

Molecule-induced interface states dominate charge transport in Si-alkyl-metal junctions

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Abstract

Semiconductor–molecule–metal junctions consisting of alkanethiol monolayers self-assembled on both p^+ and n^- type highly doped Si(111) wires contacted with a $10\text{ }\mu\text{m}$ Au wire in a crossed-wire geometry are examined. Low temperature transport measurements reveal that molecule-induced semiconductor interface states control charge transport across these systems. Inelastic electron tunneling spectroscopy also highlights the strong contribution of the induced interface states to the observed charge transport.

(Some figures in this article are in colour only in the electronic version)

The use of molecular elements as the active components of electronic devices is the underlying goal of molecular electronics. While metal–molecule–metal junctions have been extensively studied, semiconductor–molecule–metal devices have gained considerable interest in recent years since they provide a potential route to combine molecular functionality with conventional CMOS technology [1–4]. The use of semiconducting electrodes also provides increased options for tailoring the device performance by controlling the dopant type and concentration to tune the band level alignment between the molecular orbitals and conduction/valence bands of the semiconducting contact.

In this paper we employ two *in situ* spectroscopic techniques—inelastic electron tunneling spectroscopy and transition voltage spectroscopy—to study the charge transport across semiconductor–molecule–metal (SMM) junctions based on 1-dodecanethiol (C12) bound to a Si(111) surface. Inelastic electron tunneling spectroscopy (IETS) is unique in that it measures the vibronic coupling between tunneling charge carriers and the nuclear motions of molecules in the junction. This *molecular signature* enables one to prove that the molecule is present in the junction and an active participant in the charge transport process [5–7]. Furthermore, IETS can provide insight into the actual pathways that the electrons traverse when transiting a molecular junction [8], as well as how the relevant vibrations act to couple the electronic

structure of the molecule and contact electrode [9, 10]. Transition voltage spectroscopy (TVS) is a complementary technique in that it directly measures the effective barriers to charge transport for a molecular junction [11]. TVS has proven useful for probing how the barrier to charge transfer changes as the length and/or conjugation motif of a molecule is varied [11, 12].

A schematic diagram of the crossed-wire test structure used is shown in figure 1(a). The crossed-wire junctions are formed by physically placing a thin ($\approx 10\text{ }\mu\text{m}$ diameter) Au wire on top of a monolayer of C12 self-assembled on a lithographically defined silicon wire. The crossed-wire architecture avoids the damage that can occur due to evaporated top contacts [13, 14]. The silicon wires are fabricated with a width of $10\text{ }\mu\text{m}$, a length of $3000\text{ }\mu\text{m}$, and a height of $28\text{ }\mu\text{m}$ on highly doped silicon substrates by photolithography and reactive ion etching. We used both p^+ (B-doped, $10\text{ m}\Omega\text{ cm}$) and n^- (As-doped, $4\text{ m}\Omega\text{ cm}$) type Si(111) substrates. Figure 1(b) is a scanning electron microscopy (SEM) image of the as fabricated silicon wire.

The C12 monolayers are formed on the silicon wires utilizing a UV reaction procedure previously established [15–18]. The silicon wires are cleaned in acetone and methanol followed by immersion into a 6:1 buffer oxide etch ($\text{NH}_4\text{F}:\text{HF}$) for 10 s. The resulting hydrogen terminated silicon wires are then rinsed with $18.2\text{ M}\Omega\text{ cm}$ water, dried with nitrogen, and placed

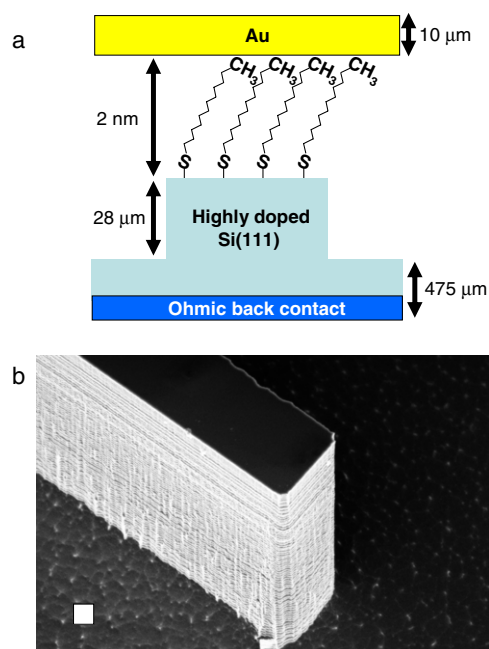


Figure 1. (a) Schematic cross section of a Si-C12-Au junction. For all transport measurements the Si substrates are grounded. (b) A scanning electron micrograph of a Si wire. The white square represent an area of $2 \mu\text{m}^2$.

immediately in a nitrogen-atmosphere glove box with <10 ppm oxygen. In the glove box, the hydrogen terminated silicon wires are immersed for 2 h in a CH_2Cl_2 solution containing ≈ 10 mM of **C12** while simultaneously being illuminated by a 6 W UV lamp ($\lambda = 254$ nm) with an intensity of $\approx 1.5 \text{ mW cm}^{-2}$ at the sample. Under these conditions the thiol undergoes a nucleophilic type reaction with surface Si-H centers resulting in molecules bound to the Si surface via covalent S-Si bonds [17]. Physisorbed molecules are removed by rinsing in CH_2Cl_2 and isopropyl alcohol. Prior to the self-assembly, Au/Ni ohmic backside contacts are deposited on the n^- Si substrates. No metal deposition is required to form ohmic backside contact to the p^+ Si substrates.

Self-assembled monolayers of **C12** on flat Si(111) substrates were characterized using water contact angle, Fourier-transform infrared (FTIR) spectroscopy, spectroscopic ellipsometry, and x-ray photoemission spectroscopy (XPS) [17, 18]. Alkyl thiol monolayers on silicon were found to have a molecular coverage of $((3 \pm 1) \times 10^{14} \text{ molecule cm}^{-2})$ comparable to that of the SAM on Au. XPS and FTIR measurements of films exposed to laboratory environment for 6 h after assembly indicate that ambient exposure of the SAM on silicon does not result in oxidation of the S-Si bond.

All transport measurement were performed at liquid He temperature in a custom-built crossed-wire apparatus previously described [5]. For all transport measurements the Si substrates are grounded. By performing our transport measurements at cryogenic temperatures with highly conductive Si substrates, we ensure that direct tunneling and field emission through the molecular layers are the dominant contribution to charge transport through the junctions. Five different SMM junctions were fabricated and measured for

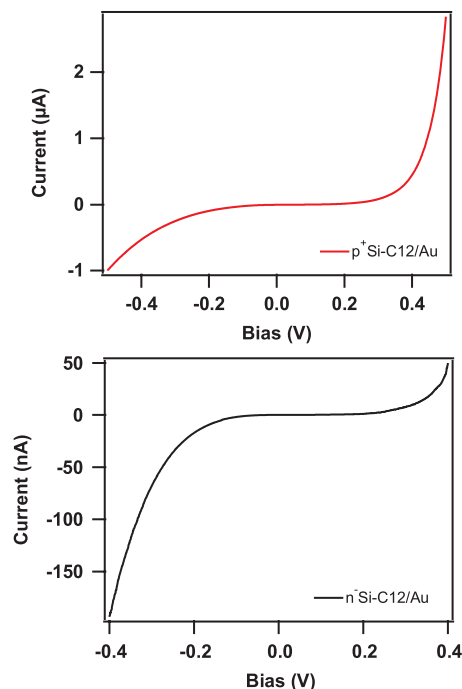


Figure 2. Current-voltage characteristics of a p^+ type SMM junction (top) and a n^- type SMM junction (bottom).

both n^- and p^+ type Si, and for each SMM junction 10–20 sets of transport data were collected and averaged. Figure 2 shows representative current-voltage characteristics for a p^+ type (top) and a n^- type (bottom) SMM junction. The rectification observed is in the same direction (although greatly reduced) as that of a bare Si/Au junction for the two dopant types.

For each SMM junctions the dI/dV and d^2I/dV^2 of the junctions are measured with standard ac modulation techniques simultaneously with the current-voltage characteristics. The amplitude of the ac modulation used is 4 mV rms. We report the normalized IET signal $(d^2I/dV^2)/(dI/dV) - V$ since it removes any dependence on junction area. This enables a direct measure of the change of junction conductance upon opening of an inelastic channel.

Figure 3 shows a representative IET spectrum for a p^+ type (top) and a n^- type (bottom) SMM junction. Observed features are assigned to specific Si and molecular vibrational modes by comparison to previous IET spectroscopic results [5, 19–22]. Silicon phonon modes dominate the spectra at energies <95 meV, and the feature appearing at 200 meV is associated with Si surface state interactions [21, 22]. All alkanethiol vibrational features observed previously in Au-alkanethiol-Au junctions [5] also appear in the IET spectra of the SMM junctions. The observed peaks are also in agreement with those reported by Vuillaume and co-workers for metal-alkanethiol-siliconoxide/silicon junctions [23, 24]. The relative intensity of the different alkyl vibrational peaks are however quite different from our earlier Au-alkanethiol-Au results (e.g. see figure 3 of [5]). While the aliphatic $\nu(\text{CH}_2)$ stretching mode near 360 meV is always the most intense feature in the IET spectra of Au-alkanethiol-Au junctions [5, 9, 25, 19, 10], with relative intensity around twice that of the other alkyl

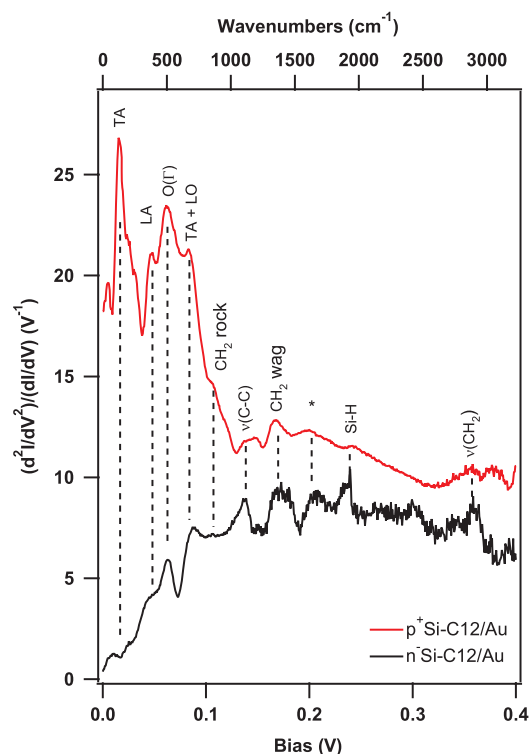


Figure 3. IET spectra of a p^+ type SMM junction (top) and a n^- type SMM junction (bottom). Mode assignments are based on previous experimental results. Note ν = stretch, TA = transverse acoustic mode, LA = longitudinal acoustic mode, $O(\Gamma)$ = vibrational mode due to the $k = 0$ optical phonons (Γ point), and LO = longitudinal optical mode. The asterisk marks a mode likely associated with surface states interactions. The spectra shown are from the negative bias region of the IET spectra, corresponding to the case where holes are emitted from the Si to the Au electrode, or where electrons are emitted from the Au to the Si electrode. The p^+ type SMM junction spectra is offset vertically for clarity.

features, the intensity of the $\nu(\text{CH}_2)$ feature of the SMM junctions has comparable intensity with the other molecular features.

Recent theoretical treatment of molecular IETS demonstrated that the contribution of a molecular vibration to the IET spectrum will be large only if the vibration involves electrons traversing through an atomic orbital that is strongly coupled to the electrodes [8]. The relatively high intensity of the $\nu(\text{CH}_2)$ feature in the IET spectra of Au–alkanethiol–Au junctions is attributed to the strong coupling between that mode and the metallic electrodes [8, 26]. Specifically, from chemical substitution it was determined that CH_2 groups near the Au–S interface dominate the observed $\nu(\text{CH}_2)$ feature [9]. The diminished relative intensity of the $\nu(\text{CH}_2)$ feature in the IETS of SMM junctions is an indication that the C–H stretching vibration is less coupled with the electrons tunneling between the substrate and the alkyl molecule when the substrate is changed to silicon from gold. The $\nu(\text{CH}_2)$ region was not examined in the metal–alkanethiol–siliconoxide/silicon junctions studied by Vuillaume and co-workers [23, 24]. Interestingly, a recent study has reported a strong $\nu(\text{CH}_2)$ mode in the IETS of alkyl molecules bound to a Si substrate via a direct Si–C bond, highlighting that the attachment chemistry plays a strong role in

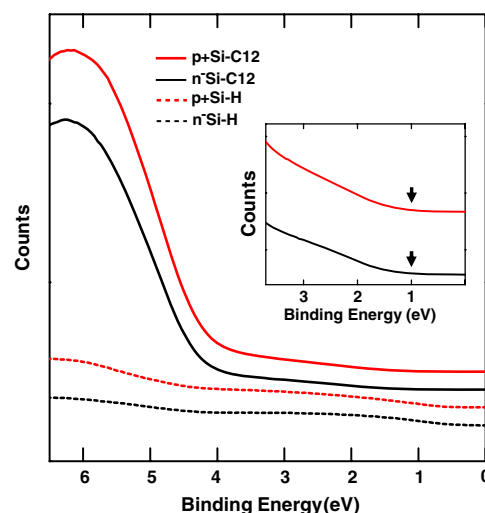


Figure 4. Ultraviolet photoelectron spectra of a p^+ type Si–C12 sample (top solid) and a n^- type Si–C12 sample (bottom solid), along with Si(111)–H substrates of both dopant types (dashed lines). Binding energies are referenced as positive for occupied states below the Fermi level of the silicon substrate (binding energy = 0 eV). The inset shows a zoomed-in view of the Si–C12 spectra close to the Fermi level. UP spectra were obtained with excitation via a He I line source (21.2 eV) with a hemispherical electrostatic analyzer (resolution ≈ 100 meV). The Si(111)–H spectra both show some density of states at roughly 2 eV below the Fermi level which is due to the Si–H bond [28].

determining what molecular vibrations are active in IETS [27]. The difference in spectral signature between an alkanethiol in a metal–molecule–metal junction and in our SMM junction suggests different electron–phonon coupling for electrons traversing the two kind of junctions.

To better understand the nature of the transport path in our SMM junctions we performed ultraviolet photoelectron spectroscopy (UPS) on Si–C12 samples to measure the energetic distribution of their occupied electronic levels. Figure 4 shows the UP spectra of a p^+ type Si–C12 (top) and a n^- type Si–C12 (bottom) sample, along with the hydrogen terminated Si(111) substrates of both dopant types. The intense feature peaked at ≈ 6 eV in the assembled monolayer spectra is attributed to the sigma bonds of the alkyl backbone [29]. A zoomed-in view of the different spectra near the Fermi level of the silicon substrate (binding energy = 0 eV) is shown in the inset of figure 4. The most important feature of the UP spectra is that for both Si–C12 systems there is a broad continuum of density of states beginning approximately 1 eV below the Fermi level (figure 4 inset). Such low energy filled states are not intrinsic to the energy levels of the molecular backbone [30], but rather are due to molecule-induced density of states from hybridization of the Si bands with the molecular orbitals [28, 31]. Segev *et al* reported similar features in UPS measurements on samples where alkyl chains of various lengths were bound directly to p^+ and n^- type Si(111) substrates, via C–Si bonds [28]. These hybridized states are the molecule/semiconductor interface analog to the induced density of interface states (IDIS) seen in inorganic heterostructures.

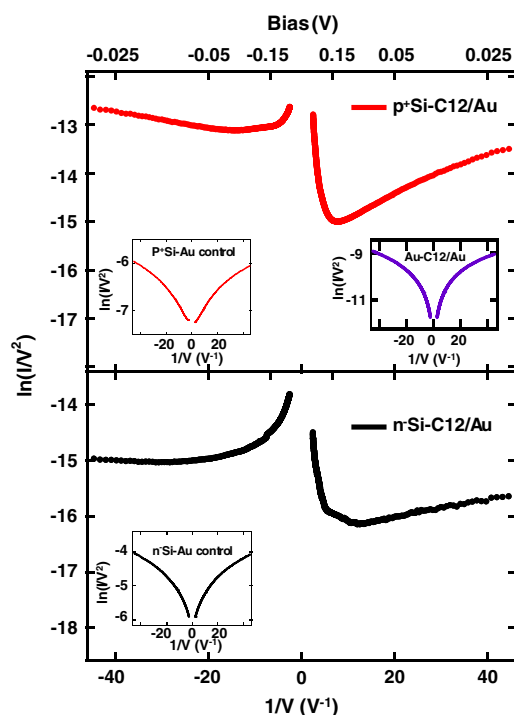


Figure 5. Transition voltage spectra of a p⁺ type SMM junction (top) and a n⁻ type SMM junction (bottom). Positive bias correspond to the case where holes are emitted from the Au to the Si electrode, or where electrons are emitted from the Si to the Au electrode. The right inset in the top panel shows the TV spectrum of a Au-C12-Au junction, and the left inset in each panel shows the transition voltage spectrum of a Si-H/Au junction.

To further explore how these molecule-induced interface states effect charge transport we use transition voltage spectroscopy to measure the effective barriers to charge transport in these junctions. TVS is an experimentally simple technique in that the normal I - V transport characteristics are transformed onto what are commonly referred to as Fowler-Nordheim axes ($\ln(I/V^2)$ versus $1/V$), where I is the current and V is the applied voltage [32]. In the direct tunneling limit $\ln(I/V^2)$ is logarithmically related to $1/V$, and in the field emission limit, $\ln(I/V^2)$ is linearly related to $-1/V$, the voltage at which the transport mechanism transition from direct tunneling to field emission can thus be easily extracted from the transport data plotted in the Fowler-Nordheim axes by finding the point on the curve where the slope changes polarity. We called the voltage where the transport mechanism changes the transition voltage, V_{trans} . Previous experiments with Au-molecule-Au junctions have resulted in a sharp transition in the charge transport characteristics and have demonstrated that V_{trans} is directly related to the barrier height of the junctions. Furthermore the magnitude of the V_{trans} could be used to probe the method and extent of molecular conjugation as well as the effect of attachment chemistry on the majority charge carrier of a junction [11, 12].

Figure 5 shows the transition voltage spectra of the two SMM junctions whose IET spectra are shown in figure 3. The right inset in the top panel shows the TV spectrum of a Au-C12/Au junction, and the left inset in each panel shows

the TV spectrum of a Si-H/Au junction. All data curves shown in figure 5 are acquired within the applied bias range of ± 400 mV. While neither the Si-H/Au nor the Au-C12/Au junction exhibit a V_{trans} within the bias range measured, the SMM junctions clearly show signs of transport mechanism transition. This is an interesting result given that previous experiments have shown the V_{trans} of Au-C12/Au junctions to be (1.2 ± 0.1) V [12]. Unlike previous experiments with Au-molecule-Au junctions where the transition voltage curve slope changes polarity abruptly [11, 12], the transition voltage curves of the SMM have a broad gradual transition. While it is difficult to assign a single value to this transition it is clear that the transition occurs for both positive and negative bias polarities at values of $< |0.2$ V|. This decrease in the energy for transport mechanism transition when an electrode of the junction is changed to silicon from gold is consistent with our assertion that the bands of the silicon substrate and the molecular orbital of the molecules are hybridized, and that the electron tunneling path through the interface is substantially modified. The broadness of the transition further suggests that the tunneling of charge carriers across the SMM junctions is mediated by a continuum of states, such as the IDIS, instead of a well defined level, such as the HOMO or LUMO of the molecules in the case of the Au-molecule-Au junctions.

In summary, through a combination of spectroscopic measurements we have demonstrated that in SMM junctions formed from alkanethiol molecules bound to highly doped Si (both p⁺ and n⁻ type), an ensemble of molecule-induced Si surface states replaces the molecular orbitals in defining the energetic manifold through which charge carriers cross the junction. These hybridized Si-molecule states lead to lowering of the effective barrier height in these molecular junctions, and changes in the electron-phonon coupling of the charge carriers traversing through the electrode-molecule interface. These results are in agreement with the previous work from the Cahen and Kahn groups for alkyl chains bound to Si via direct Si-C bonds [2, 28, 31]. Furthermore these results suggest that molecule-induced interface states may play a ubiquitous role in the charge transport properties of semiconductor-molecule-metal systems, and thus need to be fully understood in order to enable the successful integration of molecular and CMOS components into hybrid electronic devices.

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