 2002* **10433**

Figure 1. Schematic description of the junctions and molecules used in the experiments. Junction A consisted of alkanethiols adsorbed on the Hg; for junction B, alkylsilanes were assembled on the SiO_x/p-Si substrate; junction C was similar to junction A except for the use of hydrogenated Si (Si−H) as the semiconductor side of the junction.

shown to be independent of monolayer thickness.[14] Waldeck et al. used photoelectrochemistry to find very weak dependence on monolayer thickness for hole tunneling from n-Si into solution ($\beta = 0.2$ Å^{-1}).[15] Structural characterization of the monolayer ensured that the surprisingly low current attenuation was not a result of defects in the monolayers.[15] *All of the preceding Si/SiO_x studies were based on monolayers that were thought to be chemically bonded to one side of the junction, but as will be shown herein, were probably effectively decoupled from the surface on which they were assembled.*

Cui et al. showed that the conductivity of a metal/alkyl chains/ metal system increases substantially once both ends of the chains are *chemically bonded to the two contacts*.[13d] Under such conditions, conductivity does not change as a function of applied pressure on the monolayers, in contrast to when only one side is chemically bonded.[13e]

Recently, we presented preliminary results on hole tunneling through monolayers of longer alkyl chains in a Hg/alkylchain/ SiO_x/p-Si system.[11] Besides the importance of acquiring data using a different experimental system, there are two important other aspects to our approach. (1) Because of technical difficulties in measuring the low tunneling currents through long alkyl chains, Cui et al. focused on chains with not more than 12 carbons (C_{12}).[13c−e] Longer molecules, which are known to assemble better as monolayers and to have different mechanical properties, were not studied. The effect on conductivity of not having bonds at all, at both ends of the chains, was not studied, either. (2) All of these studies were based on electron, rather than hole, tunneling although theory suggests that the latter should be more efficient than electron tunneling.[16]

Here, we expand on and complement our preliminary report and describe our studies of the electrical properties of well-ordered alkyl chain monolayers sandwiched between p-Si and Hg. The different systems that were used are depicted in Figure 1. In junction A, the alkyl monolayers are chemically bonded (via a S−Hg bond) to the Hg but chemically decoupled from the Si side (no chemical bond between the terminal CH_3 group and SiO_x. In junction B, the molecules are connected to neither side of the junction. As will be described, we base ourselves here on extensive earlier work by, among others, Allara and colleagues,[17a−e] as well as by Sagiv, Maoz and co-workers,[17f,g]

who showed that the alkyl silane chains that make up the silane monolayer are anchored to the SiO_x surface only occasionally, that is, most of the chains are *not* bonded to the SiO_x (the chains are bonded between them via Si−O−Si bonds). In junction C, the monolayer is once again bonded to the Hg, and electronic coupling to the Si is changed because its surface is hydrogenated, rather than covered by an oxide layer.

The use of a p-type semiconductor ensured that *at low bias values* current through the molecules is governed by hole tunneling. That is because in the bulk the Fermi level is between 0.15 and 0.2 eV from the valence band maximum[18] so that for forward bias up to ∼0.4 V holes are the dominant charge carriers that reach the interface. As we shall show herein, there is negligible band bending at the Si/SiO_x interface, which means that the rate-determining step for hole transfer is not that of crossing the potential barrier due to the band bending (Schottky barrier) but that of tunneling through the molecules. In addition, the relatively large contact areas that we used enabled us to learn about the effect of pressure on conductivity also through long chains ($>C_{12}$), something that could not be measured with the AFM setup.

A key point in this study is the fact that the structures of all of the monolayers used here have been studied thoroughly in the past and that they are known to have the same structure, including tilt angle, regardless of the different binding chemistry.[17,19]

Experimental Section

Materials. Octadecyltrichlorosilane, dodecyltrichlorosilane, octadecanethiol, hexadecanethiol, dodecanethiol, dodecane, tetradecane, and carbon tetrachloride (all from Aldrich) and trichlorohexadecylsilane and tetradecanethiol (both from Fluka) were of the highest purity available and used as received without further purification. Mercury (Aldrich, extra pure) was taken out of its bottle into the electrode's reservoir by means of a syringe, extracting only from within the mercury pool, to avoid extraction of contaminations and oxide from the surface. p-Si wafers (⟨100⟩ or ⟨111⟩) with a nominal resistivity of 1−10 Ω cm were purchased from Virginia Semiconductors Ltd.

Si Sample Preparation. *Oxide-Covered Samples.* ⟨100⟩ Si samples (1 cm^2) were cleaned in a H_2O/H_2SO_4/H_2O_2 (5:2:1) solution at 90° for 20 min, followed by thorough washing with water. Some of the samples (group I) were used without any further treatment to construct the junctions. Other samples (group II) were treated by a 60 s dip into a 5% HF solution to strip off the native oxide layer. This step gave samples with highly hydrophobic surfaces. Following a 30 s wash with water, the samples were put in an UV-ozonator for 7 min to regrow an oxide layer. This layer was found to be 1.5−2 nm thick by ellipsometry. These samples were then used in the various junctions. *The two groups of samples turned out to be similar in terms of their I−V characteristics.*

Hydrogen-Terminated ⟨111⟩ Samples. Following an initial cleaning process as described above, the samples were immersed for 15 min in a 40% aqueous deoxygenated NH_4F solution and then transferred into the reaction vessel without rinsing.

Monolayer Formation. *Thiols.* The molecular monolayers on mercury were formed by extruding a drop of mercury (∼5 μL) from a presilanized capillary of a commercial mercury drop electrode (CGME, BAS Inc., Indiana) and exposing it to a solution of the alkylthiol (∼5 mM) in ethanol for ∼10 min. Subsequently, the drop was rinsed with ethanol, dried in air, and then used to assemble the junction.

Silanes on SiO₂. The reactive solution was composed of ~70% dodecane (or tetradecane), ~30% carbon tetrachloride, and ~10^{-3} M of the *n*-alkyltrichlorosilane. The silanes were always incorporated at the last moment to avoid prolonged contact with atmospheric humidity. Samples were immersed for periods of ~1 h, and the temperature for all modifications was kept at 4 °C, that is, under the transition temperature of all monolayers.[17a−e] As the samples were withdrawn from the silane solution, one could observe spontaneous dewetting over the whole surface. This evidenced that the treated silicon samples were covered with a dense monolayer of long alkyl chains. Routine contact-angle measurements on one sample from each modification batch ensured that the modified wafers were highly hydrophobic with a contact angle above 110°.

To improve reproducibility and to make comparison between results meaningful, care was taken that sets of measurements (with different molecules) were based on samples prepared from the same Si wafer. In this way, all of the experimental steps prior to the assembly process of the molecules (such as cleaning, controlled oxide growing, etc.) were identical.

Junctions and Measurement Setup. The Si substrates were mounted on a homemade stage that allowed both coarse and fine movement (by means of a micrometer screw) of the substrate toward the mercury drop. InGa eutectic was used to make back contacts to the samples. For this, the back of the sample was scratched with a diamond knife to ensure good contact to the eutectic so that no significant potential drop could develop at this contact. The complete setup was constructed on a vibration-free optical table. The Hg drop remained steady after a monolayer self-assembled on it. The contact area between the Hg drop and Si was monitored optically (×120 magnification), which also allowed measurement of the actual geometric contact area (~0.2 mm²). An HP4155 semiconductor parameter analyzer was used to measure *I−V* curves. At forward bias, the Hg was negative relative to p-Si. Because the measured currents were relatively high (because of the large contact area), a short integration time (0.03 s) with a scan rate of 30 mV/s was found to be sufficient to produce *I−V* curves without any significant noise. Short integration was also used to avoid deterioration of the monolayers, something that was found to result from prolonged, 1 mV/s, scans. Each set of *I−V* curves that is shown represents an average over measurements on at least 5−10 different samples for each type of molecule.

Kelvin Probe Measurements of Modified Hg. Kelvin probe measurements on alkanethiol-modified Hg were carried out on a fresh mercury pool confined in an octadecyl trichlorosilane (OTS)-silanized glass vial (2 cm in diameter), which was fixed vertically in a small Petri dish. Presilanization made the glass surface less-prone to contamination. A tungsten wire at the bottom of the vial and connected to the outside through the glass was used to establish electrical contact to the Hg pool. A second glass cylinder, slightly longer and of slightly larger diameter, was placed concentrically around the vial. Hg formed a flat meniscus extending above the edge of the vial. An ethanol self-assembly solution was poured over the mercury and allowed to make contact with it for at least 1 min. By lifting the outer glass cylinder, we allowed the self-assembly solution to drain into the Petri dish. The same method was then used to rinse the surface of mercury repeatedly with ethanol and water without disturbing it. The commercial Kelvin probe (Besocke Delta-Phi, Juelich, Germany) was then brought in close proximity to the Hg surface, and a measurement was taken. The distance between the probe and Hg was adjusted under a microscope to ensure as short a distance as possible to the sample (to limit
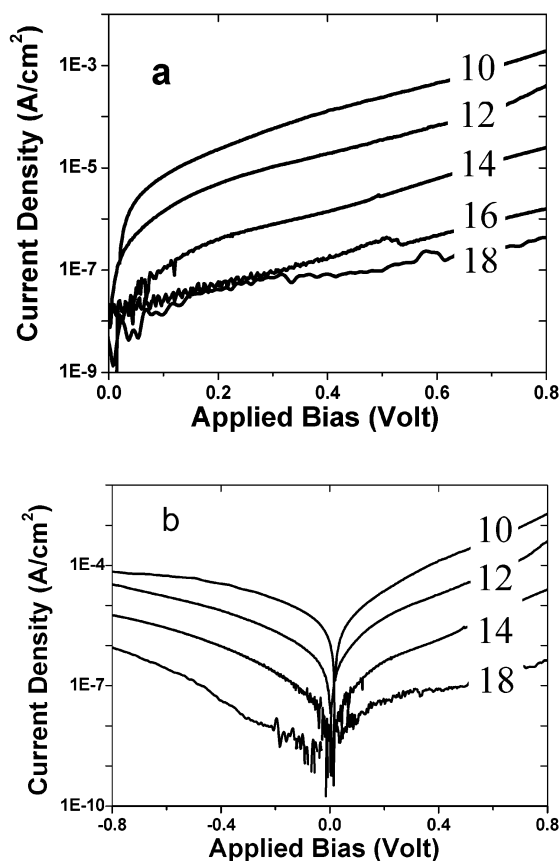

Figure 2. Experimental *I−V* curves (a) for Hg/alkylthiols/SiO$_x$/p-Si junctions (junction A). Because we use p-type semiconductors, at forward bias ($V > 0$), Hg is at a potential negative with respect to the p-Si; in reverse bias ($V < 0$), the situation is the opposite. The numbers on the curves give the length of the alkylthiol chain in terms of methylene units. The set of *I−V* curves is the average of measurements on 5−10 different samples. Panel b shows curves similar to those in panel a but for both polarities to show the relatively symmetric behavior of the *I−V* curves around 0 V.

the noise) but sufficiently large to avoid incidental contact that would have destroyed the probe by amalgamation. Details of the Kelvin probe system and the measurement technique are described elsewhere.[20] The entire apparatus was placed on a vibration isolation table. The error in these measurements is ±100 mV because a relatively large distance had to be kept between the probe and the sample to avoid ripples on the Hg surface due to the vibrations of the probe.

Results and Discussion

Figure 2a depicts a typical set of *I−V* curves measured with the thiol-based junctions of type A. The semilogarithmic plot not only shows the exponential dependence of the current on the applied voltage, but also suggests such a current dependence on the length of the molecules. Figure 2b shows that the junctions are rather symmetrical with respect to the bias polarity. The behavior is, qualitatively, in accordance with the fact that the work functions of oxide-covered Si and monolayer-covered Hg surfaces, measured by the Kelvin probe technique, were found to be the same within ±100 mV. Because Hg does not wet, or chemically react with, Si and SiO$_x$ surfaces,[21] this similarity in work function suggests that, upon contact, no major rearrangement of charge occurs between the two free surfaces and no substantial barrier should form inside the Si. Thus, we conclude that *no significant energy barrier exists inside the semiconductor side of the interface, and because care was taken*
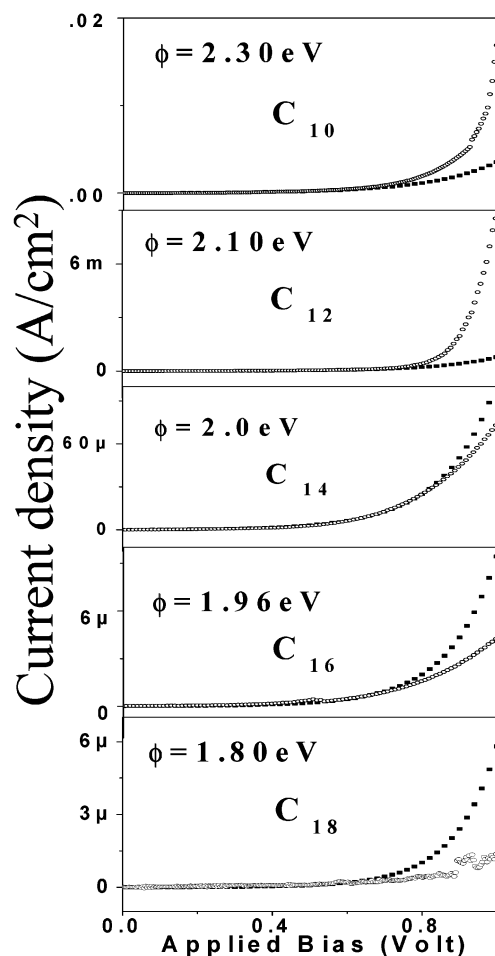
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Figure 3. Fitting of Simmons' model[22] (■) to the experimental curves (○) of junction A. All fittings were done with an effective tunneling barrier of $\phi = 2.0 \pm 0.2$ eV. The ϕ values in the graphs rule out the possibility that the results for the C_{10} and C_{12} chains are due to less-ordered monolayers (see text for further details).

to eliminate an iR drop at the back contact (see experimental details), all of the applied voltage is imposed on the molecules at the interface.

To describe the current density, J, through the junctions, we adopt Simmons' model,[22] expressed by eq 1, which is based on the Wentzel−Kramers−Brillouin (WKB) approximation for tunneling and which has proven to be a good first approach to describe tunneling through alkyl chains as tunneling through a dielectric, as long as the potential range is not larger than ± 1.5 V:[13]

$$J = \frac{q}{4\pi^2\hbar d^2}\left\{\left(q\phi - \frac{qV}{2}\right)\exp\left[-\frac{2(2m)^{1/2}}{\hbar}\left(q\phi - \frac{qV}{2}\right)^{1/2}d\right] - \left(q\phi + \frac{qV}{2}\right)\exp\left[-\frac{2(2m)^{1/2}}{\hbar}\left(q\phi + \frac{qV}{2}\right)^{1/2}d\right]\right\} \quad (1)$$

Here, ϕ (in eV) is the barrier height, V (in volts) is the applied potential, m is the mass of an electron (in kg), $\hbar$ is Planck's constant (in eV s) divided by 2π, q is the charge of an electron (in Coulombs), and d is the tunneling distance (in m).

Figure 3 shows the fit between a set of experimental $J-V$ data for Si/SiO$_x$/alkylthiol monolayer/Hg devices made with alkylthiols of different lengths adsorbed on Hg and eq 1. The tunneling distance, d, was taken as the sum of the expected length of the molecules,[7] and the oxide thickness was, as measured by ellipsometry. Optimization of the fit between the

experimental results and eq 1 was done only for low bias values. We did so for the following reasons: (1) Under these conditions, *hole* tunneling dominates. With increasing forward bias voltage, the energy difference between the Fermi level at the mercury side (which serves as a cathode) and the bottom of the semiconductor conduction band will decrease, bringing them closer and closer in resonance.[18] As a result, the probability for *electron* tunneling from the metal increases, and thus, at higher forward bias, the overall current will have both electron and hole contributions. (2) If the electric field, resulting from the potential difference across the molecules at the interface, is sufficiently large, structural changes can occur. These, in turn, can affect the tunneling efficiency (see below). Because we are interested in finding correlations between the molecules/molecular layers with known, controlled structure and their electrical characteristics, we report quantitative results only for bias values that are expected to be sufficiently low so that no major structural changes in the molecules take place.

Tunneling through alkyl chains is often treated in terms of a superexchange mechanism.[5,16] This mechanism explains how electronic conduction can be facilitated by mixing the donor/acceptor levels (in our case the Hg/Si Fermi levels) with the molecules' electronic energy levels, if these levels are *not* close enough to the donor/acceptor levels to be in resonance with them. Such mixing improves the electronic coupling between the "donor" and the "acceptor" and is more efficient when the gap between the Fermi levels and the levels in the molecules is smaller. If the Fermi levels are energetically far enough from the HOMO/LUMO levels in the molecules, that is, *at low enough voltages*, the contribution from superexchange will be relatively small. In that case, Simmons' model (eq 1) is a useful first approximation, because the process can be described as one of simple tunneling through a dielectric. It then provides a semiquantitative tool to understand *trends* in results.

While it was not possible to obtain good fits to eq 1 over the whole experimental potential range, satisfactory fits could be achieved for *all curves*, up to 0.5 V bias, using a tunneling barrier, ϕ, of 2.0 ± 0.2 eV. The errors in the barrier heights are due to the ± 2 Å uncertainty in the ellipsometrically determined oxide thickness. The ϕ values are in good agreement with values reported recently by others.[13b,c] At this stage, the simplicity of our system enables us to use this basic (two-parameter) model rather than more elaborate ones with more parameters.

Further examination of the curves in Figure 3 suggests that they can be divided qualitatively into two groups based on their behavior at high bias voltages. In the first group, which contains C_{10} and C_{12} alkyl monolayers, the theoretical fit at high voltages is lower than the experimental curves. In the second group, which contains monolayers with the rest of the alkyl chains, the behavior at high voltages is the opposite, that is, the fit is higher than the experimental curves. The fit for C_{14} can be regarded as intermediate between the two groups.

One plausible explanation for this difference is the less-organized, more poorly packed structure of the shorter alkyl chains, C_{10} and C_{12}.[7] However, if this were the case, then we would expect lower ϕ values for these than for the other junctions, because monolayers of these chains can be more easily penetrated than those made with longer chains. However, this does not explain why the junctions with the longer chains are less-conducting (at high voltages) than what is predicted theoretically. We can actually rule out this explanation completely, as follows. If we ignore the uncertainty in the oxide thickness and fit all curves by using a *similar oxide thickness* (taken in this case as 1.5 nm), we find that the resulting values

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of ϕ with C_{10} and C_{12} monolayers are higher than those of the other junctions (see values in Figure 3). This is opposite to what we expect according to the "organization" hypothesis.

Another possible explanation is that at high voltages there is a substantial contribution of electron tunneling to the already existing hole tunneling. If this were indeed the case, this added contribution should be roughly the same fraction, regardless of chain length, resulting in higher-than-theoretical currents for all curves. Such behavior is obviously not seen for all chains.

We suggest that differences in the mechanical properties of the molecular layers and in their structural response to the applied electric field (electrostriction, that is, the effect for which an electric field causes compression of the material on which it acts) are the cause for the observed differences in electrical characteristics. Similar effects were seen in AFM-mediated electronic transport measurements on Au/alkane/Au systems.[13e] The electrostriction effects can be understood as follows: The pressure on the monolayers as a function of potential is given by[10]

$$P = \left(\frac{V}{d}\right)^2 \epsilon\epsilon_0 \qquad (2)$$

where P (in pascals) is the pressure, V (in volts) is the applied voltage, d (in meters) is the thickness of the film (in this case including the oxide layer), and ϵ and ϵ_0 are the relative dielectric constant of the film and the permittivity of vacuum, respectively. At a bias of 1 V, the pressure on the monolayers (taking $\epsilon = 2.5$ and $d = 30$ Å) is on the order of 2.5 MPa. AFM and interfacial force microscopy (IFM) experiments suggest that a pressure of more than 2 GPa is needed to tilt long alkyl chains[23] ($>C_{14}$). However, several nonlinear optical experiments on a variety of self-assembled and Langmuir—Blodgett films of long alkyl chains indicate that, even at pressures of a few megapascals, terminal gauche defects are generated that tilt the CH_3 symmetric dipole of the terminal groups.[24] These results support a Monte Carlo simulation[25] of self-assembled thiol C_{16} monolayers, which suggests that with increasing pressure a dramatic increase (from 6% to 38%) in the number of molecules with such end gauche defects is expected. Slowinski et al.[7] observed on the basis of capacitance measurements that long alkylthiol chains adsorbed on Hg tend to fracture as the drop expands. Introducing gauche defects in an otherwise all-trans configuration of an alkyl chain is expected to decrease electronic coupling through bonds.[16]

We postulate that initially (at zero and low bias values) all chains are in an all-trans configuration and that the mechanism of charge transfer at these biases is one of *through-bond tunneling*. As the potential increases, electrostriction increases as well. The longer chains, $>C_{14}$, do not tilt substantially under the forces operating in this study. Instead, defects such as gauche conformations are formed in these chains, effects that lower the efficiency of through-bond tunneling. Experimentally, such a progressive process is revealed as an *I—V* curve in which the current deviates more and more (to lower currents) from exponential increase as a function of bias. *This agrees with results from electrochemical studies[26] that demonstrated that the current through these chains is highest if they are in the all-trans configuration.*

Unlike what is the case with the long alkylthiol monolayers adsorbed on Hg, it was found that the short chain ($<C_{14}$) molecules tend to tilt[7] under compression. The fact that monolayers made up of such short chains can be compressed and released without showing hysteresis in strain recovery (measured by a surface force apparatus) was ascribed to their
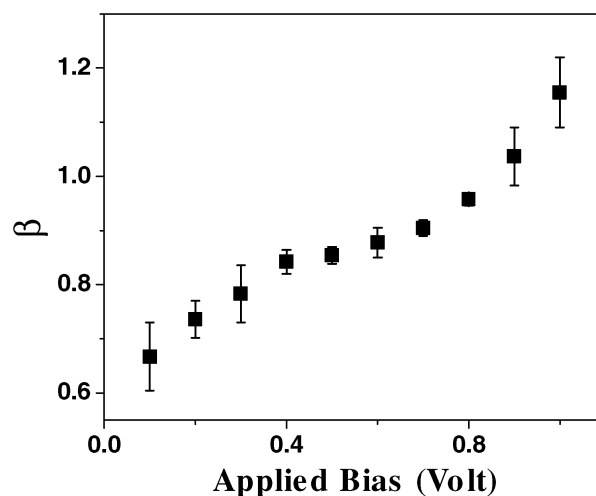

Figure 4. Variation of β ($I = I_0$ $e^{-\beta d}$; see eq 3) extracted from the experimental data for junction A samples, shown in Figure 2, with the applied voltage.

"liquidlike" structure.[23b] The increase in current that is observed once the chains are tilted has been ascribed to *additional through-space tunneling.*[7] Others found that if the pressure is high enough to tilt also long ($>C_{16}$) chains, the rate of current increase is higher with the shorter than with the longer chains.[23e]

In view of these results, we explain our findings as follows. As the potential increases, the shorter chains C_{10} and C_{12} are tilted because of electrostriction, causing the current to increase as a result of an added route to charge transfer, that is, *through-space tunneling*. The probability for this process increases progressively as the film continues to be compressed, and current increases faster than expected from its initial exponential behavior.

If we describe the current, I, through the alkyl chains as

$$I = I_0 \, e^{-\beta d} \qquad (3)$$

then β, the structure-dependent attenuation factor for the molecules, can be extracted from eq 1 to be

$$\beta = 2\sqrt{\frac{2m^*(\phi - V/2)}{\hbar^2}} \qquad (4)$$

According to eq 4, β should decrease slowly with voltage and approach zero as V approaches 2ϕ. *Lower β values mean less attenuation of the current per unit distance or, in other words, more efficient tunneling.*

The different experimental results obtained for junctions with short- and long-chain monolayers, suggest that the situation in this case is more complicated. For the short chains, β decreases with potential as the *observed* tunneling becomes more efficient, and for the long chains, it increases with potential as the *observed* tunneling becomes less efficient. However, as we showed earlier,[11] if we calculate a single "effective" β parameter by plotting $\ln(I)$ as a function of d, the two opposing effects result in an overall *increase* of β as a function of voltage, as can be seen in Figure 4.

As described above, ϕ, the barrier height for tunneling that we extract from the experimental data, is approximately 2 eV. Although this result agrees with that of others,[13b,c] this value is rather surprising considering the fact that the HOMO—LUMO gap of alkyl chains is approximately 9 eV.[14b] We postulate that, upon adsorption, this gap decreases, that is, the (chemical) contact, in this case to the Hg side, strongly affects the energy
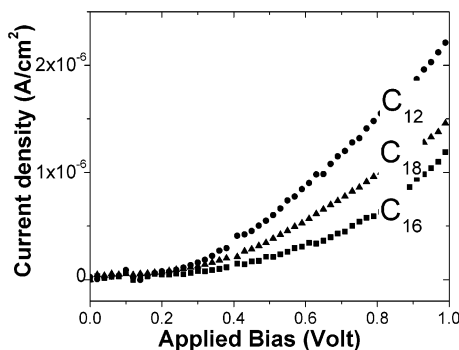
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Figure 5. Experimental *I*−*V* curves for Hg/alkylsilanes/SiO$_x$/p-Si junctions (junction B). The set of *I*−*V* curves is the average of measurements on 5−10 different samples.

levels that are relevant to the tunneling process (via a super-exchange mechanism).[27]

The importance of chemical-bonded contacts between electrodes and organic molecules has recently been reviewed.[1] One of the more striking results that has been reported was the dramatic decrease in tunneling efficiency through single alkyl chain molecules having only one contact bonded rather than both.[13d] We compare charge transport through organized monolayers of alkyl chains (chemically bonded to the electrode on one end) to that of monolayers of chains that are **not** bonded on either of the ends, that is, highly decoupled from both sides of the junction. As previously pointed out by us,[11] junction B is an appropriate system for such a study. The decoupling from the Si side is a result of the procedure for alkyl-silane assembly, which requires a temporary presence on the substrate of an ultrathin, interfacial water film.[17] In this mechanism, the water layer allows the formation of a highly organized, transient Langmuir-type film of hydrolyzed silane molecules, which subsequently forms the final polymerized film by compliant cross-linking of the *siloxy* network. The substrate-bound water is thought to promote decoupling of the organic film from the underlying solid surface. In the case of highly dense monolayers, insignificant bonding exists between the alkyl-silanes and SiO$_x$. These monolayers can be viewed as large networks of interconnected alkyl chains, which are covalently connected to the electrode at only very few points.[17]

Figure 5 shows that having none rather than one chemical bond has a dramatic effect on the *I*−*V* curves. Each curve in this plot is an average of more than five different measurements. The results shown here should be viewed in light of the experimental fact that measurements of different junctions made with monolayers of alkyl chains with the same length can differ by up to a factor of 2 from one to another. This suggests that the curves in this figure are essentially the same. As noted and justified in the experimental part, relatively fast scans were used throughout this study, using short integration times. Under these conditions, the curves in Figure 5 are just above the noise level. The observation that the currents for the junction made with the C$_{12}$-based monolayer are at this level implies that "losing" the chemical bond is equivalent to adding *six more carbons* to the chain. Exactly the same number has been suggested as the effective barrier for hopping *between* two chains in a bilayer structure.[9b,c] Using eq 1, we can represent the lack of chemical bond by adding 0.5 eV to the tunneling barrier. However, one has to be cautious when doing so because in contrast to the behavior of junctions with C$_{12}$ (Figure 3), here the experimental curve is lower at high voltages than the theoretical curve. This means that either the cross-linking bonds make cooperative tilting of C$_{12}$ under electrostriction more difficult or the
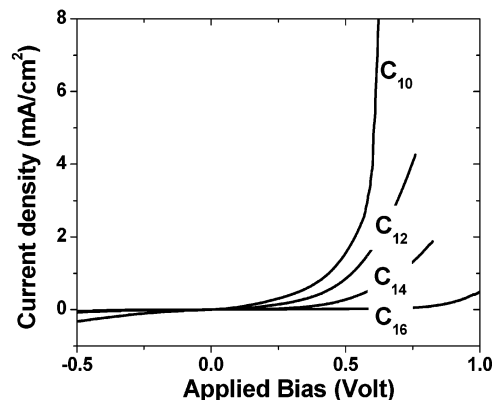

Figure 6. Experimental *I*−*V* curves for Hg/alkylthiols/p-Si−H junctions (junction C). The rectifying (Schottky) behavior is revealed by comparing the magnitude of current at numerically equal positive and negative bias voltages. The set of *I*−*V* curves is the average of measurements on 5−10 different samples.

mechanism of electronic charge transfer changes once there are no bonds to the contacts. A similar lack of length dependence has been reported earlier.[14a]

Junction C enables us to examine several additional points: (a) What is the role of the oxide in these junctions? (b) What happens to junction A when the (nonbonded) electronic coupling between the alkyl chains and the Si is improved? (**c**) Does this change have any effect on the efficiency of hole tunneling?

Figure 6 reveals that junction C is strongly rectifying (i.e., it is essentially a Schottky junction). Now we find that, in contrast to what we saw with junction B, the current depends on the barrier length because a chemical bond exists at one side of the monolayer. As expected, by eliminating the oxide layer, we shrink the width of the barrier and as a result the measured currents are higher.

Because our focus here is on the interplay between bonding and tunneling, we will not dwell on possible mechanisms (interfacial dipoles, surface and interface states, etc.) that make junction C a Schottky junction. Instead, we will concentrate on learning about tunneling through this junction.

Assuming a thermionic emission model, the current density can be described by

$$J = A^*T^2 \exp(-\beta d) \exp\left(-\frac{q\phi_b}{kT}\right) \exp\left(\frac{qV}{nkT}\right)\left[1 - \exp\left(-\frac{qV}{kT}\right)\right]$$

(5)

where A^* is the Richardson coefficient,[18] n is the ideality factor, T is the temperature, k is Boltzmann's constant, ϕ_b is the barrier height inside the semiconductor and $\exp(-\beta d)$ is the attenuation factor acting on A^* because of the tunneling process through the alkyl chains at the interface. We define ϕ_{eff} to be

$$\phi_{eff} = \phi_b + \frac{kT}{q}\beta d$$

(6)

Equation 5 then becomes

$$J = A^*T^2 \exp\left(-\frac{q\phi_{eff}}{kT}\right) \exp\left(\frac{qV}{nkT}\right)\left[1 - \exp\left(-\frac{qV}{kT}\right)\right]$$

(7)

By plotting ln(*J*) as a function of *V*, we can calculate ϕ_{eff} from the intercept at zero bias and n from the slope. By plotting ϕ_{eff} as a function of d, which in this case is the molecular length, we calculate β from the slope. All of the calculated parameters are summarized in Table 1.

TABLE 1: Analysis of $I-V$ Characteristics for Si–H/Alkylthiols/Hg (C) Junctions

number of carbons in alkyl chain	ideality factor (n)	effective barrier, ϕ_{eff} (V)	Schottky barrier, ϕ_b (V)
10	1.67	0.74	0.52
12	1.51	0.77	0.51
14	1.75	0.82	0.53
18	1.8	0.87	0.51

The last column in Table 1 is calculated backward after knowing β to check the consistency of the procedure. From the slope of eq 6, β is found to be 0.55 ± 0.06 Å^{-1}.

The structure of the monolayers in junctions A and C is the same. Hence, comparing this β value for *hole* tunneling to another value (0.65 ± 0.08 Å^{-1}) that was calculated by us earlier[11] using junction A is justified. There are two reasons why β has a lower value than reported by us earlier: (1) In the absence of an oxide layer, the electronic coupling to the Si surface, which is the *source* for the tunneling holes, is better, and as a result, tunneling is more efficient.[28] (2) In our earlier report, β was calculated on the basis of data from all chain lengths. However, from the present study, we learn that short chains are tilted under electrostriction, causing an uncertainty in the length of the barrier for tunneling. Indeed, if we recalculate β from Figure 2 only on the basis of the long chains ($>C_{12}$), we find $\beta = 0.57 \pm 0.06$ Å^{-1} in agreement with this study. The use of all chain lengths to calculate β for junction C is justified by the fact that the effect of electrostriction is less pronounced at low bias values, because most of the applied voltage drops across the barrier inside the Si and not on the molecules.

Conclusions

The results from this work can be put in a broader perspective by viewing it as complementary and in comparison to recent contributions, such as those by Cui et al. who investigated alkanethiols (and dithiols) using conducting atomic force microscopy.[13c–e] The low currents passing through long alkyl chains ($>C_{12}$) cannot be measured using an AFM setup. In this respect, our results add data about these chains showing that their behavior is fundamentally different from the behavior of short chains.

Cui et al. focused on the effect of having one as opposed to two chemical bonds at the contacts on current and charge-transfer mechanism. In our work, we compared $I-V$ behavior of similar systems having either one or no chemical bonds to the contacts.

The forces compressing the monolayers in this study are orders of magnitude less than those in previous studies. Our results suggest that even small geometrical defects produced by relatively low pressures are sufficient to make substantial changes in the electrical behavior of alkyl chains.

Current passes through alkyl chains in an all-trans configuration by through-bond tunneling. This seems to be true as long as at least one side of the chains is chemically bonded to the contacts. *Bonding seems to "force" the molecule to pass current through bonds.* This "forcing" effect of the bond(s) has two contributions: (1) Mechanically, it anchors at least one side of the chains to the surface, making it more difficult to deform them under applied forces or electrostriction. (2) Energetically, it makes through-bond tunneling more efficient than any other charge-transfer process, at least for certain geometrical arrangements. The number of these arrangements is increased upon bonding to the contacts.

Thus, for example, when the chains do not have bonds to contacts at all, they behave effectively as insulators immediately once electrostriction is applied. On the other hand if the chains are bonded at both ends,[13c,d] current does not change regardless of the force acting on the monolayers (and, probably, regardless of their configuration). In the absence of chemical bonds at both ends of the chains, small forces are probably sufficient to produce enough end-of-chain gauche deformations to suppress tunneling and to make the monolayer an insulating film.

When only one side of the chains is bonded to a contact, the behavior of the junction depends on the chains' mechanical properties, which in turn depend on their length. Short chains ($<C_{12}$) are tilted under moderate forces resulting in an increase of the probability for through-space tunneling. Long chains ($>C_{14}$), which are apparently more resilient to moderate forces, are deformed at their ends, making through-bond tunneling less effective without contributing to the current by through-space tunneling.

As important as the contact bonding aspect is our confirmation of earlier theoretical predictions[16] that hole tunneling is more efficient than electron tunneling through all-trans alkyl chains.

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(28) Junction C enables us to compare the magnitude of our measured currents to the currents measured in refs 13b,c. In these references at low voltage values (<0.4 V), current is approximately 2 pA/molecule. Assuming that the coverage is ∼20 Å²/molecule, we estimate the amount of molecules per square centimeter in our junctions to be ∼0.25 × 10¹⁴. The current density for C_{10} at 0.4 is ∼1.5 × 10⁻³ A/cm². The attenuation of the current by the barrier height inside the Si at this potential is calculated from the exponent of the Schottky equation,

$$\exp\left(\frac{q}{kT}\left(-\phi_b + \frac{V}{n}\right)\right) = \exp\left(38.9\left(-0.51 + \frac{0.4}{1.67}\right)\right) \cong 2 \times 10^{-5}$$

where 0.51 is the effective barrier height (cf. Table 1), 0.4 is the applied potential, and 1.67 is the (non)ideality factor (all for C_{10}). Hence, the *tunneling* current, after taking into account the attenuation factor/molecule, is [(1.5 × 10⁻³)/(0.25 × 10¹⁴)] × 0.5 × 105 = 3 pA/molecule.