Chemically Modified Si(111) Surfaces Simultaneously Demonstrating Hydrophilicity, Resistance Against Oxidation, and Low Trap State Densities

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Abstract.

Chemically modified Si(111) surfaces have been prepared through a series of wet chemical surface treatments that simultaneously show resistance towards surface oxidation, selective reactivity towards chemical reagents, and areal defect densities comparable to unannealed thermal oxides. Specifically, grazing angle attenuated total reflectance infrared and X-ray photoelectron (XP) spectroscopy were used to characterize allyl-, 3,4-methylenedioxybenzene-, or 4-[bis(trimethylsilyl)amino]phenyl-terminated surfaces and the subsequently hydroxylated surfaces. Hydroxylated surfaces were confirmed through reaction with 4-(trifluoromethyl)benzyl bromide and quantified by XP spectroscopy. Contact angle measurements indicated all surfaces remained hydrophilic, even after secondary backfilling with CH₃- groups. Surface recombination velocity measurements by way of microwave photoconductivity transients showed the relative defect-character of as-prepared and aged surfaces. The relative merits for each investigated surface type are discussed.

Keywords: surface chemistry, semiconductor, hydrophilic, silicon

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Introduction.

Three features are highly desirable in semiconductor interfaces when used to construct optoelectronic technologies. First, the chemical integrity of the semiconductor surface must be both compatible with all device fabrication/metallurgical steps. Second, the electrical quality of each semiconductor interface must be sufficiently good so as not to present an operational bottleneck or otherwise adversely affect the device. Third, the semiconductor surface should be (and remain) either highly conducting or insulating (depending on the application) with respect to heterogeneous charge transfer. No native semiconductor surface perfectly and simultaneously demonstrates these aspects, motivating the development of new and improved chemical modification strategies of semiconductor interfaces.

Vapor phase atomic layer deposition (ALD)[1, 2] and spin casting of aqueous metal oxo cluster solutions[3, 4] are highly advantageous for rapidly and simply constructing high quality semiconductor heterojunctions. However, they are best suited for hydrophilic semiconductor interfaces that can withstand elevated temperatures and have proton donating/accepting character. The majority of technologically relevant Groups IV and III-V have native interfaces that do not possess these attributes in addition to retaining a low defect density. Although native oxides on such semiconductors are generally hydrophilic,[5, 6] they possess deleterious levels of trap states. Of the few high quality oxides (e.g. annealed thermal oxide Si(100)[7]), they are naturally insulating. Chemical methods to eliminate electrically active surface states on Groups IV and III-V surfaces (e.g. etching with NH_4F :[8] lattice matched AlGaAs epilayers[9]) render surfaces that have too few nucleation sites for ALD[10] and/or are neither wettable nor stable towards exposure to aqueous solutions.[11-19]

This report focuses on the potential of wet chemical surface modification to yield semiconductor surfaces that are jointly hydrophilic, resistant against oxidation, and possesses a low level of surface defects. Using single crystalline Si(111) as a model surface, we demonstrate organically modified interfaces prepared through a sequence of reactions involving Grignard reagents[20, 21] and subsequent activation steps. Specifically, we show the preparation of Si(111) surfaces decorated with either a terminal primary alcohol, a terminal diol, or a terminal amine group (Scheme 1). Distinctions between the surfaces prepared here and the prior art in organically-modified Si surfaces[22-33] are drawn through measurements of oxide growth via X-ray photoelectron spectroscopy, contact angle wetting measurements, reactivity towards model test reagents, and

surface recombination velocities, S , of photogenerated carriers. The purpose of the work is to not only identify the attainable physicochemical properties of these modified Si interfaces but more generally to show that semiconductor surfaces that are reactive towards modification by Grignard reagents can be deterministically tailored as needed.

Experimental.

Materials and Chemicals. All chemicals were purchased from Sigma-Aldrich and used as received unless noted. Methanol (anhydrous >99.8%), chlorobenzene (Acros, 99.8%), tetrahydrofuran (THF) (anhydrous $\geq 99.9\%$, inhibitor free), acetone (Fisher, HPLC grade), hexanes (Macron Chemicals, ACS grade), dichloromethane (anhydrous > 99.8%), phosphorus (V) oxychloride, borane-tetrahydrofuran (1 M), diethyl ether (anhydrous), potassium bis(trimethylsilyl)amide (KHMDs), 40% ammonium fluoride (Transene Electronic Chemicals, semiconductor grade), sodium hydroxide (Fisher, 95.0 to 100.5% FCC grade), 30wt% in H_2O hydrogen peroxide (ACS grade), trifluoroacetic acid (TFA) (99%), 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (98%), and 37% hydrochloric acid (ACS grade) were used as received. Methylmagnesium chloride (3.0 M), allyl magnesium chloride (2.0 M), and 4-[bis(trimethylsilyl)amino]phenyl magnesium bromide (0.5 M) were used as received. 3,4-(methylenedioxy)phenylmagnesium bromide (1.0 M) was diluted to 0.5 M with THF to help prevent polymerization during reaction. 4-(trifluoromethyl)benzyl bromide (Sigma-Aldrich, 98%) was outgassed by three freeze-pump-thaw cycles before use. Benzoyl peroxide (Fluka, $\geq 97\%$) was dried under a vacuum of < 200 mTorr for at least 24 h and placed in the nitrogen-atmosphere glovebox. Water with a resistivity of $18.2 M\Omega\text{ cm}^{-1}$ (Barnsted Nanopure system) was used throughout. For surface characterization studies, one-side polished, n-type Si (111) wafers doped with As were purchased from Wafer Works Corp. and had thickness of $525 \pm 15\text{ }\mu\text{m}$. For SRV measurements, float-zone (FZ), intrinsically-doped Si(111) (El-Cat) wafers with a resistivity equal to $16500 \pm 3500\text{ }\Omega\cdot\text{cm}$, a thickness of $460 \pm 15\text{ }\mu\text{m}$, and both sides polished were used.

Sample Preparation. Samples were diced into 0.5 cm by 0.5 cm squares for surface characterization and into 1 cm by 1.5 cm rectangles for SRV measurements. Si(111) samples were etched prior to use in 40% NH_4F solution for 5 minutes while continuously purging with nitrogen gas, rinsed with water, and dried in a stream of nitrogen gas. Immediately after etching, wafers were transferred to a nitrogen-purged glove box. Freshly etched wafers were chlorinated at 90°C for 50 minutes using a saturated solution of phosphorous (V) pentachloride in chlorobenzene, to which a few grains of benzoyl peroxide were added.[34] Following the chlorination step, samples were

washed with THF, dried in the glovebox, and transferred to reaction vessels to which designated Grignard reagents were added (Scheme 1).

Preparation of 1 and 1a. Chlorinated wafers were transferred to closed reaction vessels to which a solution of allylmagnesium chloride was added. Reaction solution was heated for 13 h at $110 \pm 5^\circ\text{C}$. Samples were rinsed with THF and methanol (**1**). To prepare **1a** surfaces, **1** surfaces were hydroborated and hydroxylated with a procedure modified from Toledano, *et al.*[30] In a nitrogen-purged glove box, **1** wafers were immersed in a solution of $\text{BH}_3 \cdot \text{THF}$ complex at room temperature for 5 h, rinsed with THF and allowed to dry, and transferred to a round bottom flask, sealed with a rubber stopper and taken out of the glove box. To the flask, 1 mL 3 M NaOH and 1 mL 30% H_2O_2 injected through a rubber septum via syringe were added stepwise. After 20 min at room temperature, the wafers were removed from the flask, washed with water and methanol, and dried under a stream $\text{N}_{2(\text{g})}$.

Preparation of 2 and 2c. Chlorinated wafers were transferred to closed reaction vessels to which a solution of 3,4-(methylenedioxy)phenylmagnesium bromide was added and diluted to 0.5 M. Reaction temperature was reduced to $90 \pm 5^\circ\text{C}$ to prevent polymerization of the reagent. Upon completion, samples were rinsed with THF and methanol (**2**). Samples were either backfilled with methylmagnesium chloride in a new reaction vessel for additional 13 h at $110 \pm 5^\circ\text{C}$, rinsed with THF and methanol, and dried in the glovebox (**2b**) or deprotected with a solution of TFA:THF: H_2O (1:20:5) for 4 h at room temperature outside of the glovebox (**2a** and **2c**).[35]

Preparation of 3 and 3b. Chlorinated wafers were transferred to closed reaction vessels to which a solution of 4-[bis(trimethylsilyl)amino]phenyl magnesium bromide was added. Reaction vessel was heated to $110 \pm 5^\circ\text{C}$ for 12-16 h, samples were rinsed with THF and methanol, and allowed to dry in the glovebox (**3**). Samples were either backfilled with methylmagnesium chloride in a new reaction vessel for additional 3 h at $90 \pm 5^\circ\text{C}$, rinsed with THF and methanol, and dried in the glovebox (**3b**) or deprotected with a 20% v/v HCl solution for 1 h at room temperature outside of the glovebox (**3a** and **3c**).

Nucleophilic Reaction with 4-(trifluoromethyl)benzyl bromide. In the glovebox, samples were reacted with 0.02 M TFB with <1 mg KHMDS in hexanes at 60°C for 1 h. Samples were rinsed with hexanes, diethyl ether, and methanol, sonicated in methanol for 2 min, and dried with a stream of nitrogen gas.

X-ray Photoelectron Spectroscopy. Elemental composition of functionalized Si(111) surfaces was collected using a PHI 5400 analyzer equipped with Al K α (1486.6 eV) source, without a

monochromator. Acquisition took place at a pressure of $< 2.5 \times 10^{-9}$ torr, without the need for charge neutralization due to the natural conductivity of the samples. A 6 mA current emission and a 12 kV anode high tension were used. For each sample survey scans were recorded between 0 and 1350 eV at pass energy of 117.40 eV. While high resolution spectra were collected at pass energy of 23.5 eV. All binding energies were referenced to the expected binding energy for adventitious carbon (284.6 eV).[36] Spectrum analysis was performed with CASA XPS 2.3.13 software. Further characterization of the surfaces were performed by calculating oxide thickness using a simplified substrate/overlayer model[37] and calculating fractional monolayer coverage of the surface using three-layer model.[38] Calculations are shown in detail in the Supporting Information.

Infrared Spectroscopy. Infrared spectra were acquired using a Thermo- Fisher 6700 FT-IR spectrometer equipped with a deuterated triglycerine sulfate (DTGS) detector and a Ge hemisphere grazing angle attenuated total reflectance (GATR) accessory. P-polarized light at an incident angle of 65° was applied and spectra were recorded with 4 cm^{-1} resolution and referenced to spectrum of clean Ge hemisphere.

Static Sessile Drop Contact Angle Measurements. Surface wettability was determined by recording the contact angles of water droplets formed on functionalized surfaces. CAM 100 optical contact angle meter (KSV instrument, Helsinki, Finland) and KSV software analysis package were utilized during data collection and analysis.

Surface Recombination Velocity Measurement A custom-built microwave photoconductivity system[38, 39] was used to measure the minority carrier lifetime in Si wafer sections after various surface treatments. Float-grown Si with low resistivity ($R > 13000 \text{ ohm cm}$) and a thickness of 0.046 cm was used exclusively for these measurements. A Continuum Minilite Nd:YAG laser operating at $\lambda = 1064 \text{ nm}$ was used to produce excitation pulses with a full-width at half-maximum of $< 10 \text{ ns}$. Photoexcitation was performed on the sample side opposite of where microwave radiation was incident. The microwave source was a HP 8350B Sweep Oscillator with a 83570A module operating at a frequency of 18.670 GHz and a nominal output power of 3.16 mW. The reflected signal was measured with an Advanced Control Devices diode (ACSP2644NZ, rise time $< 1 \text{ ns}$) connected to a Tektronix TDS 1002B digital oscilloscope. The transient responses were normalized by the reflected signal at $t = 0$ and plotted as ' $\Delta P/P_0$ '. The apparent photoconductivity lifetime, τ , was then determined from plots of $\Delta P/P_0$ vs t through a fit with a single exponential function. The explicit relation between τ and the surface recombination velocity, S , is given in eq 1,[40]

$$\frac{1}{\tau} = \frac{1}{\tau_b} + \left(\frac{2S\pi^2 D}{W\pi^2 D + 2SW^2} \right) \quad (1)$$

where τ_b is the bulk lifetime of the Si wafer section, D is the ambipolar diffusion constant in crystalline Si ($10 \text{ cm}^2 \text{ s}^{-1}$ at $T = 300 \text{ K}$)[41], and W is the wafer thickness. Eq 1 defines several important bounds. The shortest time constant ($= W^2 \pi^{-2} D^{-1}$) occurs when S is infinitely large. For the materials used here, the shortest measurable value of τ is $2 \times 10^{-5} \text{ s}$. The largest possible value of τ occurs when $S = 0 \text{ cm s}^{-1}$ and corresponds exactly to τ_b . According to the manufacturer, $\tau_b > 2 \times 10^{-3} \text{ s}$ for the wafers used here. All values of τ measured between these two bounds thus report on S . Since $\pi^2 D \gg 2SW$ for $S < 10^3 \text{ cm s}^{-1}$ for all measured samples, the following approximation was used to estimate S .

$$\frac{1}{\tau} = \frac{1}{\tau_b} + \frac{2S}{W} \quad (2)$$

Results.

Three different surface terminations were evaluated for achieving a hydrophilic, stable, and electronically passivated surface (Scheme 1). After etching with $\text{NH}_4\text{F}(\text{aq})$ and then chlorination with PCl_5 in chlorobenzene, samples were reacted with one of three Grignard reagents to achieve surfaces decorated by either an allyl group, a cyclic diether, or a bis(trimethylsilyl)amino group. We henceforth refer to these surfaces as types **1**, **2**, and **3** (Scheme 1). These surfaces were subsequently modified by introducing Bronsted-Lowry functionality without affecting the underlying putative Si-C bond. The resultant surfaces were selectively decorated with primary alcohols, diols, and amine groups. These surfaces are henceforth denoted as types **1a**, **2a**, and **3a**. The characterization and properties of each surface are described individually below.

Passivated Surfaces Featuring Chemisorbed Primary Alcohols (1a) The preparation of Si surfaces decorated with allyl groups was first described by Lewis and co-workers.[42] In this work, we specifically set out to selectively oxidize the terminal olefin to a primary alcohol, i.e. the anti-Markovnikov addition of an alcohol across the ‘-C=C-’ group. A hydroboration/hydroxylation method was employed, similar to an approach used to oxidize surface-grafted 1-decene reported previously by Cahen and co-workers.[30] That procedure was modified for surface **1** by extending both hydroboration times ($>5 \text{ h}$) and subsequent hydroxylation (20 min) as long as possible without

inducing surface oxidation, as monitored by high resolution Si 2p XP spectra. These surfaces are denoted as type ***1a***. The oxide thickness inferred from the integrated intensity of the shoulder centered at 103 eV was below <0.09 nm (Figure 1a). Before reaction, a peak for the C=C-H stretch at 3051 cm⁻¹ was observable in the infrared spectrum but was absent after reaction (Figure 1b). Further, analysis of GATR-IR spectra of ***1a*** resulted in a peak at 1265 cm⁻¹ ascribed to COH bend of primary alcohols and no signatures at 2500-3000 cm⁻¹ that indicated oxidation to a terminal carboxylic acid group (Supporting Information). The wetting properties of type ***1*** and ***1a*** surfaces were decidedly different, with the sessile contact angles with water of 75 ± 5° to 42 ± 3°, respectively (Table 1). This contact angle value for type ***1a*** surfaces is broadly in agreement with the value of 50° demonstrated by Zhong and Bernasek for Si surfaces decorated with long primary alcohols.[43] The reactivity of type ***1a*** surfaces was probed with test reagents so as to identify the predominant surface group (e.g. alcohol, carboxylic acid). Specifically, we attempted to perform both an etherification reaction with an organic halide and an esterification reaction with a primary alcohol. The hypothesis was that a surface decorated with primary alcohols is only reactive (under the employed reactions) towards organic halides for ether bond formation and wholly unreactive towards molecular alcohols. Upon reaction of ***1a*** with 4-(trifluoromethyl)benzyl bromide (TFB), a new signal was observed in the F 1s XP spectrum (Scheme 2, Figure 1c). Fractional coverage was calculated to be 0.19 molecules per Si atom (Supporting Information). Conversely, exposure to 2,2,3,3,4,4,5,5-octafluoro-1-pentanol yielded no change in the recorded F 1s XP spectra (Supporting Information). These cumulative observations strongly suggest that type ***1a*** surfaces were populated by terminal alcohol groups.

The presence of surface-based electrical traps on these two surfaces was assessed through contactless microwave photoconductivity transients (Figure 1d). The measured value of *S* for type ***1*** surfaces was 40 ± 30 cm s⁻¹, consistent with prior estimates of *S* for allyl-terminated Si.[42, 44] The values of *S* for ***1*** slightly increased over the course of 4 days (Table 2). After conversion to ***1a***, the value of *S* increased significantly to 220 ± 150 cm s⁻¹, well above any *S* value measured for ***1***. However, for type ***1a*** surfaces, the values of *S* slightly *decreased* to 90 ± 50 cm s⁻¹ after 4 days. Concurrently, the measured oxide thickness over the same time frame increased substantially to 0.55 nm (Supporting Information).

Passivated Surfaces Featuring Chemisorbed Diols H-terminated Si(111) was converted to a surface decorated with 3,4-(methylenedioxy)phenyl groups (type ***2*** surfaces). These surfaces could be reacted with trifluoroacetic acid without substantially increasing the surface oxide content (Figure 2a). However, the wetting character became slightly more hydrophilic, decreasing from 64 ± 2° to 57 ± 3° (Table 1). Further, after reaction with trifluoroacetic acid, new modes corresponding to a CO

stretch at 1288 cm^{-1} , an OH bend at 1198 cm^{-1} , and a CH bend at 1076 cm^{-1} in the GATR-IR spectra were observed (Figure 1b), consistent with deprotection of the 3,4-(methylenedioxy)phenyl groups to a 3,4-benzenediol. These type **2a** surfaces were then reactive towards 4-(trifluoromethyl)benzyl bromide. F1s XP spectra of these surfaces showed a clear signature indicative of grafted trifluoromethyl groups (Figure 2c). The integrated intensity of these spectra corresponded to a total fractional surface coverage of 0.22 per atop Si atom (assuming no surface roughness and each 3,4-benzenediol was functionalized with two 4-(trifluoromethyl)benzyl groups).

Because these surface groups have a large areal footprint (0.8 nm^2 , assuming phenyl ring plane is perpendicular to the surface plane and freely rotates about the putative Si-C bond), a significant fraction of the available atop Si atoms remain unreacted. A mixed monolayer approach based on the premise of using CH_3 - groups to occupy unreacted sites was established previously.[44-47] We sought to apply this premise on type **2** surfaces. Reaction of **2** with CH_3MgCl yielded surface **2b**. The measured water contact angles for **2b** were only slightly changed relative to **2** (Table 1). Reaction of type **2b** surfaces with trifluoroacetic acid (yielding type **2c** surfaces) and then 4-(trifluoromethyl)benzyl bromide yielded signal in the F1s the XP spectrum (Supporting Information) comparable to that for type **2a**, corresponding to a fractional coverage of 0.21 surface groups per atop Si atom.

The photoconductivity transients for type **2**, **2a**, **2b**, and **2c** surfaces exposed to the laboratory ambient are shown in Figures 2e,f. Type **2** surfaces showed slightly larger initial S values than type **1** surfaces (Table 3) but still demonstrated reasonable levels of passivation on the order of 10^2 cm s^{-1} . Over 4 days, the surface recombination velocities fluctuated with time and increased slightly for type **2** surfaces. Type **2a** surfaces exhibited S values measurably larger than for type **2** but these values *decreased* over the course of 4 days. In comparison, the methylation ‘back-fill’ step yielded noticeably lower S values for types **2b** and **2c** surfaces relative to types **2** and **2a** surfaces. Type **2b** surfaces (i.e. functionalized with 3,4-(methylenedioxy)phenyl and methyl groups) showed a general trend of slightly increasing surface recombination velocities over time. Conversely, type **2c** surfaces (i.e. functionalized with 3,4-benzenediol and methyl groups) like type **2a** surfaces showed S values that slightly *decreased* over time.

Passivated Surfaces Featuring Chemisorbed Phenylamine Type **3** surfaces were prepared after reaction with 4-[bis(trimethylsilyl)amino]phenyl magnesium bromide. As-prepared **3** surfaces showed a detectable but low N 1s signal intensity. A peak at 925 cm^{-1} was observed in the IR spectrum which agreed with the Si-N stretch in trimethylsilyl groups (Supporting Information).[48, 49] Deprotection of the surface groups by reaction with acid (i.e. H- replaced the trimethylsilyl

groups) resulted in type **3a** surfaces. These surfaces did not initially possess substantial oxide (Figure 3a) and the N 1s signal in the XP spectrum became more pronounced (Figure 3b). The integrated intensity of this signal corresponded to a fractional coverage of 0.49 phenylamine groups per atop Si atom. Further, the wettability towards water increased, with a change in the water contact angle from $70 \pm 6^\circ$ to $57 \pm 4^\circ$ (Table 1). In addition, a peak at 3330 cm^{-1} consistent with NH_2 symmetric stretches was now evident in the IR spectra (Figure 3c). After aging in ambient conditions for 48 h, types **3** and **3a** surfaces had oxide layer thicknesses of 0.21 and 0.033 nm, respectively. Type **3a** surfaces were selectively reactive towards 4-(trifluoromethyl)benzyl bromide, yielding a surface coverage of 0.22 grafted groups per atop Si atom (Figure 3d), indicating not all underlying phenylamine groups were alkylated. Reaction of **3** with CH_3MgCl prior to deprotection of the phenylamine groups yielded type **3b** surfaces. After deprotection to give type **3c** surfaces, the integrated intensity in the N 1s spectra corresponded to a fractional coverage of phenylamine groups of 0.5 per atop Si atom, similar to type **3a** surfaces. Type **3c** surfaces were similarly reactive towards alkylation via reaction with 4-(trifluoromethyl)benzyl bromide (Supporting Information), yielding a surface coverage of 0.18 grafted groups per atop Si atom.

Type **3** surfaces exhibited an initial surface recombination velocity ($100 \pm 40\text{ cm s}^{-1}$), which steadily increased over time. The deprotection step that converted type **3** to type **3a** surfaces increased the measured value of S even though the measured oxide content had not substantially increased (*vide supra*). In addition, these surfaces deteriorated significantly over 4 days, yielding the largest value of S among all the surface types that were analyzed ($345 \pm 100\text{ cm s}^{-1}$). Unexpectedly, type **3b** surfaces (i.e. functionalized with [bis(trimethylsilyl)amino]phenyl and methyl groups) did not possess lower S values as compared to type **3** surfaces either initially and after 4 days in air (Table 2). Steric blocking by the bis(trimethylsilyl)amino]phenyl groups may have prevented sufficient access to populate unreacted sites with $-\text{CH}_3$ groups. Still, type **3c** surfaces (i.e. functionalized with phenylamine and methyl groups) demonstrated more stable and lower values of S relative to type **3a** surfaces, implying a sufficient amount of $-\text{CH}_3$ groups to render some improved passivating effect.

Discussion.

The presented data cumulatively show three separate surface types that achieve some level of chemical stability, possess proton donating/accepting character, and have low defect density. Here we discuss their respective virtues, the observed correlations between surface stability and electronic passivation, and the prospects for employing such surface chemistry to interfaces beyond Si.

Lewis and co-workers previously showed allyl-terminated Si(111) prepared by a Grignard reaction possesses surface recombination velocities ranging from 50 to 90 cm s⁻¹, [42, 44] in line with what was observed here. They later proved that mixed monolayers with allyl-groups demonstrate *S* values as small as 30 cm s⁻¹ if 10% of the surface is decorated with allyl groups and the remaining 90% is covered by CH₃- groups. [44] A more recent advancement by this same group was the oxidation of the fraction of allyl groups to primary aldehydes, resulting in a low defect surface amenable for ALD coating. [45] However, the wetting properties were not detailed. The type **1a** surfaces reported here are designed to achieve a similar goal but are simpler to prepare (i.e. fewer reaction steps) and have a defined hydrophilicity. However, the initial surface recombination velocity is decidedly higher for these type **1a** surfaces, which may or may not be tolerable depending on the specific application. For reference, the initial *S* value for type **1a** surfaces is still reasonably good compared to the native oxide of Si and is in fact on par with unannealed thermal oxides. [50] For further comparison, a recent report demonstrating Si(111) surfaces terminated with 4-trifluoromethylsulfonylbenzene exhibited surface recombination velocities of 1372 ± 30 cm s⁻¹. [51] Still, if a lower initial surface recombination velocity is necessary, surface types **2a**, **2c**, **3a**, and **3c** are all viable options. Again, surface types **2a** and **3a** retain the practical advantage of a minimal number of preparative steps. Further, type **2a** surfaces exhibit the greatest wettability towards water in comparison to surface **3a**, a feature which may aid in coatings cast from aqueous solutions. In comparison to alkyl-terminated Si surfaces rendered hydrophilic by oxidation with oxygen-containing plasmas, [52, 53] the wet chemical approach shown here is both controllable and more amenable to ‘short’ surface layers suited for heterogeneous charge transfer.

The surface stability and surface recombination velocities of some of the surfaces studied here tracked with time in unexpected ways. Surfaces that did not intentionally have any proton donating/accepting character (i.e. type **1**, **2**, **2b**, **3**, and **3b**) all exhibited surface recombination velocities that either remained statistically unchanged or slightly increased over time. This observation itself is unsurprising given these surfaces are not indefinitely stable against oxidation and the act of oxidation should introduce strained bonding that act as electronic traps. However, the majority of surfaces that did have explicit proton donating/accepting character (i.e. type **1a**, **2a**, and **2c**) had surface recombination velocities that *decreased* over time even though the underlying surface oxide layer *increased*. That is, even though these surfaces were somewhat susceptible to oxidation of the underlying substrate, the resultant oxide growth did not add significant numbers of new electrical traps. Surface type **1a** is a noteworthy example, as the surface oxide that grew after 24 h (0.55 nm) in

air was greater than the thickness of a complete oxide monolayer on Si(111) (0.4 nm),[54] yet the measured surface recombination velocity was actually lower than the initial value. Although the present dataset does not provide any direct microscopic insight on the cause of this observation, we comment on two possibilities. First, the presence of the grafted surface groups imparted some directing effect on the growth of any new oxide. Similar arguments have been made previously for modified surfaces whose surface recombination velocities decrease over time[55, 56] and there is no data to conclusively rule out this scenario. Still, since the physicochemical nature of the modifying groups in these three sets of surfaces differ significantly, an equivalent ‘oxide templating’ effect seems unlikely. Second, the acid/base functionality of the modified surfaces influences/introduces charge within the growing oxide. Such oxides could artificially lower the observable surface recombination velocity through charge screening.[8] A hallmark of such an effect is a strong dependence of the surface recombination velocity with illumination intensity.[8] The accessible illumination intensities were limited by the linearity of the microwave reflection method only at low charge carrier concentrations.[57] Nevertheless, we did not observe any significant dependence of the measured lifetimes with changes in laser intensity, arguing against this possibility. Hence, additional studies are necessary to explain this curious phenomenon.

The wet chemical strategies applied here are not limited to just Si interfaces. The approaches demonstrated in this work to convert the grafted moieties into alcohols and amines should generally apply to these same groups when bonded to other semiconductors. We have shown previously that III-V semiconductor surfaces (e.g. GaAs(111)A, GaP(111)A, GaN(0001)) [58-60] are reactive towards Grignard reagents and therefore these interface could be initially functionalized in a similar manner as explored here. Since the intrinsic instability of the native surfaces of these III-V semiconductors substantially complicates coating these semiconductors with either solid dielectrics[61, 62] or molecular films,[63] such wet chemical methods should prove useful. Work in our group to attain similar levels of control over wetting, stability, and interfacial defect densities on III-V semiconductor surfaces is ongoing.

Conclusions.

Three separate wet chemical reaction sequences were performed on Si(111) to achieve hydrophilic, chemically stable, and electronically passivated surfaces. These general features were attained although an unexpected improvement in the apparent surface recombination velocities was observed for many of the surfaces with acid/base character. These modified Si surfaces should be

amenable for contacting methods such as ALD or spin-casting of solutions of oxo-clusters. With regards to ALD, these interfaces ought to provide a high number of nucleating sites during the initial deposition cycles, potentially leading to more uniform films. In the context of solution-cast oxides, the low level of initial defects and good chemical stability should improve the quality of the resultant junction. Separate studies are needed to rigorously test these hypotheses. This study adds three sets of Si surfaces to the number of interfaces that are quantitatively categorized in terms of their stability, wettability, and electrical quality. This work thus defines protocols and benchmarks so as to evaluate these surfaces in heterojunctions as well as to apply to other semiconductor interfaces.

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Supporting Information

Additional information describing control experiments and XPS data analysis is available free of charge via the Internet.

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Figures and Schemes.

Scheme 1. Chemical modification routes for Si surfaces employed in this work.

Scheme 2. Representative etherification reaction, showing reaction *1a* with TFB with base promotor (KHMDs).

Figure 1. Comparison of (a) Si 2p XP and (b) infrared spectra for freshly prepared type **1** and **1a** surfaces. (c) Comparison of F 1s XP spectra before and after reaction of a type **1a** surface with 4-(trifluoromethyl)benzyl bromide. All spectra offset vertically for clarity. Representative microwave photoconductivity transients presented as (d) normalized and (e) natural log signal vs time.

Figure 2. (a) Comparison of Si 2p XP spectra for freshly prepared type **2** and **2a** surfaces. (b) Infrared spectra showing the CO stretches, -OH bend, and CH bend for type **2a** surfaces. (c) Comparison of F 1s XP spectra before and after reaction of a type **2a** surface with 4-(trifluoromethyl)benzyl bromide. (d) Comparison of Si 2p XP spectra for freshly prepared type **2b** and **2c** surfaces. All spectra offset vertically for clarity. Representative microwave photoconductivity transients presented as (e) normalized and (f) natural log signal vs time.

Figure 3. (a) Comparison of Si 2p XPS spectra for freshly prepared type **3** and **3a** surfaces. (b) High resolution N1s XPS spectrum of a freshly prepared type **3a** surface. (c) Comparison of infrared spectra for freshly prepared type **3** and **3a** surfaces. (d) Comparison of F 1s XPS spectra before and after reaction of a type **3a** surface with 4-(trifluoromethyl)benzyl bromide. (e) Comparison of Si 2p XPS spectra for freshly prepared type **3b** and **3c** surfaces. All spectra offset vertically for clarity. Representative microwave photoconductivity transients presented as (f) normalized and (g) natural log signal vs time.

Tables

Table 1. Contact Angle Data for Modified Si(111) Surfaces.

Surface Type	Number of Samples Measured	Contact Angle /°
1	10	75±5
1a	16	42±3
2	10	64±2
2a	7	57±3
2b	10	57±3
2c	4	53±4
3	11	70±6
3a	7	57±4
3b	3	76±1
3c	3	64±2

Table 2. Calculated SRV Values in cm s^{-1} Over Time in Ambient Conditions for N=3.

ime/hr	1	1a	2	2a	2b	2c	3	3a	3b	3c
0	40 ± 30	200 ± 150	150 ± 120	170 ± 40	75 ± 2	110 ± 40	140 ± 90	190 ± 50	190 ± 80	180 ± 90
1	40 ± 30	210 ± 170	110 ± 70	190 ± 60	82 ± 3	90 ± 20	170 ± 60	170 ± 40	140 ± 20	180 ± 100
4	40 ± 10	220 ± 150	110 ± 90	170 ± 50	130 ± 40	130 ± 60	400 ± 200	170 ± 50	210 ± 70	200 ± 120
24	70 ± 60	160 ± 120	170 ± 120	120 ± 50	120 ± 10	110 ± 50	210± 120	170 ± 70	200 ± 110	220 ±110
48	40 ± 40	150 ± 90	220 ± 170	140 ± 50	90 ± 20	100 ± 40	--	300 ± 140	160 ± 40	180 ± 80
96	70 ± 70	90 ± 50	180 ± 110	110 ± 30	100 ± 2	80 ± 40	--	350 ± 100	170 ± 80	173 ± 130