

Electrical Properties of Junctions between Hg and Si(111) Surfaces Functionalized with Short-Chain Alkyls[†]

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Received: January 25, 2007; In Final Form: June 29, 2007

Metal–semiconductor junctions between Hg and chemically modified n- and p-Si(111) surfaces have been prepared and analyzed using current–voltage and differential capacitance–voltage methods. To understand the role of the interfacial dipole on interfacial charge transfer, silicon surfaces were modified with either nonstoichiometric oxide (SiO_x), terminal monohydride, short (C_nH_{2n+1}–, *n* = 1, 2, 3) saturated alkyl chains, or propynyl (CH₃–C≡C–) groups. X-ray photoelectron spectra of the modified Si electrode surfaces taken before and after exposure to Hg contacts showed no evidence of irreversible chemical interactions between the Si and the Hg. Hg/Si contacts made using H-terminated Si(111) surfaces exhibited Schottky junctions having barrier heights (Φ_b) that were consistent with the known surface electron affinity of Si and the work function of Hg. In contrast, Si coated with a thin, chemically grown oxide formed Hg/Si junctions having barrier heights suggestive of Fermi level pinning. Si(111) surfaces modified with methyl groups yielded Hg junctions having barrier heights in accord with expectations based on the electron affinity (3.67 eV) and surface dipole (0.38 eV) measured on such surfaces by photoemission spectroscopy, attesting to the degree of chemical control that can be exerted over the barrier heights of such systems by surface functionalization methods. Incomplete coverages of functional groups produced by alkylation with ethyl or *iso*-propyl groups did not greatly impact the observed values of Φ_b relative to Φ_b values observed for CH₃-terminated Si(111) surfaces. However, the observed variation in Φ_b between nominally identical samples increased as the number of carbons in the functionalizing alkyl group increased. Junctions between Hg and Si(111) surfaces modified with propynyl groups showed nearly identical behavior to that of CH₃–Si(111)/Hg contacts, both in average Φ_b values and standard deviation between samples. The behavior of Si/Hg interfaces modified with short organic functional groups is consistent with the efficacy and utility of passivated surfaces in modifying the properties of surface-based Si devices.

I. Introduction

The ability to exert molecular-level control over the energetics and kinetics of charge-transfer processes across semiconductor surfaces is of interest in developing ultrathin insulating or gating films for high-speed and nanoscale electronics^{1–5} and in modifying semiconductor surfaces for chemical sensing applications.^{6,7} Covalently attached organic moieties can, in principle, affect both the barrier height and the transmission coefficient for electron tunneling at chemically modified semiconductor surfaces,^{5,8–12} with concomitant effects on the energetics and kinetics, respectively, of electron flow across such interfaces.

Covalently attached long (C_nH_{2n+1}, *n* ≥ 5) alkyl groups have been used to modify the charge-transfer properties of Si/metal Schottky contacts.^{2,4,9,12–16} Two inherent phenomena limit straightforward analysis of Si surfaces modified with long alkyl groups. Through-bond tunneling across the alkyl group contributes significantly to the current density (*J*) vs voltage (*V*) response.^{14,15} In addition, steric repulsion between adjacent methylene units of any saturated alkyl chains C_nH_{2n+1}, with *n* > 1, precludes functionalization of every atop site on an unreconstructed Si(111) with Si–C bonds. The unalkylated Si

atoms are either H-terminated, oxidized, or a combination thereof, leading to a mixed surface both in composition and in electrical tunneling properties.^{17,18}

Methyl (CH₃–) terminated Si(111) surfaces are attractive systems to investigate the electron-transfer properties of contacts between metals and alkylated Si surfaces. CH₃–Si(111) surfaces prepared by a two-step chlorination/alkylation process^{19,20} are, essentially, completely terminated by Si–C bonds,^{1,21} as shown by a variety of spectroscopic and electrical measurements.^{22–24} Such surfaces are resistant to Si oxidation after prolonged exposure to ambient conditions and/or aqueous solutions,^{19,22,25} and possess negligible surface-related mid-gap trap states or electronic defect sites.^{24,26,27} Synchrotron photoemission studies have shown that CH₃–Si(111) surfaces possess a net positive surface dipole of 0.38 ± 0.01 eV that arises from the formation of the covalent Si–CH₃ surface bonding.²⁴ Hence, H–Si and CH₃–Si(111) surfaces possess significantly different electron affinities (χ_{eff}) of 4.17 and 3.67 eV, respectively.^{24,28} The different energetics for such surfaces should, in principle, be directly reflected in different barrier heights for electron transfer across metal Schottky junctions with these two different semiconductor surfaces.

Potential confounding factors in the analysis of Si/metal junctions, however, arise from defects in the surface coverage of the passivating layer and/or in the presence of interfacial

[†] Part of the special issue “Richard E. Smalley Memorial Issue”.

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chemical reactions that generally accompany the deposition of metals on Si surfaces. Any direct Si/metal contacts through pinholes in the alkyl overlayer can produce regions possessing different energetics than those of the alkyl-Si/metal contacts. If the direct Si/metal regions constitute any fraction of the total junction area, then the exponential weighting of such regions on the observed current could significantly contribute to, or even dominate, the total measured junction current.²⁹ Additionally, metal silicide formation at ambient conditions is well-known for most Si/metal Schottky contacts.³⁰ The resultant Fermi level pinning at such Si/metal contacts will complicate interpretation of the observed electron tunneling barrier height in terms of the respective energetics of the isolated Si and metal phases.

An interesting approach to obviate the metal contact issues at functionalized Si surfaces is to use liquid Hg as the metal contacting phase. In contrast to the formation of silicides with coinage metals such as gold, no metallurgical evidence has been obtained for silicide formation when Hg contacts are formed at ambient conditions on Si.^{31,32} Hg is readily contacted to Si at room temperature, gives conformal junctions without the possibility of trap state-inducing lattice mismatch, and possesses a high surface tension ($408 \text{ dynes cm}^{-1}$)^{33–36} that should reduce the sensitivity of the metal contact to pinholes in the passivating layer. Furthermore, the work function of Hg ($W_{F,\text{Hg}}$) is located energetically between the bottom of the conduction band and the top of the valence band of Si; so, in an ideal system, both n-type and p-type Si surfaces should form contacts with Hg, which are in depletion rather than accumulation or inversion, allowing meaningful barrier height analysis.³⁷

Accordingly, we have investigated the electrical behavior of a series of Hg/Si junctions. The properties of H-Si(111) surfaces have been compared to those of CH₃-Si(111) surfaces, C₂H₅-terminated Si(111) surfaces, and *iso*-C₃H₇-terminated Si surfaces. In addition, the electrical responses of Si(111)/Hg contacts employing intentionally defective, oxidized Si surfaces have been investigated for comparative purposes. Finally, Hg junctions employing Si(111) modified with propynyl (CH₃CC-) groups have also been evaluated. Propynyl moieties are interesting because, like CH₃-groups, they are sterically capable of terminating every atop site on an unreconstructed Si(111) surface.³⁸

II. Experimental

A. Materials. Si samples were obtained from single-side polished, (111)-oriented (to $\pm 0.5^\circ$) wafers having thicknesses of $525 \pm 25 \mu\text{m}$. The n-Si wafers, doped with phosphorus to a resistivity of 1–8 $\Omega \text{ cm}$, were purchased from Virginia Semiconductor Inc. The p-Si wafers, doped with boron to a resistivity of 1–2 $\Omega \text{ cm}$, were purchased from ITMS. Wafers used in this study were obtained from the same two cassettes. For a given surface functionalization, each subset of samples was obtained from a single wafer. Unless noted otherwise, all chemicals were used as received without further purification. Water was 18 M $\Omega \text{ cm}$ resistivity, as obtained from a Barnsted Nanopure system.

B. Surface Functionalization. Prior to chemical modification, all Si surfaces were degreased by sequential rinses with water, methanol (Aldrich), acetone (Aldrich), 1,1,1-trichloroethane (Aldrich), dichloromethane (Aldrich), 1,1,1-trichloroethane, acetone, methanol, and water. Samples were then dried under a stream of N₂ (g).

H-terminated Si(111) surfaces were obtained through wet chemical etching for 10 min in 11 M (48% wt/wt) NH₄F (aq).

The samples were agitated periodically to minimize the formation of etch pits.³⁹ Following etching, the monohydride-terminated surfaces were rinsed with flowing H₂O, dried under a stream of N₂(g), and immediately tested or further modified. A nonstoichiometric silicon oxide layer, SiO_x, was prepared on some samples by soaking the H-Si(111) surfaces in 3:1 (v/v) H₂SO₄/(30% v/v, aq) H₂O₂ at 60 °C for 60 min, followed by a rinse with H₂O.

Si samples were alkylated using a two-step chlorination/alkylation protocol.^{20,24} First, H-Si(111) surfaces were transferred into a flush box and immersed in a saturated solution of PCl₅ (Fluka) in chlorobenzene (Aldrich) for 50 min at 90 ± 10 °C under an atmosphere of dry N₂ (g). The chlorinated samples were rinsed sequentially with chlorobenzene and tetrahydrofuran (THF, Aldrich) and were then dried under a stream of N₂ (g). The samples were subsequently immersed for 2–8 h at 70 ± 10 °C in a THF solution of 1 M C_nH_{2n+1}-MgCl ($n = 1$ to 3, Aldrich). Alkylated silicon samples were rinsed with flowing THF and then immersed in methanol. The alkylated samples were transported out of the flush box and were further rinsed with methanol, sonicated in fresh methanol, rinsed with H₂O, and dried under a stream of N₂ (g). Propynylated samples were prepared in a similar fashion,³⁸ employing the same initial chlorination step. Propynyl groups were grafted by immersion of the Cl-Si(111) surface into 0.5 M propynyl magnesium bromide (H₃C-C≡CMgBr, Aldrich) in THF for 24 h at 120–130 °C.

C. Surface Characterization. X-ray photoelectron spectra (XPS) of representative samples from each class of surface modification were obtained after the samples were exposed to Hg for 20 min and/or several current density versus voltage (J - V) curves had been recorded. Spectra were obtained using an MProbe XPS, employing a 1486.6 eV Al K α X-ray source. Emitted photoelectrons were collected at 35° from the sample surface, and their measured kinetic energy is reported in terms of binding electron volts (BeV). The pressure was 10⁻⁸ Torr during measurements. Low-resolution survey scans were collected between 0 and 1000 BeV, with a resolution of approximately 1.5 eV. High-resolution scans were collected between 350 and 370 BeV for the Hg 4d_{5/2} peak and between 302 and 312 BeV for the Mg Auger peak, with a spectrometer resolution of ~ 0.8 eV.

D. Junction Formation Between Hg and Si(111) Surfaces. Except for H-terminated surfaces, ohmic contacts to n-Si samples were made following surface modification. Contacts were formed by scratching the back (non-polished) side of the sample with 100 grit sandpaper, etching for 5 min with a drop of 48% HF (aq, Transene), rinsing with H₂O, and then rubbing in an In/Ga eutectic. Ohmic contacts to p-Si samples were made prior to surface functionalization by sputtering <100 nm of Al onto the back side of the sample and then annealing the contact at 450 °C in 5% H₂ (g) in N₂ (g) (Air Liquide). Schottky junctions were formed with high-grade Hg (>99.999%, Alfa Aesar). Contact areas for Hg junction formation were nominally 0.05–0.1 cm², as defined by either a nitrile O-ring or by a ring of insulating epoxy (1C Hysol, Loctite) on the front surface of the sample. Electrical contact to the Hg drop was made with a platinum wire, thereby preventing the Hg drop from making contact with any amalgamating materials. For current-voltage testing, the time between preparing the Si-H surface and forming the Hg junction was short (~ 20 s). The time between preparation and testing for the oxidized and alkylated samples ranged from 10 min to 12 h, except for studies with intentionally aged samples.

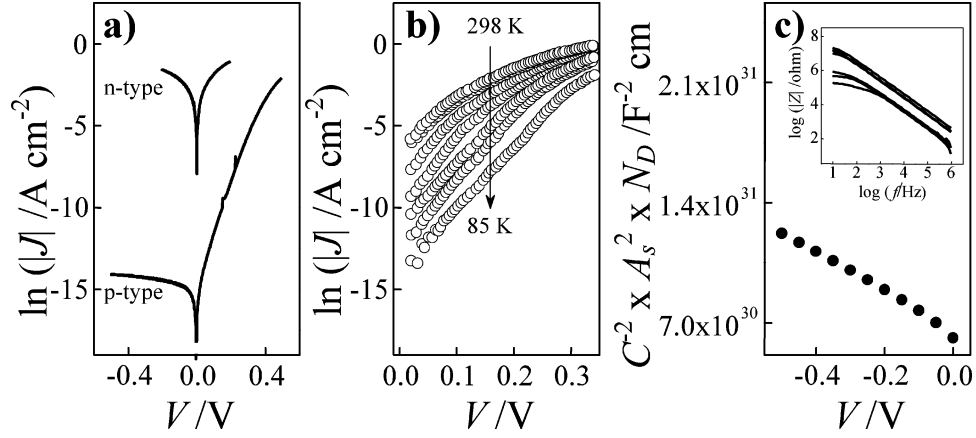


Figure 1. Representative electrical responses of Hg junctions with H-terminated Si(111). (a) J - V data for n-Si and p-Si, $T = 296 \pm 2$ K. (b) J - V data for n-Si, $85 \text{ K} \leq T \leq 296 \text{ K}$ (c) Mott-Schottky (C^{-2} - V) plots of Hg/p-Si junctions. Inset: Bode plots of the total impedance magnitude ($|Z|$) over the range of frequencies (f) tested for all tested p-Si junctions. $T = 296 \pm 2$ K, and $V = 0$.

E. Electrical Measurements. Measurements were recorded either at ambient temperature (23 ± 2 °C) or near the boiling point of liquid nitrogen (i.e., at -188 °C). A Teflon cell was used for low-temperature measurements, with a type K thermocouple placed directly underneath the back ohmic contact for the Si sample (see Supporting Information). The cell was immersed in a shallow liquid nitrogen reservoir and cooled. J - V data were obtained periodically as the system returned to room temperature.

The J - V data were obtained at a scan rate of 0.020 V s^{-1} and a sampling of 1 mV per data point, with a Solartron Model 1287 potentiostat controlled by CorrWare software. Measurements were conducted with the silicon substrate as the working electrode. Barrier heights (Φ_b) and ideality factors were estimated by fitting the linear portion of the forward-bias currents to the thermionic emission model of eq 1:³⁰

$$J = A^{**} T^2 e^{-q\Phi_b/k_B T} (e^{qV/k_B T} - 1) \quad (1)$$

where k_B is Boltzmann's constant, T is the temperature in degrees K, and A^{**} is the modified Richardson's constant for Si ($A^{**} = 112 \text{ A cm}^{-2} \text{ K}^{-2}$ for n-Si, and $A^{**} = 32 \text{ A cm}^{-2} \text{ K}^{-2}$ for p-Si). When necessary, the raw data were corrected for series resistance (R_s) losses.

Impedance measurements were obtained with a Schlumberger Model SI 1260 frequency response analyzer controlled by ZPlot software. Differential capacitance measurements were collected with a 5–10 mV amplitude sinusoidal signal at frequencies (f , typically 1 MHz) at which the measured phase angle was much greater than 80° . For all samples, the Nyquist plots collected under open-circuit conditions were observed to be hemispherical, indicating a simple parallel RC circuit in series with a series resistance, R_s (see Supporting Information). The value of R_s was estimated from the high-frequency intercept to the real impedance axis. R_s values were nominally 10–100 Ω for all Hg/Si junctions, and $4\pi^2 f^2 R^2 C^2$ was $\ll 1$ for all measurements.⁴⁰ Minimal frequency dispersion was observed for all samples, except for the oxide-coated Si interfaces.

The impedance data were analyzed using the Mott-Schottky equation (eq 2),

$$C^{-2} = \frac{2}{q\epsilon\epsilon_0 N_D A_s^2} \left(\frac{\mathbf{E}_{fb}}{q} + \frac{k_B T}{q} - V \right) \quad (2)$$

where C is the differential capacitance, q is the unit Coulombic charge, ϵ and ϵ_0 are the Si dielectric constant and vacuum

permittivities, respectively, N_D is the dopant density (cm^{-3}), A_s is the junction area (cm^{-2}), and \mathbf{E}_{fb} is the flat-band energy of the Si. The barrier height was then calculated from eq (3),

$$\Phi_{b,n} = \frac{\mathbf{E}_{fb}}{q} + \frac{k_B T}{q} \ln \left(\frac{N_D}{N_C} \right) \quad (3a)$$

$$\Phi_{b,p} = \frac{\mathbf{E}_{fb}}{q} + \frac{k_B T}{q} \ln \left(\frac{N_D}{N_V} \right) \quad (3b)$$

where N_C and N_V are the effective density of states in either the valence or conduction bands, respectively.

All reported figures depict as-collected, uncorrected data. For simplicity, all data are presented with positive currents and positive potentials, corresponding to forward bias conditions, for both n-type and p-type silicon samples. All Mott-Schottky plots are shown with the y-ordinate adjusted by the electrode geometric surface area and wafer dopant density (i.e., $C^{-2} A_s^2 N_D$ vs V).

III. Results

A. Hg Contacts to H-Si(111) Surfaces. 1. J - V Measurements. Figure 1 shows representative J - V data for freshly prepared contacts between Hg and p-type H-Si(111) surfaces. The devices showed strongly rectifying behavior, evidenced by a small and near-constant current at reverse bias ($V < 0$) and by an exponentially increasing current at forward bias. Distortion due to IR_s drop limited the linearity of the forward bias $\ln J$ vs V data to $V < +0.35 \text{ V}$ (corresponding to $J < 10^{-2} \text{ A cm}^{-2}$ and $A_s \sim 0.05 \text{ cm}^2$). A fit of the forward bias data to the thermionic emission-diffusion model produced an average ideality factor (n) of 1.16 ± 0.03 . The barrier height ($\Phi_{b,J-V}$) calculated from the forward bias J - V data was $\Phi_{b,J-V} = 0.82 \pm 0.02 \text{ V}$, which is in agreement with literature values for this system.^{3,13,16,37,41,42}

In contrast to the behavior of p-type H-Si(111)/Hg contacts, n-type H-Si(111)/Hg contacts exhibited a nearly ohmic response at room temperature (Figure 1a). Both forward and reverse biases greater than $|0.05| \text{ V}$ resulted in currents in excess of 10^{-2} A , limiting the precision of identifying a linear portion of the current response. The J - V behavior clearly indicated a much lower barrier height for n-type H-Si(111)/Hg contacts than for p-type H-Si(111)/Hg junctions.

To more precisely estimate an apparent barrier height for n-type H-Si(111)/Hg contacts, J - V data were also obtained

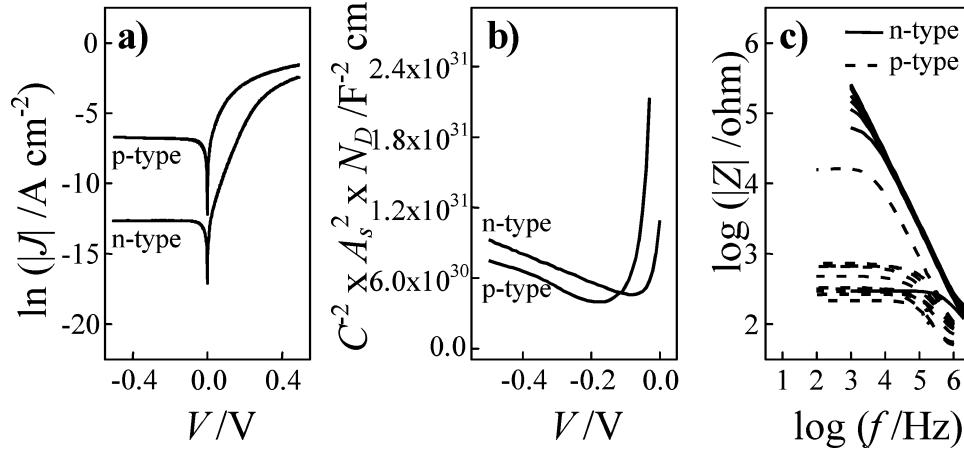


Figure 2. Representative electrical responses of Hg junctions with chemically oxidized Si(111). (a) J - V responses at reverse and forward bias. $T = 296 \pm 2$ K (b) C^{-2} - V responses at reverse bias. $T = 296 \pm 2$ K (c) Bode plots for all tested oxidized Si samples. $T = 296 \pm 2$ K, and $V = 0$.

near the boiling point of $N_2(l)$. At 85 K, a clear linear region of the $(\ln J)$ - V data was observed at forward bias (Figure 1b). As the temperature was slowly increased to room temperature, the shape of the $(\ln J)$ - V data became increasingly ohmic. Analysis of the data at 85 K according to eq 1 yielded a barrier height of 0.17 ± 0.02 V, with $n = 2.6 \pm 0.8$.

The large diode quality factor indicates a strong deviation from pure thermionic emission and a potentially large error in the barrier height. In addition to the large value of n , the nonlinearity of the $(\ln J)$ - T^{-1} plots (not shown) was also indicative of an anomalously low and imprecise estimation of Φ_b .^{43,44} High n values have been reported previously for low-temperature J - V measurements of metal/semiconductor junctions.^{43,45,46} In such cases, the experimentally measured Φ_b at low ($\ll 300$ K) temperatures systematically underestimated the value of Φ_b at 300 K. Werner and Guttler proposed a method for correction of the experimentally measured values of Φ_b at low temperatures (eq 4);⁴³

$$\Phi_{b,\text{corr}} = n\Phi_{b,\text{exp}} + (n-1)\frac{k_B T}{q} \ln\left(\frac{N_D}{N_C}\right) \quad (4)$$

where $\Phi_{b,\text{exp}}$ is the experimentally measured barrier height at the temperature T , and $\Phi_{b,\text{corr}}$ is the corrected barrier height. Using this correction, a value of $\Phi_b = 0.3 \pm 0.1$ V was obtained for the n-type H-Si(111)/Hg junction. This barrier height value is slightly smaller than barrier heights for H-Si(111)/Hg contacts previously reported^{2,16,47} but is in good agreement with the barrier height measured for Hg on p-type H-Si(111) with the expectation that the barrier heights on n-type Si and p-type Si, multiplied by q , should add up to the band gap (1.12 eV) of Si.⁴⁸

2. Impedance Data. Mott-Schottky analysis was also used to assess the barrier heights of these junctions (Figure 1c). Bode plots for p-type H-Si(111)/Hg contacts at 0 V showed excellent linear behavior, with unit slope over a large frequency range (Figure 1c, inset).⁴⁹ C^{-2} - V plots obtained in reverse bias yielded a barrier height of 0.86 ± 0.08 V for such contacts. The poorly rectifying behavior of n-type Si(111)/Hg contacts precluded straightforward Mott-Schottky analysis of the barrier height of this system.

B. Hg Contacts to Oxidized Si(111) Surfaces. 1. J - V Measurements. Figure 2 depicts representative J - V data for chemically oxidized SiO_x -Si(111)/Hg contacts. Unlike the H-terminated surfaces, both n-type and p-type SiO_x -Si(111)/

Hg contacts demonstrated rectifying character at room temperature. Junctions made from n-type SiO_x -Si(111) were more strongly rectifying, as evidenced by a lower saturation current in reverse bias and a stronger linear correlation between $\ln J$ and V at forward bias (Figure 2a). The J - V responses were moderately well-described by simple thermionic emission (after correction for R_s), with n values of 1.2 ± 0.1 . From the forward bias portion of the J - V responses, the average Φ_b with Hg for n-type SiO_x -Si(111) surfaces was 0.73 ± 0.06 V. Barrier heights on p-type SiO_x -Si(111) were somewhat lower, with $\Phi_b = 0.56 \pm 0.04$ V.

2. Impedance Data. Figure 2b displays representative C^{-2} - V responses collected at reverse bias for contacts between Hg and n-type and p-type SiO_x -Si(111), respectively. Both n- and p-Si samples showed linear responses for $V < -0.2$ V. The barrier height measured from the C^{-2} - V plots for p-type SiO_x -Si/Hg contacts was 0.6 ± 0.2 V, in reasonable agreement with the value obtained for such junctions from analysis of the J - V data. In contrast, the mean value of $\Phi_b = 0.56 \pm 0.07$ V for n-type SiO_x -Si/Hg contacts was significantly different (by 0.17 \pm 0.09 V) from the value deduced from the J - V data.

For both types of doping of the Si substrate, for $V > -0.2$ V, the C^{-2} - V data exhibited a significant deviation from linearity, with C^{-2} increasing rapidly at increasingly positive biases (Figure 2b). Such behavior was observed for all tested p-type SiO_x -Si/Hg contacts, whereas some n-type SiO_x -Si/Hg contacts did not show any obvious increase in C^{-2} in this bias range. Bode plots for both n-type and p-type SiO_x -Si/Hg contacts exhibited poor linearity over a large range of frequencies (Figure 2c). Additionally, the erratic $\log(|Z|) - \log(f)$ responses demonstrate the inherent variability, irreproducibility, and low electronic quality of chemically oxidized Si surfaces. Unlike thermal oxides, chemically prepared oxides on Si are known to be electronically defective⁵⁰ and compositionally inhomogeneous.⁵¹⁻⁵⁴ Thus, the data are consistent with surface defect sites dominating the energetics and kinetics of interfacial charge-transfer at such interfaces.

C. Hg Contacts to CH_3 -Si(111) Surfaces. 1. Electrical Properties. Figure 3 displays representative J - V behavior for CH_3 -Si(111)/Hg contacts. In contrast to the behavior of contacts between Hg and H-Si(111) (Figure 1), the n-type CH_3 -Si(111)/Hg contacts exhibited strongly rectifying behavior, whereas p-type CH_3 -Si(111)/Hg contacts exhibited no rectification, and an ohmic response, at room temperature.

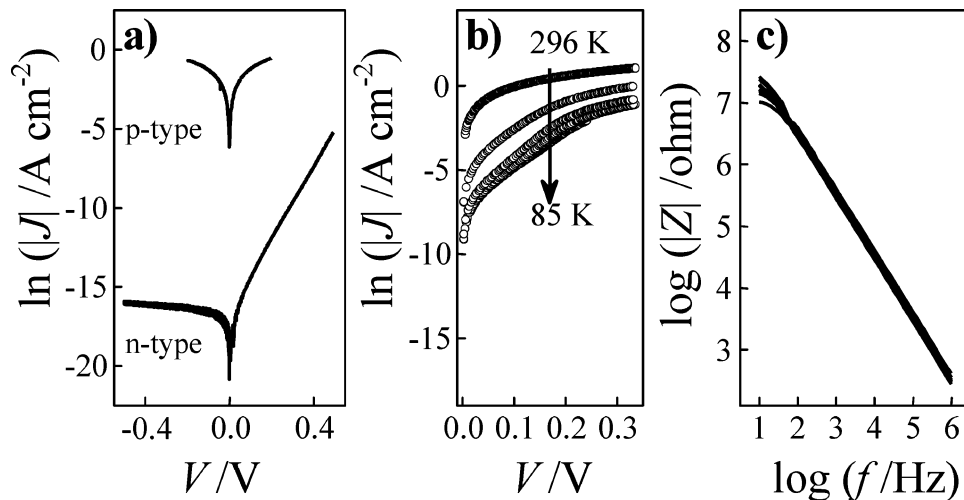


Figure 3. Representative electrical responses of Hg contacts to CH_3 -terminated Si(111). (a) J - V responses of Hg junctions with n-Si and p-Si, $T = 296 \pm 2$ K (b) J - V response of p-Si, $85 \text{ K} \leq T \leq 296 \text{ K}$ (c) Bode plots for all tested Hg junctions with n-Si, $T = 296 \pm 2$ K, and $V = 0$.

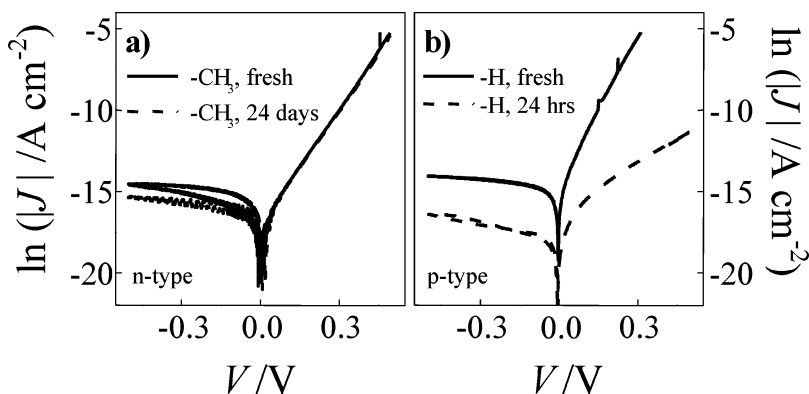


Figure 4. J - V data for Hg/n-Si(111) junctions freshly prepared and aged at ambient conditions. (a) Hg junctions with CH_3 -terminated n-Si(111) freshly prepared (top) and exposed to ambient for 24 days prior to Hg junction formation (bottom). (b) Hg junctions with H-terminated p-Si(111) freshly prepared (top) and exposed to ambient 24 h after preparation (bottom). $T = 296 \pm 2$ K.

The measured forward bias current for p-type CH_3 -Si(111)/Hg contacts was $>10^{-2}$ A at $V = 0.01$ V ($A_s \sim 0.05 \text{ cm}^{-2}$); hence, a quantitative analysis of the room temperature J - V behavior for p-type CH_3 -Si(111)/Hg contacts was not attempted. Unlike H-terminated n-Si, the dependence of the J - V response on temperature was less pronounced for CH_3 -Si(111)/Hg contacts (Figure 3b). Extrapolation of the forward bias J - V data for this system yielded an average uncorrected barrier height of $\Phi_b = 0.15$ V. However, several samples showed nominally the same (ohmic) J - V behavior at 85 K as was observed at 296 K, preventing precise determination of the barrier heights for such contacts. Even with series resistances as low as $10^1 \Omega$, currents in excess of 10^{-3} A will produce an IR_s distortion of the J - V data of $\geq 10^{-2}$ V, placing an upper bound on the practical measurement of J_0 values (where J_0 is the exchange current density) from the forward bias J - V data of $J_0 \leq 5 \text{ mA cm}^{-2}$, which in turn places a lower bound on the measurable barrier height of $\Phi_b > 0.11$ V for p-Si at 85 K. Hence, the mean experimental value of Φ_b for p-type CH_3 -Si(111)/Hg contacts is an upper limit, with $\Phi_b < 0.15$ V.

All tested n-type CH_3 -Si(111)/Hg junctions showed linear $(\ln J)$ - V behavior and a small standard variation in the sample set of measured Φ_b values. The mean value of the barrier height obtained from the forward-bias portion of the J - V response of n-type CH_3 -Si(111)/Hg contacts was $\Phi_b = 0.85 \pm 0.02$ V. Although these contacts exhibited a rather large diode quality factor ($n = 1.6 \pm 0.2$) that further degreasing steps did not lower measurably, brief soaks in 49% wt/wt HF (aq) following

alkylation, but before the Hg contacts had been formed, lowered the mean value of n to 1.13 ± 0.06 without changing the value of Φ_b .

2. Impedance Behavior. Bode plots for n-type CH_3 -Si(111)/Hg contacts at 0 V showed linear behavior, with a unit slope over a large frequency range (Figure 3c).⁴⁹ C^{-2} - V plots obtained in reverse bias yielded a barrier height of 0.91 ± 0.02 V for such contacts. The poorly rectifying behavior of p-type CH_3 -Si(111)/Hg contacts prevented Mott-Schottky analysis of the barrier height of this system.

3. Junction Stability. Figure 4 compares the J - V behavior of Hg junctions between freshly prepared H-Si(111) and CH_3 -Si(111) surfaces with that of junctions formed using H-Si(111) and CH_3 -Si(111) surfaces that had been allowed to age under ambient conditions prior to contact with Hg. The J - V behavior of the CH_3 -Si(111)/Hg contacts was essentially independent of whether the CH_3 -Si(111) samples had been aged or used immediately after preparation (Figure 4a). In contrast, H-Si(111) surfaces showed a deterioration of the J - V response even after 24 h of exposure to air prior to formation of the Si/Hg contact. The altered J - V response (Figure 4b) is consistent with the degradation of H-Si(111) surfaces previously reported as a result of exposure to ambient conditions.¹³

C. Hg Contacts to C_nH_m -Si(111) Surfaces. 1. J - V Properties. The behavior of Si/Hg junctions was also investigated using n-type Si(111) surfaces that had been modified by alkylation with C_2H_5 - (ethyl), *iso*- C_3H_7 - (*iso*-propyl), or CH_3CC - (propynyl) groups. Figure 5 compares the J - V responses of a

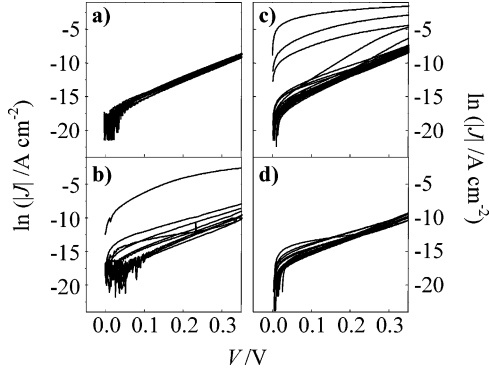


Figure 5. Forward bias J - V data for Hg/n-Si(111) junctions with different terminal surface functionalities: (a) methyl, (b) ethyl, (c) *iso*-propyl, and (d) propynyl. $T = 296 \pm 2$ K.

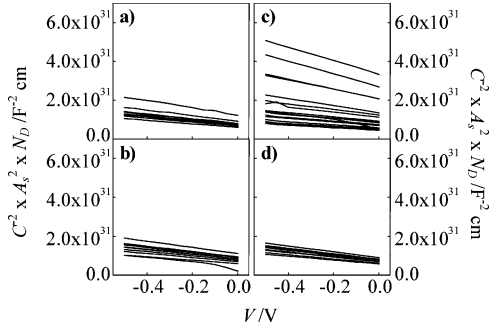


Figure 6. Mott-Schottky (C^{-2} - V) plots of Hg/n-Si(111) junctions with different terminal surface functionalities: (a) methyl, (b) ethyl, (c) *iso*-propyl, and (d) propynyl. The y-axis scale is normalized to the wafer dopant density. $T = 296 \pm 2$ K.

collection of such junctions with the behavior of a collection of n-type CH_3 -Si(111)/Hg contacts. The collection of n-type C_2H_5 -Si(111)/Hg contacts (Figure 5b) exhibited a significantly wider variability in both the slope and intercept of $(\ln J)$ vs V plots than did the collection of n-type CH_3 -Si(111)/Hg contacts. A mean value of $\Phi_b = 0.82 \pm 0.07$ V was determined for the n-type C_2H_5 -Si(111)/Hg junctions.

An even larger dispersion in the shape of the J - V data between samples was observed for n-type *iso*- C_3H_7 -Si(111)/Hg contacts (Figure 5c). A small fraction of the recorded J - V curves for such contacts were suggestive of low barrier height junctions, but a significant fraction of the *iso*- C_3H_7 -Si(111)/Hg junctions showed J - V behavior suggestive of high barrier heights. The mean barrier height value for n-type *iso*- C_3H_7 -Si(111)/Hg contacts was $\Phi_b = 0.8 \pm 0.1$ V.

Figure 5d depicts the data for n-type CH_3CC -Si(111)/Hg contacts. The relative spread of the J - V data between samples was much smaller than that observed for the C_2H_5 -Si(111)/

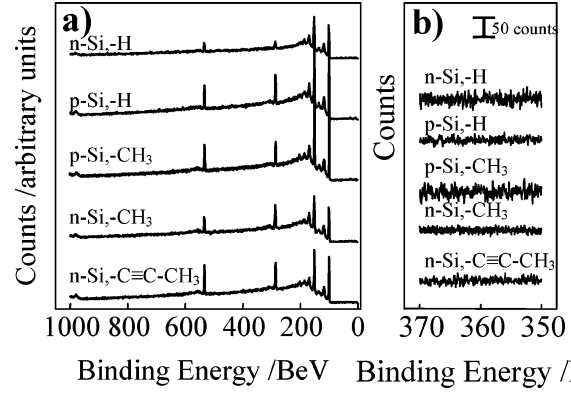


Figure 7. XP spectra of functionalized Si(111) surfaces after exposure to Hg. (a) Survey scans for monohydride-, methyl-, and propynyl-terminated Si(111) surfaces. (b) High-resolution XP spectra demonstrating the absence of a Hg 4d_{5/2} signature for all tested surfaces. The spectra in both figures have been offset for clarity.

Hg or *iso*- C_3H_7 -Si(111)/Hg junctions (Figures 5b,c). Analysis of the J - V data for the n-type CH_3CC -Si(111)/Hg contacts yielded an average barrier height of $\Phi_b = 0.85 \pm 0.03$ V, nominally identical in magnitude and standard deviation to the barrier height observed for n-type CH_3 -Si(111)/Hg contacts.

2. C^{-2} - V Behavior. Figure 6 depicts the C^{-2} - V behavior of these four distinct sets of surface functionalities. As in Figure 5, both the methyl- (Figure 6a) and propynyl- (Figure 6d) functionalized Si(111) surfaces exhibited a smaller spread in measured response than did the ethyl- (Figure 6b) or the *iso*-propyl- (Figure 6c) functionalized Si(111) surfaces. The barrier heights obtained from the data in Figures 5 and 6 are reported in Table 1.

D. XPS Data on Si(111) Surfaces After Contact With Hg.

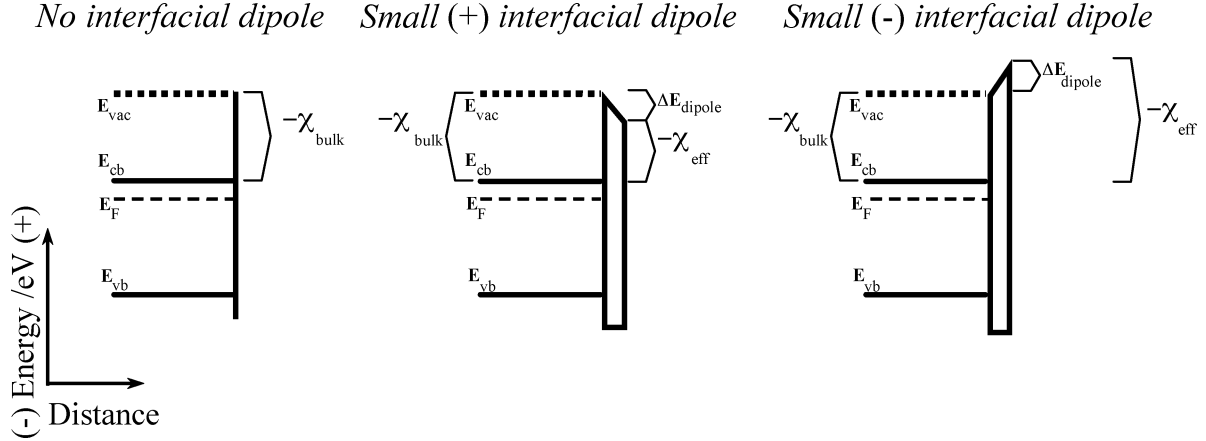
The formation of Hg silicides or Hg-Si amalgams at room temperature is not known,³¹ and silicon has generally been regarded as an inert material with respect to chemical attack by liquid or vapor Hg.³² However, following prolonged exposure, persistent and deleterious Hg adsorption onto silicon interfaces has been observed by electrical measurements and by scanning electron microscopy (SEM).⁵⁵

Figure 7 displays XPS survey scans of chemically modified Si(111) surfaces after they were contacted with Hg, with the Hg removed prior to insertion of the sample into the vacuum chamber. The only observed peaks were ascribable to Si 2p, Si 2s, C 1s, and O 1s emissions. For the H-Si(111) surface, the C 1s and O 1s emissions were present due to adventitious C and O that arose from exposure to the ambient environment following etching, Hg contact, and transport to and insertion into the sample holding chamber of the XP spectrometer (~ 20 min).²¹ High-resolution Si 2p XP spectra (see Supporting

TABLE 1: Measured Junction Properties for Functionalized Si (111) Surfaces in Contact with Hg

surface functionalization	number of tested junctions	$\ln J_0$ (A cm^{-2}) ^a	$q\Phi_{b,J-V}$ (eV) ^a	n^a	V_{bi} (V) ^d	$q\Phi_{b,\text{Mott-Schottky}}$ (eV) ^d	$\Delta q\Phi_b$ (eV) ^e
n-Si, Si-H	7	-21 ± 3^b	0.17 ± 0.02 (0.3 ± 0.1) ^{b,c}	2.6 ± 0.8^b			
n-Si, SiOx	10	-13 ± 2	0.73 ± 0.06	1.2 ± 0.1	0.39 ± 0.07	0.65 ± 0.07	0.08 ± 0.09
n-Si, Si-CH ₃	17	-17.1 ± 0.5	0.85 ± 0.02	1.6 ± 0.2	0.65 ± 0.02	0.91 ± 0.02	-0.06 ± 0.03
n-Si, Si-C ₂ H ₅	10	-16 ± 3	0.82 ± 0.07	2.1 ± 0.8	0.63 ± 0.08	0.88 ± 0.07	-0.07 ± 0.10
n-Si, Si- <i>iso</i> -C ₃ H ₇	20	-14 ± 5	0.8 ± 0.1	1.6 ± 0.3	0.64 ± 0.19	0.93 ± 0.20	-0.2 ± 0.2
n-Si, Si-C≡C-CH ₃	9	-18 ± 1	0.87 ± 0.01	1.8 ± 0.4	0.57 ± 0.04	0.84 ± 0.01	0.01 ± 0.03
p-Si, Si-H	5	-15.8 ± 0.8	0.82 ± 0.02	1.16 ± 0.03	0.6 ± 0.2	0.8 ± 0.2	-0.01 ± 0.08
p-Si, SiOx	10	-7 ± 2	0.56 ± 0.04	1.2 ± 0.1	0.5 ± 0.2	0.7 ± 0.2	-0.14 ± 0.2
p-Si, Si-CH ₃	20	$\geq -7^b$	$< 0.15^b$				

^a Determined from the forward bias portion of J - V data, assuming thermionic emission-diffusion. ^b Measured at $T = 85$ K. ^c The value in the parentheses is after correction, see text. ^d Measured from the reverse bias portion of C^{-2} vs. V data. ^e $q\Phi_{b,J-V} - q\Phi_{b,\text{Mott-Schottky}}$.

SCHEME 1. Energy-band Diagrams at Flat-band Conditions of Three Ideal, Uncontacted n-type Semiconductor Interfaces That are Devoid of Surface States


E_{vac} is the vacuum level energy, E_{cb} is the conduction band edge energy, E_{F} is the fermi level energy, E_{vb} is the valence band edge energy, χ_{bulk} is the energy difference between E_{vac} and E_{F} in the bulk, ΔE is the change in the vacuum level energy at the surface effected by a net surface dipole, and χ_{eff} is the adjusted difference between E_{vac} and E_{F} at the surface as a result of the surface dipole. (Left) an interface with no net dipole at the surface. (Center) an interface with a small positive dipole at the surface. (Right) an interface with a small negative dipole at the surface. The surface dipole layer width is exaggerated for viewing and is not to scale.

Information) verified the absence of appreciable silicon oxide formation. The absence of any other spectral features in Figure 7 indicates that formation of a junction with Hg did not lead to significant persistent chemisorbed or physisorbed Hg at the studied Si(111) interfaces.

Figure 7b displays high-resolution XP spectra in the Hg 4d_{5/2} region. For H-terminated, CH₃-terminated, and CH₃CC-terminated Si surfaces, no discernible signals ascribable to adsorbed Hg were evident above the background. The large cross section (12.17 referenced to C) for the Hg 4d_{5/2} emission implies that a signal for surficial Hg would be much more easily detected than for surficial C and O, which have cross sections of 1.00 and 2.93, respectively. The detection limit of Hg is ~ 0.1 atom % within the sampled depth of the Si substrate; hence, the lack of an observed Hg 4d_{5/2} signal implies that, for the conditions used in this study, the near-surface content of Hg must be $< \sim 0.1$ atom % within the topmost ~ 12 Å of the Si substrate.^{56,57} Analogous high-resolution scans taken at 290–310 eV demonstrated a similar lack of spectroscopic evidence of residual Mg on surfaces that had been exposed to the precursor Grignard reagents.

IV. Discussion

A. Barrier Heights of Hg Contacts to CH₃-Si(111) and H-Si(111) Surfaces. Systematic control over the barrier height of Si/metal contacts is well-known to be extremely difficult. Barrier heights for traditional metal/Si Schottky contacts exhibit strong Fermi level pinning because of a combination of metal silicide formation, metal induced gap states, and/or defect states at the metal/Si interface.³⁰ Correspondingly, experimentally observed barrier heights for Si/metal contacts are relatively insensitive to the work function of the contacting metal phase, with a variety of metals having differing work functions showing barrier heights of 0.6–0.9 V on n-type Si and 0.3–0.5 V on p-type Si.³⁰ Only metals having very low work functions, such as In or Hg, yield ohmic contacts on n-type Si at room temperature.³⁰

Alkylation of the Si surface offers a potential route to controlling the barrier height of metal contacts on Si surfaces by precluding direct contact and/or chemical bonding between the Si and the contacting metal phase. Ideally, the intervening

layer would be sufficiently thin that subsequent layers of, for example, high dielectric constant materials or electronically conducting or insulating materials could be deposited on top of the passivated Si surface to allow systematic control over the properties of the resulting electrical device structures.

In addition, manipulation of the chemical bonding of the topmost atoms on the Si surface offers the possibility of further controlling the energetics of the resulting Si/metal contact through controlled introduction of a dipole layer at the Si surface as a result of surface alkylation. For example, mixed monolayers of Rb and O on Si(100) have been shown to lower the vacuum-level energy below the conduction band edge at the Si surface, substantially facilitating emission of thermalized electrons at the surface.⁵⁸ The observed phenomenon is a consequence of the net dipole effected by the Rb/O modifying layers, where the magnitude of the electron affinity at the surface (χ_{eff}) changes relative to that in the bulk (χ_{bulk}) by an amount equal to ΔE_{dipole} .

In principle, a covalently bonded passivating layer can either raise or lower χ_{eff} , depending on the sign of the associated dipole (Scheme 1). The barrier height of a metal contact to an n-type semiconductor is given by eq 5.

$$q\Phi_{\text{b}} = W_{\text{F}} - \chi_{\text{eff}} \quad (5)$$

Thus, for Schottky barriers with moderately doped semiconductors, the extent of the band bending and the width of the depletion layer are strong functions of χ_{eff} .

As shown herein, introduction of one CH₃-group between the metal and the Si has a pronounced effect on the energetics of the resulting Si/Hg contacts. The barrier heights changed by ~ 0.5 V for methylated n-Si(111) surfaces, relative to H-Si(111) surfaces, and the J - V behavior at room temperature changed from an ohmic contact to a highly rectifying contact. Similarly, the J - V behavior for p-type Si(111) samples changed from a high barrier height for H-Si(111)/Hg contacts to a low barrier height for CH₃-Si(111)/Hg contacts.

The electron affinity of Si in the bulk is 4.05 eV,²⁴ and the work function of Hg is 4.49 eV.³³ Synchrotron photoemission methods indicate that the interfacial dipole at the CH₃-Si(111) surface is 0.38 eV.²⁴ Hence, use of eq 5 predicts that the barrier height of CH₃-Si(111)/Hg contacts should be 0.8 ± 0.1 V for n-type Si(111) surfaces and 0.3 ± 0.1 V for p-type Si(111)

surfaces. These expectations are in excellent agreement with the barrier heights determined experimentally from the J - V and C^{-2} - V data for these systems (Figure 3, Table 1).

The barrier heights of Si/metal Schottky contacts are also very sensitive to the presence of contamination, such as silicon oxides, at the Si surface. For example, Hg contacts with chemically oxidized Si(111) surfaces showed nonideal behavior (Figure 2) and exhibited evidence for Fermi level pinning that was not observed for CH_3 -Si(111)/Hg contacts. Similarly, H-Si(111) samples that were exposed to ambient air for 24 h before Hg junction formation showed much different barrier heights than Hg contacts to freshly prepared H-Si(111) surfaces (Figure 4). In contrast, barrier heights on CH_3 -Si(111) surfaces were the same regardless of whether the samples were freshly prepared or exposed to air for extended periods of time. This behavior is consistent with the insensitivity to oxidation imparted to the Si(111) surface by alkylation with CH_3 - groups.²¹ The bonding of CH_3 - groups to every Si atop site thus also imparts greater kinetic robustness and stability toward metal-silicide formation to the CH_3 -terminated Si(111) surface, as compared to the H-Si(111) or chemically oxidized Si(111) surfaces.¹³

B. Hg Contacts to Si(111) Surfaces Functionalized with Ethyl and Other Alkyl Groups. The ethyl and *iso*-propyl groups have effective diameters (≥ 4.5 Å) larger than the internuclear distance (3.8 Å) between atop sites on an unreconstructed Si(111) surface.⁵⁹ Hence, these alkyls are not sterically capable of forming Si-C bonds to every atop atom without introducing a prohibitive degree of surface strain.¹⁸ Consistently, XPS analysis has shown that C_2H_5 - groups exhibit 70–90% of the coverage of CH_3 - groups, whereas *iso*-propyl groups exhibit 40% of the coverage of CH_3 - groups on Si(111) surfaces. Use of the two-step chlorination/alkylation method to produce such surfaces has been shown to result in Si-H bonds on the unalkylated atop sites of such Si(111) surfaces.⁶⁰

The J - V and C^{-2} - V data of Hg contacts to such surfaces are consistent with the expectations for a chemically mixed bonding overlayer in such systems. Both the C_2H_5 - and *iso*- C_3H_7 -terminated Si(111) surfaces showed more scatter and larger n values in their Hg junction characteristics, with a sizable portion of the sample sets showing barrier heights and band bending values comparable to H-terminated Si. Nevertheless, on average, surface modifications yielded junctions with comparable electrical properties to those formed on CH_3 -surfaces, presumably reflecting the equivalent chemical nature of the Si-C bonds in both systems.

The measurement of high barrier heights on such partially alkylated surfaces, which also contain a significant degree of H-termination, is somewhat surprising. Discrete, isolated patches of H-Si(111) would be expected to produce very low barrier heights in contact with Hg (Figure 1). The ~ 0.5 V difference in barrier heights effected by the alkyl and H- groups is tantamount to 9 orders of magnitude difference in exchange current densities, at room temperature (i.e., 10^2 A cm^{-2} vs 10^{-7} A cm^{-2}). If the regions of differing barrier height are non-interacting, then such a large discrepancy in J_0 implies that the current measured through the total junction will be dominated by that through the Hg/H-Si(111) regions, even if such regions constitute as low as 3.5×10^{-9} of the total contact surface area.⁶¹

Two mechanisms likely prevent such behavior from being observed. The surface tension of Hg is sufficiently high that pinholes in the passivation layer are not as directly accessible as they are with other liquid contacting phases (e.g., water).⁵ A significant fraction of the residual H-terminated regions may

thus be physically inaccessible to the Hg contact. Additionally, current flowing through patches of H-Si(111) in direct contact with Hg may be effectively screened or “pinched-off” by the higher barrier height alkylated-Si/Hg regions.^{29,62–64} High fractional areas of low barrier-height regions will not contribute significantly to the total interfacial current of a junction, provided that the low barrier-height regions are comprised of small patches having widths less than a critical effective radius, R_0 ;

$$R_0 < \frac{(\Phi_{\text{b,high}} - \Phi_{\text{b,low}}) \sqrt{\frac{2\epsilon_0\epsilon_{\text{Si}}V_{\text{bi}}}{qN_{\text{D}}}}}{2\left(\Phi_{\text{b,high}} - \frac{k_{\text{B}}T}{q} \ln\left(\frac{N_{\text{C}}}{N_{\text{D}}}\right) - V_{\text{app}}\right)} \quad (6)$$

where R_0 is the radius of a low barrier height ($\Phi_{\text{b,low}}$) patch, $\Phi_{\text{b,high}}$ is the high barrier height value for the majority of the surface, V_{app} is the applied bias, and V_{bi} is the built-in voltage of the contact at equilibrium. For the respective barrier heights of H- and CH_3 - terminated Si(111) surfaces with Hg, and for the nominal doping level of the Si substrates, the critical length at 0 V is $R_0 \sim 400$ nm. Hence, regions of low barrier height H-Si(111)/Hg contact smaller than this dimension are expected to be “pinched off” by the surrounding high barrier height alkylated Si/Hg contact regions. The likelihood that one or both of these screening processes will fail increases with lower coverage of the alkyl groups. This likely accounts for the increased dispersion in the behavior of surfaces alkylated with larger alkyl groups, with the observed dispersion increasing in the order $\text{CH}_3 < \text{C}_2\text{H}_5 < \text{iso-C}_3\text{H}_7$ - (Figures 5 and 6).

C. Contacts Between Hg and Si(111) Surfaces Functionalized with Propynyl Groups. The propynyl group is believed to be oriented normal to the Si(111) surface plane.³⁸ Hence, although the vertical height of the propynyl group is greater than that of a CH_3 - group, the projected areal cross section is the same in each case. Passivation with propynyl groups can also, in principle, produce 100% coverage of Si-C bonds to every atop Si atom on an unreconstructed Si(111) surface.

Junctions between Hg and CH_3CC -Si(111) surfaces exhibited J - V behavior that was quite similar to that of CH_3 -Si(111)/Hg contacts. As expected from the low tunneling barriers exhibited by alkynyl compounds,⁶⁵ the triply bonded carbon atoms ($-\text{C}\equiv\text{C}-$) between the Si surface and the terminal CH_3 - group, apparently, do not add significant resistance to charge transfer. The data reported herein also demonstrate that propynyl groups can passivate Si(111) surfaces with comparable effectiveness to CH_3 - groups, as evidenced by the much lower variability in J - V behavior observed for propynyl-Si(111)/Hg contacts as compared to C_2H_5 -Si(111)/Hg or *iso*- C_3H_7 -Si(111)/Hg contacts. This behavior is consistent with the preliminary characterization of CH_3CC -Si(111) surfaces reported elsewhere,³⁸ and an extensive characterization of Si surfaces modified with propynyl groups is currently in progress.⁶⁶

D. Comparison with the Behavior of Hg Contacts to Other Alkylated Si Surfaces. Several other reports have recently described the electrical characteristics of Hg/Si junctions on related, but not identically alkylated, Si(111) surfaces. The findings and interpretations in these various reports differ from each other and also differ from those reported herein. For p-type Si(111) grafted with $\text{C}_n\text{H}_{2n+1}$ groups ($n = 10, 12, 16, 22$), the measured barrier heights for all long alkyl chains were in the range of 0.5 – 0.7 V,¹⁶ whereas high (≈ 0.85 V) barrier heights were also measured for alkylated n-type Si(111) surfaces. No clear dependence of either the barrier heights or V_{bi} values was

observed with chain length. In contrast, a monotonic increase in barrier heights (0.76–0.85 V) has been reported for n-type Si(111) alkylated with $n = 6, 8, 10, 12$.^{2–4} In that study, analogously modified p-Si yielded higher barrier heights (i.e., 0.56 V for p-Si modified with C₁₀H₂₁ groups) than would be expected based on having the barrier heights of n-type and p-type Si, multiplied by q , sum to the 1.12 eV band gap of Si. Extrapolating the data of Yu et al. to $n = 1$ (–CH₃), yields an estimate for the barrier height between Hg junctions and CH₃–Si(111) of ~0.68 V, as opposed to the ~0.8 V barrier height measured in this work for CH₃–Si(111) surfaces. One likely source of these differences is that the Grignard chemistry employed for surface modification in these other studies did not utilize the preliminary chlorination step employed in the two-step chlorination/alkylation method.⁶⁷ Previous work has suggested the chlorination is important for achieving consistent surface coverages with long alkyl groups and to achieve full coverage for methyl groups on Si(111) surfaces.¹⁹ Additionally, it is difficult, from charge-transfer rate measurements alone, to separate a reduction in the electron-tunneling coefficient from changes in the barrier height at the semiconductor surface.¹⁵ The well-behaved C^{-2} – V plots, as well as the expected complementarity between barrier heights on n-type and p-type alkylated surfaces and the ability to directly separate the energetics and kinetics of the charge-transfer process for the CH₃-terminated Si(111)/Hg junctions of interest, lend credence to the approach employed herein for understanding the electrical and chemical effects that accompany replacement of H–Si bonds by C–Si bonds on Hg junctions with Si(111) surfaces.

V. Conclusions

XP spectra and the electrical responses of the H–, CH₃–, and SiO_x– terminated Si(111) surfaces have shown that Hg is an excellent contact material that does not introduce extrinsic defects in the resultant metal/semiconductor junctions. The observed barrier heights and built-in voltages of H– and CH₃–Si(111) surfaces are consistent with their respective electron affinities and previously reported low electronic defect densities. The equivalent electrical responses of Hg junctions made with recently prepared and aged CH₃–Si(111) surfaces has demonstrated the robust nature of the CH₃-terminated Si(111) surface. Variability in the properties of Hg junctions with more sterically hindered ‘short’ alkyl groups underscores the necessity for complete surface coverage in the passivating layer. Si(111) surfaces modified with propynyl groups yielded Hg junctions having electrical properties comparable to those of CH₃–Si(111) terminated surfaces. In the absence of complications from the formation of the metal contact, metal/semiconductor junctions involving either the CH₃– or CH₃CC– terminated Si(111) surfaces can display ideal Schottky-type behavior.

Acknowledgment. We acknowledge the National Science Foundation, grant No. CHE-0604894, for support of this work. S.M. also acknowledges financial support from the Ford Foundation, through the National Academy of Sciences.

Supporting Information Available: Additional information regarding the low temperature J – V data acquisition, analysis of impedance data, and high-resolution Si 2p spectra are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

(1) Aswal, D. K.; Lenfant, S.; Guerin, D.; Yakhmi, J. V.; Vuillaume, D., *Anal. Chim. Acta* **2006**, *568*, (1–2), 84–108.

- (2) Liu, Y. J.; Yu, H. Z., *Chemphyschem* **2002**, *3*, 799–802.
 (3) Liu, Y. J.; Yu, H. Z., *J. Phys. Chem. B* **2003**, *107*, 7803–7811.
 (4) Liu, Y. J.; Yu, H. Z., *Chemphyschem* **2003**, *4*, 335–342.
 (5) Yu, H. Z.; Morin, S.; Wayner, D. D. M.; Allongue, P.; de Villeneuve, C. H., *J. Phys. Chem. B* **2000**, *104*, 11157–11161.
 (6) Rohde, R. D.; Agnew, H. D.; Yeo, W. S.; Bailey, R. C.; Heath, J. R., *J. Am. Chem. Soc.* **2006**, *128*, 9518–9525.
 (7) Zhu, Z. Q.; Zhang, J.; Zhu, J. Z., *Sens. Lett.* **2005**, *3*, 71–88.
 (8) Vilan, A.; Shanzer, A.; Cahen, D., *Nature* **2000**, *404*, 166–168.
 (9) Cohen, R.; Zenou, N.; Cahen, D.; Yitzchaik, S., *Chem. Phys. Lett.* **1997**, *279*, 270–274.
 (10) Allongue, P.; de Villeneuve, C. H.; Cherouvrier, G.; Cortes, R.; Bernard, M. C., *J. Electroanal. Chem.* **2003**, *550*, 161–174.
 (11) He, T.; He, J.; Lu, M.; Chen, B.; Pang, H.; Reus, W. F.; Nolte, W. M.; Nackashi, D. P.; Franzon, P. D.; Tour, J. M., *J. Am. Chem. Soc.* **2006**, *128*, 14537–14541.
 (12) Seitz, O.; Bocking, T.; Salomon, A.; Gooding, J. J.; Cahen, D., *Langmuir* **2006**, *22*, 6915–6922.
 (13) Liu, Y. J.; Yu, H. Z., *J. Electrochem. Soc.* **2003**, *150*, G861–G865.
 (14) Salomon, A.; Boecking, T.; Chan, C. K.; Amy, F.; Girshvitz, O.; Cahen, D.; Kahn, A., *Phys. Rev. Lett.* **2005**, *95*, 2668071–2668074.
 (15) Salomon, A.; Boecking, T.; Gooding, J. J.; Cahen, D., *Nano Lett.* **2006**, *6*, 2873–2876.
 (16) Faber, E. J.; de Smet, L. C. P. M.; Olthuis, W.; Zuilof, H.; Sudholter, E. J. R.; Bergveld, P.; van den Berg, A., *Chemphyschem* **2005**, *6*, 2153–2166.
 (17) Webb, L. J.; Nemanick, E. J.; Biteen, J. S.; Knapp, D. W.; Michalak, D. J.; Traub, M. C.; Chan, A. S. Y.; Brunschwig, B. S.; Lewis, N. S., *J. Phys. Chem. B* **2005**, *109*, 3930–3937.
 (18) Nemanick, E. J.; Solares, S. D.; Goddard, W. A.; Lewis, N. S., *J. Phys. Chem. B* **2006**, *110*, 14842–14848.
 (19) Bansal, A.; Li, X. L.; Yi, S. I.; Weinberg, W. H.; Lewis, N. S., *J. Phys. Chem. B* **2001**, *105*, 10266–10277.
 (20) Bansal, A.; Li, X. L.; Lauer, I.; Lewis, N. S.; Yi, S. I.; Weinberg, W. H., *J. Am. Chem. Soc.* **1996**, *118*, 7225–7226.
 (21) Webb, L. J.; Lewis, N. S., *J. Phys. Chem. B* **2003**, *107*, 5404–5412.
 (22) Webb, L. J.; Rivillon, S.; Michalak, D. J.; Chabal, Y. J.; Lewis, N. S., *J. Phys. Chem. B* **2006**, *110*, 7349–7356.
 (23) Yu, H. B.; Webb, L. J.; Ries, R. S.; Solares, S. D.; Goddard, W. A.; Heath, J. R.; Lewis, N. S., *J. Phys. Chem. B* **2005**, *109*, 671–674.
 (24) Hunger, R.; Fritsche, R.; Jaeckel, B.; Jaegermann, W.; Webb, L. J.; Lewis, N. S., *Phys. Rev. B* **2005**, *72*, 0453171–7.
 (25) Bansal, A.; Lewis, N. S., *J. Phys. Chem. B* **1998**, *102*, 4058–4060.
 (26) Yu, H. B.; Webb, L. J.; Heath, J. R.; Lewis, N. S., *Appl. Phys. Lett.* **2006**, *88*, 2521111–3.
 (27) Royea, W. J.; Juang, A.; Lewis, N. S., *Appl. Phys. Lett.* **2000**, *77*, 1988–1990.
 (28) Hunger, R.; Pettenkofer, C.; Scheer, R., *J. Appl. Phys.* **2002**, *91*, 6560–6570.
 (29) Rossi, R. C.; Lewis, N. S., *J. Phys. Chem. B* **2001**, *105*, 12303–12318.
 (30) Sze, S. M., *Physics of Semiconductor Devices*, 2nd ed.; John Wiley & Sons: New York, 1981.
 (31) Hansen, M., *The Constitution of Binary Alloys*, 2nd ed.; McGraw Hill: New York, 1958.
 (32) Battistoni, C.; Bemporad, E.; Galdikas, A.; Kaciulis, S.; Mattogno, G.; Mickevicius, S.; Olevano, V., *Appl. Surf. Sci.* **1996**, *103*, 107–111.
 (33) Lide, D. R., *Handbook of Chemistry and Physics*, 75th ed.; CRC Press, Inc.: Boca Raton, 1994; pp 9–2 through 9–5.
 (34) Rampi, M. A.; Schueller, O. J. A.; Whitesides, G. M., *Appl. Phys. Lett.* **1998**, *72*, 1781–1783.
 (35) Haag, R.; Rampi, M. A.; Holmlin, R. E.; Whitesides, G. M., *J. Am. Chem. Soc.* **1999**, *121*, 7895–7906.
 (36) McCreery, R. L., *Chem. Mater.* **2004**, *16*, 4477–4496.
 (37) Severin, P. J.; Poedt, G. J., *J. Electrochem. Soc.* **1972**, *119*, 1384–1389.
 (38) Hurley, P. T.; Nemanick, E. J.; Brunschwig, B. S.; Lewis, N. S., *J. Am. Chem. Soc.* **2006**, *128*, 9990–9991.
 (39) Allongue, P.; de Villeneuve, C. H.; Morin, S.; Boukherroub, R.; Wayner, D. D. M., *Electrochim. Acta* **2000**, *45*, 4591–4598.
 (40) Goodman, A. M., *J. Appl. Phys.* **1963**, *34*, 329–338.
 (41) Wittmer, M.; Freeouf, J. L., *Phys. Rev. Lett.* **1992**, *69*, 2701–2704.
 (42) Wittmer, M.; Freeouf, J. L., *Phys. Lett. A* **1993**, *173*, 190–194.
 (43) Werner, J. H.; Gutler, H. H., *J. Appl. Phys.* **1993**, *73*, 1315–1319.
 (44) Aydogan, S.; Saglam, M.; Turut, A., *Appl. Surf. Sci.* **2005**, *250*, 43–49.
 (45) Aboelfotoh, M. O., *Solid St. Electron.* **1991**, *34*, 51–55.
 (46) Lee, T. C.; Chen, T. P.; Au, H. L.; Fung, S.; Beling, C. D., *Semicond. Sci. Technol.* **1993**, *8*, 1357–1360.
 (47) Choi, J. Y.; Ahmed, S.; Dimitrova, T.; Chen, J. T. C.; Schroder, D. K., *IEEE T. Electron. Dev.* **2004**, *51*, 1380–1384.
 (48) $q(\Phi_{b,n} + \Phi_{b,p}) = 1.12$ eV for Si at $T = 296$ K.

- (49) Fajardo, A. M.; Lewis, N. S., *J. Phys. Chem. B* **1997**, *101*, 11136–11151.
- (50) Ikari, T.; Fukuyama, A.; Murata, T.; Suemitsu, M.; Haddad, N.; Reita, V.; Roger, J. P.; Fournier, D., *Mat. Sci. Eng. B Solid St. Mater. Adv. Technol.* **2005**, *124*, 345–348.
- (51) Ogawa, H.; Hattori, T., *Appl. Phys. Lett.* **1992**, *61*, 577–579.
- (52) Asuha; Kobayashi, T.; Takahashi, M.; Iwasa, H.; Kobayashi, H., *Surf. Sci.* **2003**, *547*, 275–283.
- (53) Bertagna, V.; Petitdidier, S.; Rochat, N.; Rouchon, D.; Besson, P.; Erre, R.; Chemla, M., *J. Electroanal. Chem.* **2005**, *584*, 54–62.
- (54) Petitdidier, S.; Bertagna, V.; Rochat, N.; Rouchon, D.; Besson, P.; Erre, R.; Chemla, M., *Thin Solid Films* **2005**, *476*, 51–58.
- (55) Jones, P. L.; Corbett, J. W., *Appl. Phys. Lett.* **1989**, *55*, 2331–2332.
- (56) Seah, M. P., Quantification of AES and XPS. In *Practical Surface Analysis*, Briggs, D., Seah, M. P., Eds; John Wiley & Sons: Chichester, United Kingdom, 1990; vol. 1, pp 201–255.
- (57) The electron escape depth (I_{Si}) can be estimated from $I_{Si} = k a_{Si}^{3/2} E_{Si}^{1/2} \sin \theta$; where $k = 0.41 \text{ nm}^{-1/2} \text{ eV}^{-1/2}$, $a_{Si} = 0.272 \text{ nm}$, $E_{Si} = 1386 \text{ eV}$, and $\theta = 35$.
- (58) Martinel.Ru, *J. Appl. Phys.* **1973**, *44*, 2566–2570.
- (59) Yu, H. B.; Webb, L. J.; Solares, S. D.; Cao, P.; Goddard, W. A.; Heath, J. R.; Lewis, N. S., *J. Phys. Chem. B* **2006**, *110*, 23898–23903.
- (60) Nemanick, E. J.; Hurley, P. T.; Brunshwig, B. S.; Lewis, N. S., *J. Phys. Chem. B* **2006**, *110*, 14800–14808.
- (61) For a heterogeneous junction composed purely of two non-interacting contact regions (low barrier height and high barrier height), the thermionic emission–diffusion model predicts that the current through the fractional area of the low barrier height regions (A_{low}) will equal the current across the majority high barrier height regions when $A_{low} = 1/(1 + e^{(\Delta\Phi_b)q/k_bT})$; where $\Delta\Phi_b$ describes the difference between the two barrier heights. For H[−] and CH₃[−] surfaces, $\Delta\Phi_b \sim 0.5 \text{ V}$.
- (62) Tung, R. T.; Sullivan, J. P.; Schrey, F., *Mat. Sci. Eng. B Solid St. Mater. Adv. Technol.* **1992**, *14*, 266–280.
- (63) Tung, R. T., *J. Vac. Sci. Technol. B* **1993**, *11*, 1546–1552.
- (64) Rossi, R. C.; Tan, M. X.; Lewis, N. S., *Appl. Phys. Lett.* **2000**, *77*, 2698–2700.
- (65) Ren, T., *Organometallics* **2005**, *24*, 4854–4870.
- (66) Plass, K.; Lewis, N. S., **2007**, manuscript in preparation.
- (67) Boukherroub, R.; Morin, S.; Bensebaa, F.; Wayner, D. D. M., *Langmuir* **1999**, *15*, 3831–3835.