

# 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) spectroscopies 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 CH<sub>3</sub>— 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.

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## 1. 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

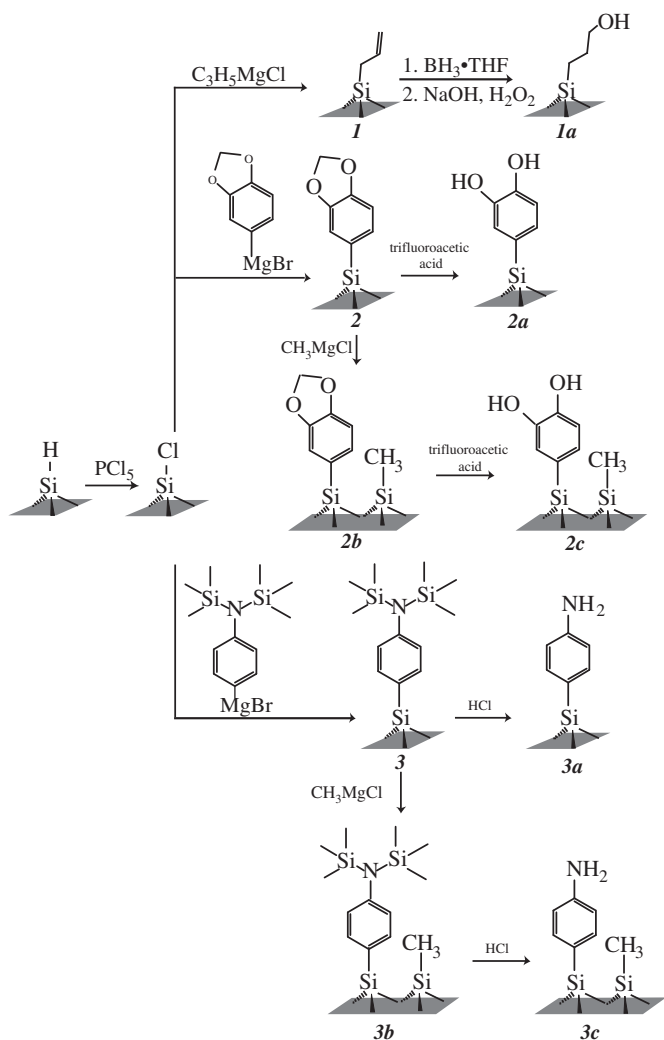
native oxides on such semiconductors are generally hydrophilic [5,6], they possess deleterious levels of trap states. Of the few high quality oxides (e.g., annealed thermal oxide Si(100) [7]), they are naturally insulating. Chemical methods to eliminate electrically active surface states on Groups IV and III–V surfaces (e.g., etching with NH<sub>4</sub>F; [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 not only to identify the attainable physico-chemical properties of these modified Si interfaces more generally but also to show that semiconductor surfaces that are reactive towards Grignard reagents can be deterministically tailored as needed.

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

## 2. Experimental

### 2.1. 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), 30 wt.% in  $\text{H}_2\text{O}$  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  $18.2 \text{ M}\Omega \text{ cm}^{-1}$  (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  $525 \pm 15 \mu\text{m}$ . For SRV measurements, float-zone (FZ), intrinsically-doped Si(111) (El-Cat) wafers with a resistivity equal to  $16,500 \pm 3500 \Omega \cdot \text{cm}$ , a thickness of  $460 \pm 15 \mu\text{m}$ , and both sides polished were used.

### 2.2. 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%  $\text{NH}_4\text{F}$  solution for 5 min 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  $90^\circ\text{C}$  for 50 min 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).

### 2.3. 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%  $\text{H}_2\text{O}_2$  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  $\text{N}_2(\text{g})$ .

### 2.4. 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: $\text{H}_2\text{O}$  (1:20:5) for 4 h at room temperature outside of the glovebox (**2a** and **2c**) [35].

### 2.5. 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**).

### 2.6. 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  $60^\circ\text{C}$  for 1 h. Samples were rinsed with hexanes,

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