



Chemical and electrical passivation of Si(1 1 1) surfaces

Fangyuan Tian^a, Dan Yang^b, Robert L. Opila^b, Andrew V. Teplyakov^{a,*}

^a Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

^b Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA

ARTICLE INFO

Article history:

Received 11 August 2011

Received in revised form 4 November 2011

Accepted 8 November 2011

Available online 18 November 2011

Keywords:

Silicon single crystal
Charge-carrier lifetime
Surface preparation

ABSTRACT

This paper compares the physical and chemical properties of hydrogen-passivated Si(1 1 1) single crystalline surfaces prepared by two main chemical preparation procedures. The modified RCA cleaning is commonly used to prepare atomically flat stable surfaces that are easily identifiable spectroscopically and are the standard for chemical functionalization of silicon. On the other hand electronic properties of these surfaces are sometimes difficult to control. A much simpler silicon surface preparation procedure includes HF dipping for a short period of time. This procedure yields an atomically rough surface, whose chemical identity is not well-defined. However, the surfaces prepared by this approach often exhibit exceptionally attractive electronic properties as determined by long charge carrier lifetimes. This work utilizes infrared spectroscopy and X-ray photoelectron spectroscopy to investigate chemical modification of the surfaces prepared by these two different procedures with PCl₅ (leading to surface chlorination) and with short- and long-alkyl-chain alkenes (1-decene and 1-octadecene, respectively) and follows the electronic properties of the starting surfaces produced by measuring charge-carrier lifetimes.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The detailed procedures for silicon surface preparation have been investigated substantially over the past half a century, since silicon has been at the heart of the microelectronics industry. The concerns over the subtle variations in the electronic properties of the surfaces, the role of defects, and the novel applications for this semiconductor have driven the continuous search for improved and simplified surface preparation approaches, as even a trace amount of impurities can result in losses in such applications as ultra-large-scale integrated (ULSI) and integrated circuit (IC) technologies. During the surface preparation steps it is important to remove any contaminants, such as hydrocarbons, metals, ions, and small particles, from the semiconductor surfaces. In addition, the effect of the impurities must be minimized during the subsequent surface modification steps, such as oxidation, vapor deposition, epitaxial growth, etc. The starting point, a well-defined silicon single crystalline surface will be the focus of this paper.

Normally, the silicon preparation procedures can be categorized into two classes: wet-chemistry and dry-clean (gas-phase) methods [1]. Wet-chemistry normally involves a classic RCA method [2] based on hydrogen peroxide solution, HF-dip process [3], ultrasonic water technique [2], or choline cleaning [4]. Chemical vapor etching [5] and UV/ozone treatment [6] are the two primary

processes utilized in dry-clean methods. Among all these methods, RCA cleaning cycle is likely the most widely applied. In 1970, Werner Kern (from Radio Corporation of America) published the first paper describing this hydrogen peroxide solution-based process. Over the following 20 years, silicon surface cleaning chemistry based on this method kept being refined by many research groups. During the main three steps of the RCA method, the following objectives are achieved: removal of hydrocarbons, metallic impurities, silicon oxide layer, and ionic contamination [2]. The first step in the RCA clean (called SC-1, where SC stands for standard clean) is performed with a solution of NH₄OH, H₂O₂, and H₂O at typically 80 °C for 10 min. This treatment results in the removal of hydrocarbons and may cause some oxidation and metal contamination of the surface. The second step is an immersion in a solution of HF in H₂O at 25 °C, in order to remove the thin oxide layer and the ionic contaminants dissolved in the oxide. The last step (called SC-2) is performed with a solution of HCl, H₂O₂, and H₂O at 80 °C. This treatment effectively removes the remaining metallic contamination.

An alternative wet cleaning method is based on a simple HF dip, which follows a pre-cleaning step that involves hot H₂O₂–H₂SO₄ solution (so-called Piranha clean) to clean up heavily contaminated silicon wafers that have visible impurities. The wafers are then subjected to a dilute HF water solution treatment. This treatment results in the majority species produced on the surface being silicon hydrides, although in selected cases, the procedure could be modified to incorporate about 30% Si–F onto a silicon surface [7]. An appropriate reaction mechanism was first proposed by Ubara et al. [8] and was later confirmed by detailed computational

* Corresponding author. Tel.: +1 302 831 1969; fax: +1 302 831 6335.
E-mail address: andrewt@udel.edu (A.V. Teplyakov).

investigations. The concentration of HF water solution proved to be a key point in determining the distribution of surface species. Etching with very dilute HF solution (<1%) alters morphology of silicon surface, and causes oxygen to diffuse into bulk silicon substrate [4]. High concentration (>10%) HF solution treatment results in a very reactive silicon surface that easily reacts with water and contaminants in solutions and in ambient.

In this paper, we compare the modified RCA cleaning procedure (also known as HF-last) and HF-dip approach used to produce clean hydrogen-terminated Si(111) surfaces. Following these preparation procedures, we investigate the reactions of the surfaces produced with PCl_5 , commonly used for silicon chlorination, and with 1-alkenes (1-decene and 1-octadecene) leading to the formation of self-assembled monolayers (SAMs), whose order is highly sensitive to the quality of the surface.

An outstanding interface between the silicon single crystal in its (100) orientation and the surface silicon oxide made this surface highly desirable in many technological applications. However, with the required thickness of this oxide decreasing below the practical limit, other substrate orientations and alternative material platforms start receiving substantial attention. From a practical standpoint, H-terminated Si(111) is a very good model system because of its stability, compared with H-terminated Si(100). The former can be stable in ambient for hours (depending on its preparation), while the latter normally only has several minutes before surface oxidation becomes noticeable [9–13]. The well-ordered and atomically flat H-terminated Si(111) surface prepared by a modified RCA cleaning procedure provides almost exclusively monohydride Si–H surface sites for further modification. This surface is truly a gold standard of the silicon surface preparation; however, it is sometimes difficult to control the electronic properties produced by this approach. The Si(111) surface produced by a simpler HF-dip procedure, as will be shown below, can possess very attractive electronic properties; however, the chemical identity of this surface is much more complex, compared to the Si(111) substrate prepared by a modified RCA clean. The investigation of chemical and physical properties of the surfaces prepared by these two approaches will provide a balance between the complexity of surface preparation procedures and chemical or physical properties achieved as a result of this preparation.

In order to compare the chemical properties of the two silicon surfaces prepared by different procedures, we use the reaction of chlorination of the Si(111) surface with PCl_5 that has been investigated previously by Lewis and co-workers [14], and the process of the formation of SAMs starting with 1-alkenes proposed by Chidsey and co-workers [15,16]. During the PCl_5 chlorination, a perfectly ordered H-terminated Si(111) surface is expected to yield a surface where every single hydrogen atom is replaced by chlorine, with the Si–Cl bond oriented perpendicular to the surface plane. If the starting Si–H surface is not well-defined (mono-, di-, tri-hydride-terminated silicon surface), it is likely that due to the large size of chlorine atom not all the Si–H bonds will react with PCl_5 and the remaining surface Si–H bonds following the chlorination procedure will easily oxidize in ambient to form Si–OH or surface silicon oxide. Another possible experimental way to assess the quality of the H-terminated Si(111) surface produced by different preparation procedures is to use 1-alkene self-assembly to form an ordered monolayer (SAM) via hydrosilylation process. Although the process of the monolayer formation is different from, for example, thiols on gold, where the thio-group is mobile on gold surface following S–H dissociation, the hydrosilylation with 1-alkenes on silicon produces ordered monolayers that are commonly referred to as SAMs and this paper will continue to use the same terminology. In fact, the degree of the order of such a SAM can be easily assessed by infrared spectroscopy and the alignment of the alkyl chains on a flat surface is the cause of self-assembly despite the fact that the

functional head-group is covalently tethered to the surface. In this paper, we chose 1-decene and 1-octadecene as test alkenes. Both these molecules could form a SAM via hydrosilylation with hydrogenated Si surface by a propagating radical chain mechanism [17]. It is important to note, however, that the SAM built based on 1-decene is more sensitive to the quality of H-terminated Si surface, while the longer chains of 1-octadecene would align themselves better even on a less well-defined surface [18]. If the H-terminated Si surface is atomically rough, the SAM based on 1-decene will likely be disordered. On the other hand, 1-octadecene would be expected to produce a relatively well-ordered SAM on either a rough or an atomically smooth surface. In addition, due to the long alkyl chain of 1-octadecene, it is expected to provide a good electrical passivation layer [19,20].

In this work, we utilized Fourier-transform infrared spectroscopy (FT-IR) to investigate the vibrational frequencies of surface Si–H species (to assess chemical identity of the surfaces produced), as well as to assess the order of the SAMs produced following surface reactions with 1-decene and 1-octadecene. Atomic force microscopy (AFM) was employed to examine the surface roughness before and after the formation of SAMs. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical species present on the silicon surfaces prepared by different procedures and following PCl_5 chlorination. Charge-carrier lifetime of H-terminated silicon surfaces produced by two methods was also measured, followed by calculations of the surface recombination velocity.

2. Experimental

2.1. Materials

The silicon samples used for charge-carrier lifetime measurements were float zone grown, double-side polished (111)-oriented Si with thickness of 1000 μm . All additional measurements and modifications were carried on the n-doped double-side polished Si(111) wafers (>0.1 Ωcm resistance, 500 μm thickness) (Virginia Semiconductor, VA). All chemicals were reagent grade or better and used as received: ammonium hydroxide (Fisher, 29% certified ACS plus grade), hydrochloric acid (Fisher, 37.3% certified ACS grade), sulfuric acid (Fisher, 95.7% certified ACS plus grade), 10% HF solution (diluted with Milli-Q water from 48 wt% hydrofluoric acid, Aldrich), hydrogen peroxide (Fisher, 30% certified ACS grade), buffer-HF improved (Transene Company, Inc.), chlorobenzene (Acros), PCl_5 (Aldrich), benzoyl peroxide (Acros), 1-decene (Acros, 95%), 1-octadecene (Acros, 90%), methylene chloride (Fisher, 99.9%), petroleum ether (Fisher, certified ACS), THF (Fisher, distilled from Na/benzophenone) and methanol (Fisher, 99.9%). The deionized water used to rinse the surfaces and containers was from a first generation Milli-Q water system (Millipore) with 18.2 M Ωcm resistivity.

2.2. Preparation of hydrogen-terminated Si(111) surface

2.2.1. RCA cleaning cycle

The first preparation method for H-terminated Si(111) surface was based on the RCA cleaning cycle [2]. The Teflon beakers and Si(111) wafers were cleaned in a solution of 4:1:1 Milli-Q water, hydrogen peroxide, and ammonium hydroxide for 30 min and 10 min, respectively, on an 80 °C water bath. After rinsing with Milli-Q water, the clean wafer was etched in 5% HF buffer water solution for 2 min and rinsed again with Milli-Q water. Then, the wafer was placed in a freshly prepared solution of 4:1:1 Milli-Q water, hydrogen peroxide, and hydrochloric acid for 10 min to grow a silicon oxide layer at 80 °C. After that, the rinsed wafer was etched in HF buffer solution again for 1 min, followed by 6 min in ammonia

fluoride solution, and then rinsed with Milli-Q water again thoroughly to form a well-ordered hydrogen-terminated Si(111) surface.

2.2.2. HF-dip method

The HF-dip method was used as an alternative to the RCA cleaning procedure described above. The Si(111) wafer was cleaned at room temperature in a 1:4 mixture of hydrogen peroxide and sulfuric acid for 5 min, followed by 5 min Milli-Q water rinsing. After that, the rinsed silicon wafer was dipped into a 10% HF aqueous solution for 2 min, followed by rinsing with Milli-Q water once to form the H-terminated Si(111) surface.

2.3. Preparation of chlorine-terminated Si(111) surface

The chlorine-terminated Si(111) surface was prepared by a previously described procedure using PCl_5 [21]. The solution of PCl_5 in chlorobenzene solvent with a trace amount of benzoyl peroxide as a reaction initiator was bubbled through with nitrogen for at least 30 min. Hydrogen-terminated Si(111) wafer was placed into this solution immediately after blowing dry with N_2 . Then, the entire setup was placed in an oil bath at 105°C for 1 h. Finally, the stable chlorine-terminated Si(111) sample was removed from the solution, rinsed with dry THF and blown dry with N_2 .

2.4. Preparation of self-assembled monolayers (SAMs) on Si(111) surface

5 ml of 1-decene (or 1-octadecene) was placed in a 25 ml flask with a reflux condenser and kept under flowing N_2 . The liquid was deoxygenated with dry N_2 for at least 1 h. Subsequently, the hydrogen-terminated Si(111) wafer was placed in the flask. Then, the flask was immersed in an oil bath, and the solution was refluxed for 2 h with a slow N_2 flow at 170°C (for 1-decene) or 180°C (for 1-octadecene). Afterwards, the silicon sample was removed from the solution and cleaned in dichloromethane, petroleum ether ($40\text{--}60^\circ\text{C}$), and methanol. Then, the surface was immediately blown dry with N_2 .

2.5. Characterization techniques

2.5.1. Charge-carrier lifetime measurements

The effective minority carrier lifetime is measured by WCT-120 Lifetime Tester with a 60 W light power source. The carrier lifetime is determined at an injection level of $1 \times 10^{15} \text{ cm}^{-3}$. An rf-bridge circuit, which is coupled by a coil to the measured specimen, senses the conductance in terms of permeability. The time dependence of illumination and excess photoconductance of the measured sample are calibrated by the reference solar cell. For the measurement the sample is cut into $2 \text{ cm} \times 2 \text{ cm}$.

2.5.2. X-ray photoelectron spectroscopy

The XPS spectra were collected on a PHI 5600 X-ray Photoelectron Spectrometer equipped with a $\text{Al K}\alpha$ X-ray source ($h\nu = 1486.6 \text{ eV}$) at a 45° take-off angle. The measurements were performed in a vacuum chamber with a base pressure of 1×10^{-9} Torr. The survey spectra were collected over the energy range of 0–1000 eV at 187.5 eV pass energy. The high-resolution spectra for each element, Si 2p, C 1s, O 1s, Cl 2p, and Cl 2s were collected over the range of 20 eV with 0.1 eV/step at a voltage of 13.5 keV and pass energy of 46.7 eV. The data analysis was performed using Casa software. All peak positions were calibrated to the C 1s peak, which was assumed to have the binding energy of 284.6 eV.

Table 1

Charge carrier lifetime and surface recombination velocities for H-terminated Si(111) surfaces prepared by two different procedures.

Surface preparation	Charge-carrier lifetime, τ (μs)	Surface recombination velocity, S (cm s^{-1})
RCA	60.7 ± 28.9	1002.7 ± 577.3
HF-dip	169.9 ± 14.0	295.3 ± 24.4

2.5.3. Fourier-transform infrared spectroscopy (FTIR)

Single beam spectra were collected using a Nicolet Magna-IR 560 spectrometer with a liquid-nitrogen-cooled external MCT-A detector. The FT-IR spectra were collected in the spectral range $4000\text{--}650 \text{ cm}^{-1}$ with a 60° angle with respect to the incoming infrared beam. 512 scans per spectrum and a resolution of 8 cm^{-1} were used to collect all the spectra. The native-oxide covered and hydrogen terminated Si(111) wafers were used as backgrounds, as indicated below.

2.5.4. Atomic force microscopy

Tapping mode AFM imaging was performed on a Multimode SPM (Veeco) with NanoScope V in air at room temperature. Aluminum coated silicon tips at a resonance frequency of 300 kHz (Budget Sensors) with a force constant of 40 N/m and a resonance frequency of 300 kHz were used. The AFM images were collected at $256 \text{ pixels} \times 256 \text{ pixels}$ per image and were analyzed using the Gwyddion software.

3. Results and discussion

3.1. Surface recombination velocity measurements

Table 1 shows the minority carrier lifetime of H-terminated Si(111) surfaces prepared using HF-dip and modified RCA procedures and respective surface recombination velocities. H-terminated Si(111) surface prepared by the HF-dip procedure exhibits much higher minority carrier lifetime ($169.9 \pm 14.0 \mu\text{s}$) compared to the surface prepared by the RCA clean ($60.7 \pm 28.9 \mu\text{s}$). The surface recombination velocity (S) can be expressed by the following equation:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2S}{W}$$

where τ_{eff} is effective minority carrier lifetime, τ_{bulk} is the minority carrier lifetime within bulk and W is the thickness of the silicon wafer.

Surface recombination velocity can be calculated by assuming the bulk lifetime τ_{bulk} is infinite, which is a reasonable approximation for float zone intrinsic wafers. As shown in Table 1, silicon wafer prepared by HF-dip pathway exhibited a lower surface recombination velocity ($295.3 \pm 24.4 \text{ cm s}^{-1}$) compared the wafer prepared by the RCA clean ($1002.7 \pm 577.3 \text{ cm s}^{-1}$).

Thus, it appears that compared to the RCA cleaning method, using HF-dip method we eliminate the surface sites and defects that decrease the carrier lifetime or that the surfaces prepared by this approach may have charge centers that repel carriers. Since the charge-carrier lifetime measurement focuses on the minority sites in this case, it seems that the surface that is well defined from the chemical perspective (RCA clean) contains the minority sites that decrease the carrier lifetimes. On the other hand, the surface that is less well defined chemically (HF-dip), likely has fewer surface sites that actually affect the carrier lifetime measurements. The studies presented below address these differences.

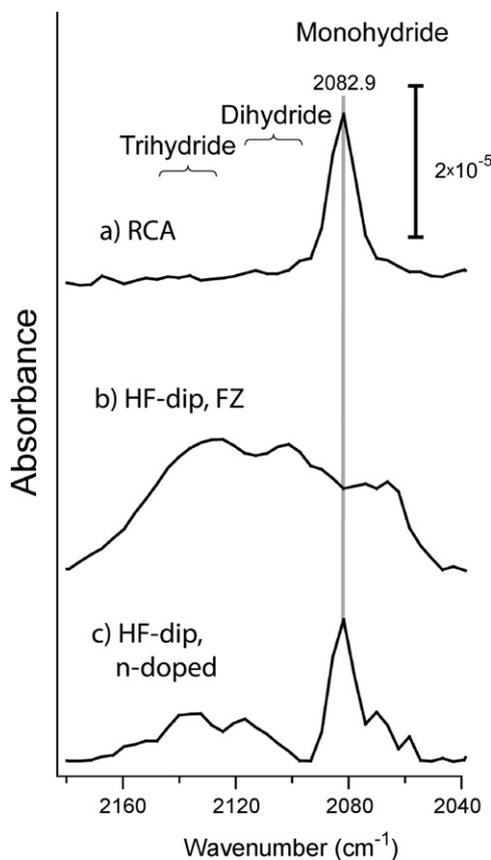


Fig. 1. Infrared studies of the Si–H stretching spectral region of H-terminated Si(1 1 1) surfaces prepared with (a) RCA method; (b) HF-dip method with a float zone crystal; and (c) HF-dip method with n-doped crystal.

3.2. Fourier-transform infrared spectroscopy (FTIR) studies

As was shown in Section 3.1, the electronic properties of the H-terminated Si(1 1 1) surfaces prepared by RCA clean are very different from those prepared by HF-dip method. The most likely explanations for these differences can be possibly different chemical state or morphology of these surfaces. The cleanliness of both types of surfaces and the absence of surface oxidation was first confirmed by XPS but the chemical state can be easily assessed by infrared spectroscopy, since a clean and well-ordered H–Si(1 1 1) surface is expected to exhibit a single Si–H stretch absorption band at 2083 cm^{-1} . Fig. 1 presents the Si–H stretching region of H-terminated Si(1 1 1) samples following the preparation by RCA and HF-dip methods. The sharp absorption peak observed at 2082.9 cm^{-1} for the surface prepared by RCA procedure is a signature of a clean and well-ordered mono-hydride terminated Si(1 1 1) [22,23].

On the other hand, we found that HF-dip method produced a poorly defined H–Si(1 1 1) surface. In addition to the identifiable mono-hydride stretch at 2083 cm^{-1} , a variety of other species is observed, including symmetric and antisymmetric stretching of dihydride species in the 2100 cm^{-1} region, and even Si–H absorption features corresponding to surface tri-hydride within the range of $2130\text{--}2140\text{ cm}^{-1}$ [13]. Also it should be pointed out that the relative intensity of all these features varied from sample to sample as the chemical state of the surface is likely extremely sensitive to the local HF concentration and the exact time of the HF dip.

Now that it has been established that the two preparation procedures do not yield chemically identical surfaces, it is important to understand how crucial these differences are for further surface modification. A reaction of H-terminated silicon with 1-alkenes can

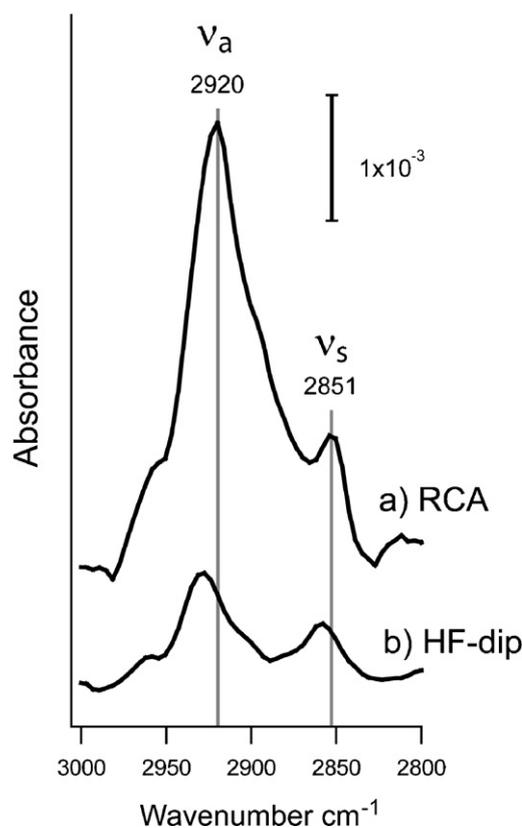


Fig. 2. IR investigation of the C–H stretching spectral region of the 1-decene modified Si(1 1 1) surface produced by (a) RCA method and (b) HF-dip procedure.

help us probe these differences as the order of the SAM produced in this reaction can also be probed by infrared spectroscopy. The C–H stretching vibrations at $\nu_s = 2850\text{ cm}^{-1}$ and $\nu_a = 2920\text{ cm}^{-1}$ (close to the vibrational signature of solid hydrocarbons [17,24]) would indicate a high degree of SAM order, while the deviations towards higher wavenumbers for both absorptions would correspond to a disordered layer (similar to the vibrational signatures of liquid hydrocarbons [25]). Figs. 2 and 3 show the –CH stretching region of 1-alkene SAM for H–Si(1 1 1) surfaces modified with 1-decene and 1-octadecene, respectively. In Fig. 2, both H–Si(1 1 1) samples obtained following RCA and HF-dip were modified with pure 1-decene. The –CH stretching region can be used to assess the quality of the SAM produced on both surfaces. The results summarized in Fig. 2 clearly indicate that the SAM formed on a H–Si(1 1 1) surface prepared by RCA clean is nearly ideal. On the other hand, the SAM prepared on the surface obtained by the HF-dip procedure lacks order, as confirmed by the shift of the absorption bands towards higher wavenumbers, 2857.8 and 2928.5 cm^{-1} , respectively. Since the two sets of vibrational studies (with RCA clean and HF-dip) were not performed on the same exact sample, the absolute intensities of the absorption bands observed cannot serve as a reliable indicator of the surface SAM coverage (although the absorption intensity of the RCA-prepared sample is indeed noticeably higher). Nevertheless, the absorption frequencies definitely confirm the formation of a well-ordered SAM on a H–Si(1 1 1) sample prepared by RCA clean and the poor order of a SAM obtained on a HF-dip-prepared sample. Thus, the most likely reason for such a difference is that RCA clean produced nearly exclusively mono-hydride terminated surface, most amenable for a reaction mechanism proposed by Chidsey's group for SAM formation [15,16]. The HF-dip method gave a relatively rough silicon surface with multiple types of Si–H-containing species, which may cause competitive reactions to disrupt the order of the SAM produced. Despite the chemical differences between the

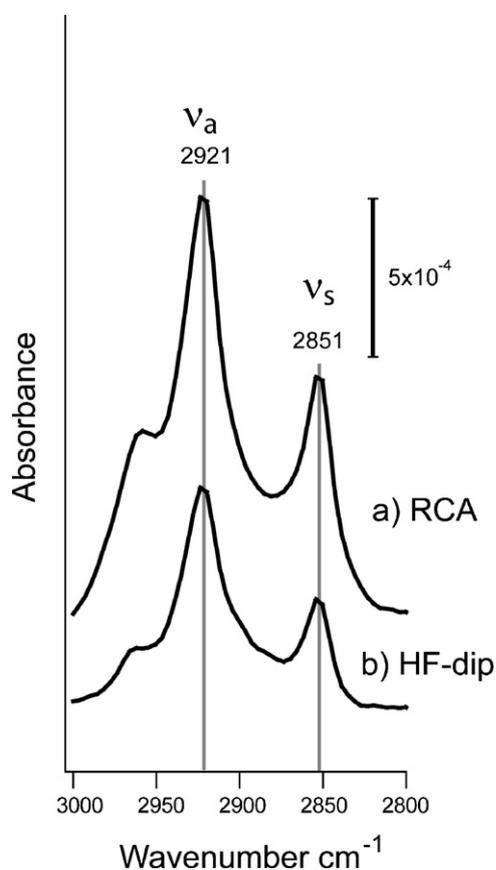


Fig. 3. IR investigation of the C–H stretching spectral region of the 1-octadecene modified Si(1 1 1) surface produced by (a) RCA method and (b) HF-dip procedure.

two types of surfaces considered here, it is also important to understand if these differences could be overcome to achieve a better functionalization platform for a surface whose electronic properties are superior. In other words, is it possible to alter the modification procedure for the SAM formation to obtain an ordered monolayer on a surface prepared by the HF-dip approach. If the monolayer produced on the silicon surfaces by 1-alkene with a relatively short alkyl chain exhibited a high sensitivity to the properties of the surface, perhaps using a longer chain alkene could overcome this disadvantage and the molecular assembly of higher order could be produced on a less well-defined H–Si(1 1 1) surface prepared by the HF-dip method. As shown in Fig. 3, this is indeed the case. The application of 1-octadecene to form a SAM on the H–Si(1 1 1) surfaces prepared by both approaches yields highly ordered monolayers, as indicated by the positions of the absorption bands (2921 and 2851 cm⁻¹) in both cases. Thus, the formation of the SAM using long-chain linear alkenes can serve as an appropriate starting point for uniform functionalization of either the H–Si(1 1 1) surface prepared by the RCA clean or for the HF-dipped silicon crystals.

3.3. Atomic force microscopy studies

The results of the infrared spectroscopy studies presented in Section 3.2 imply that the ordered SAM can only be produced by a short-chain alkene, 1-decene, if the starting surface is atomically flat, as prepared by the RCA clean. However, it is also important to rule out the effects of topography on the order of the monolayers produced. To interrogate the structure of the surfaces prepared by two different methods and modified with alkenes, atomic force microscopy was employed. Top two images in Fig. 4 show the AFM images of H-terminated Si(1 1 1) surfaces prepared by the HF-dip

method and RCA clean, respectively. Both methods produced flat surfaces with the RMS roughness substantially less than 0.5 nm. However, the surface prepared by RCA clean clearly exhibits atomic steps, as also illustrated in the top part of Fig. 5. This figure also gives an example of atomic height step on that surface. These steps are not obtained on the surface prepared by HF-dip procedure. This part of the microscopy study confirms that RCA clean produces atomically flat H-terminated Si(1 1 1) surface. The HF-dip preparation does not result in atomically flat surface but neither of the two methods produces any observed topographical features at larger scales.

To investigate if the surface topography would change following the formation of a SAM, AFM was also used to image the surfaces of both types following SAM formation with 1-decene (middle images in Fig. 4) and 1-octadecene (two bottom images in Fig. 4). Similar results with similar RMS roughness were obtained in all cases. The RMS roughness of 1-octadecene monolayers was slightly higher than for 1-decene; however, no evidence of extended domains or changes in surface topography caused by SAM formation was found. In fact, as illustrated by the two bottom images in Fig. 5, the Si(1 1 1) surface prepared by RCA clean procedure and modified with 1-octadecene exhibited the presence of the atomic height steps that were initially observed on the clean H-terminated Si(1 1 1) surface prepared by this procedure. The step height in both cases is in agreement with the step height reported previously on H-terminated Si(1 1 1) and SAM-covered Si(1 1 1) [26–28]. Thus, the microscopy investigation suggests that the local order of the SAM formed on both the surfaces prepared by RCA clean and by HF-dip procedures depends on the local chemical structure of each surface and is not defined by surface topography on larger scales [4].

3.4. X-ray photoelectron spectroscopy investigation of chlorinated Si(1 1 1) surfaces

In addition to the formation of a SAM, single crystal silicon surface chlorination is also a common path for further surface functionalization. Using PCl₅ as a mild chlorinating agent allows for a formation of well-defined Cl–Si(1 1 1) surface with every monohydride replaced by a Si–Cl bond on an atomically flat H–Si(1 1 1) prepared by an RCA clean [21]. Comparison of the chlorinated surfaces produced with H-terminated Si(1 1 1) crystals obtained with different preparation procedures should demonstrate if this approach could be used on both types of surfaces efficiently. We used XPS to monitor Cl 2s, Cl 2p, Si 2p, C 1s, and O 1s spectral regions of the surfaces prepared by RCA clean and HF-dip procedures followed by PCl₅ chlorination. Representative Cl 2p and Si 2p spectra are shown in Fig. 6. O 1s and C 1s regions only demonstrate the presence of impurities from ambient transfer of the samples following the last modification step into the XPS setup and are essentially identical. Based on the Si 2p edge shown in Fig. 6, it can also be concluded that no observable surface oxidation in ambient was recorded on the timescale of the experiments, meaning that both types of surfaces remain stable in ambient, at least for a short time. The Cl 2p region confirms that both surfaces are chlorinated and that the surface reactive sites produced by the chlorination procedures are similar. Thus, both H–Si(1 1 1) surfaces prepared by the RCA clean and by HF-dip undergo surface chlorination with PCl₅ leading to similar chlorinated surfaces amenable to further modification despite the fact that the starting H-terminated Si(1 1 1) surfaces are dissimilar at the local atomic scale. This last observation has substantial practical implications since a wide range of surface functionalities can be utilized for silicon substrates if the Cl-terminated surface is obtained. It is possible that the atomically rough H–Si(1 1 1) surface prepared by the HF-dip procedure undergoes different types of surface reactions compared to the atomically flat H–Si(1 1 1) surface prepared by RCA clean, but it is also

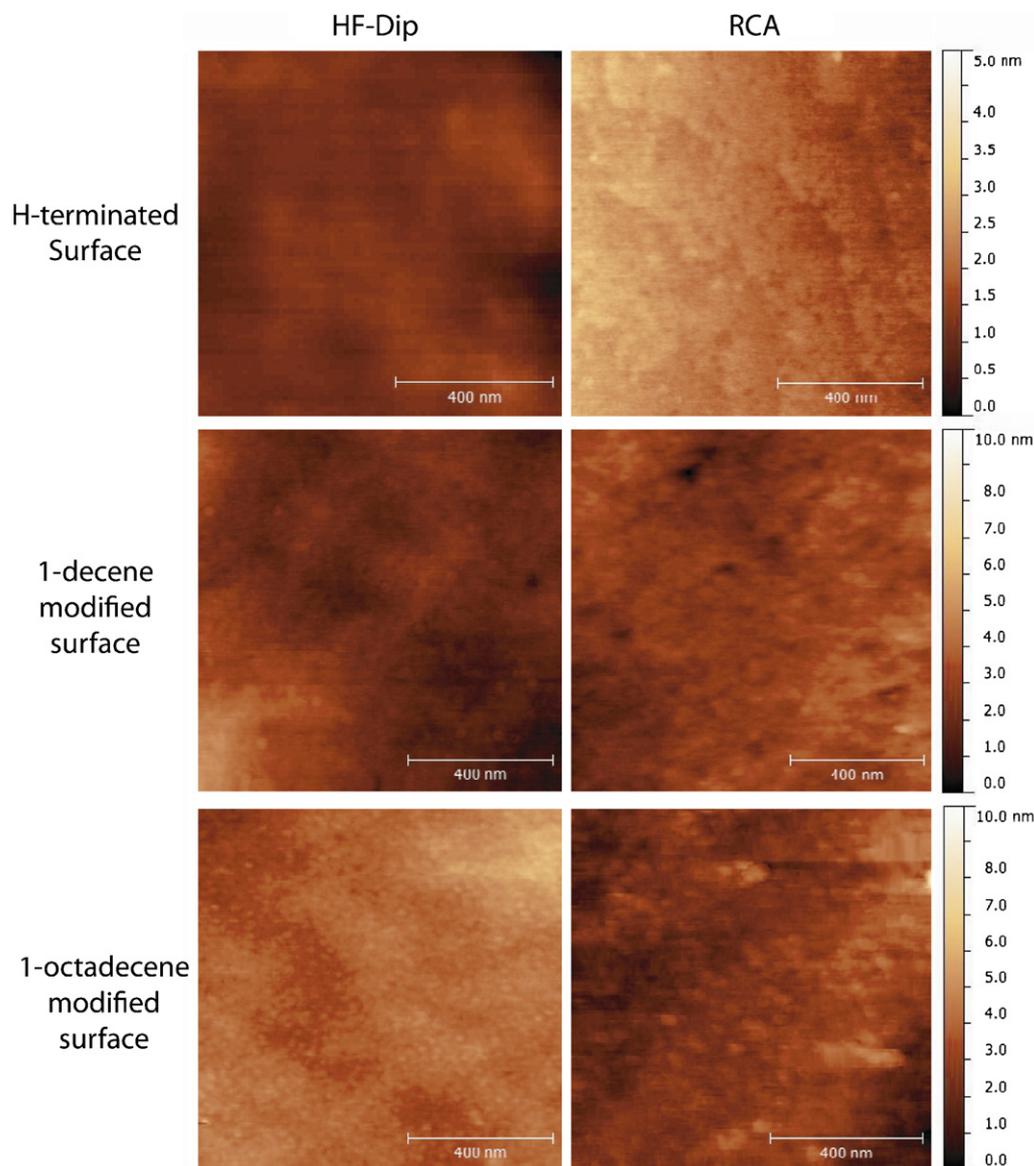


Fig. 4. AFM images of the modification of the Si(111) surface prepared by HF-dip procedure (left) and RCA clean (right). Top images shows the surfaces before alkene modification, middle images show the same surfaces modified with 1-decene and the bottom images show the surfaces shown in the top two images modified by 1-octadecene.

possible that some of the silicon dihydride and trihydride species are eliminated during the PCl_5 treatment, thus making the two resulting surfaces chemically very similar. An overlayer–substrate model was employed to estimate the chlorine coverage on both silicon surfaces [29,30]. Based on Cl 2p and Si 2p spectra, 0.72 relative apparent monolayer Cl was produced on H–Si(111) surface prepared by RCA (approximate 95.6% of the surface was occupied by chlorine atoms [16,25,26]). Similarly, about 0.65 relative apparent monolayer Cl was produced on H–Si(111) surface prepared by HF-dip method (approximate 86.0% of the surface was occupied by chlorine atoms).

One of the interesting points that is also worth mentioning is that if the RCA-prepared surface was subsequently dipped into HF (the last step of HF-dip procedure), its electronic properties became similar to the surface obtained entirely by HF-dip. This likely suggests that the surface reactions during the HF-dip procedure are more “aggressive” compared to the modified RCA clean used here and that the initial topography of the surface does not affect the ultimate surface species formed, regardless of the specific surface preparation procedure.

4. Conclusions and final remarks

In this work we have investigated the chemical and electronic properties of H-terminated Si(111) surfaces prepared by two commonly used surface preparation approaches: modified RCA clean and HF-dip. The former exhibited a well-defined chemical behavior with essentially a single monohydride surface site leading to exclusive surface chlorination by PCl_5 and the formation of an exceptionally ordered SAM in a reaction with 1-alkenes. The latter was shown to be atomically rough but to possess a very attractive set of electronic properties. This surface prepared with HF-dip procedure was shown to yield a very similar surface to that for RCA clean-prepared in a chlorination reaction and also could produce a well-ordered SAM in a reaction with 1-alkene when a long-chain alkene molecule, 1-octadecene, was used. It was shown that only local atomic structure and not the topography of the H–Si(111) surfaces influences their chemical properties and that the selected surface functionalization procedures could be used to produce chemically similar platforms for further chemical functionalization of silicon regardless of the

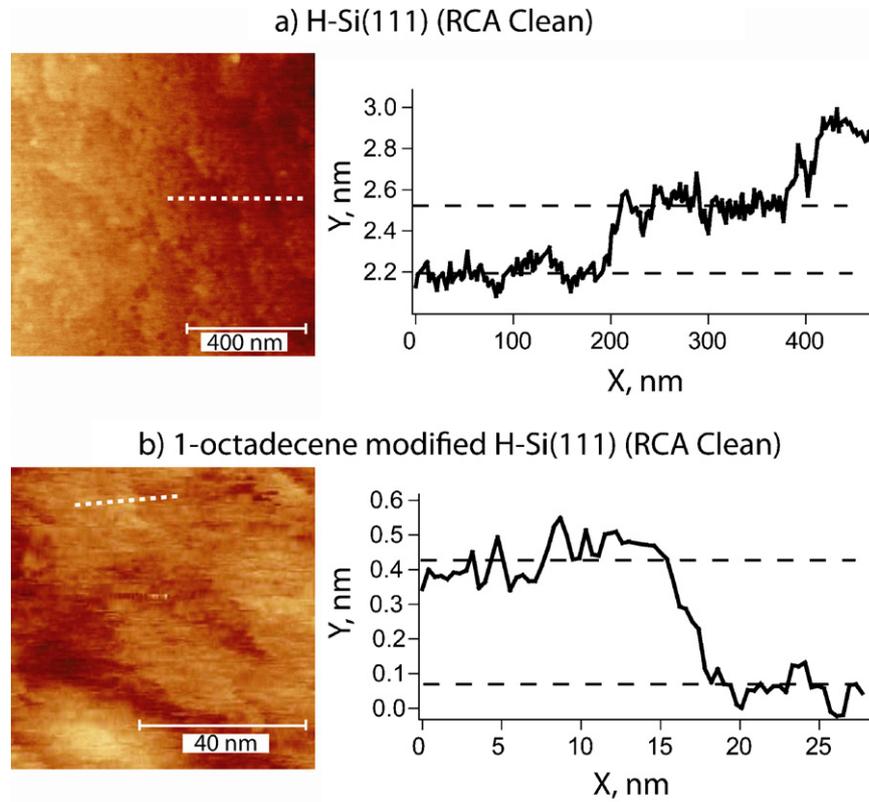


Fig. 5. AFM images and corresponding line-profiles of (a) H-Si(1 1 1) surface prepared by the modified RCA procedure and (b) the same surface modified with of 1-octadecene.

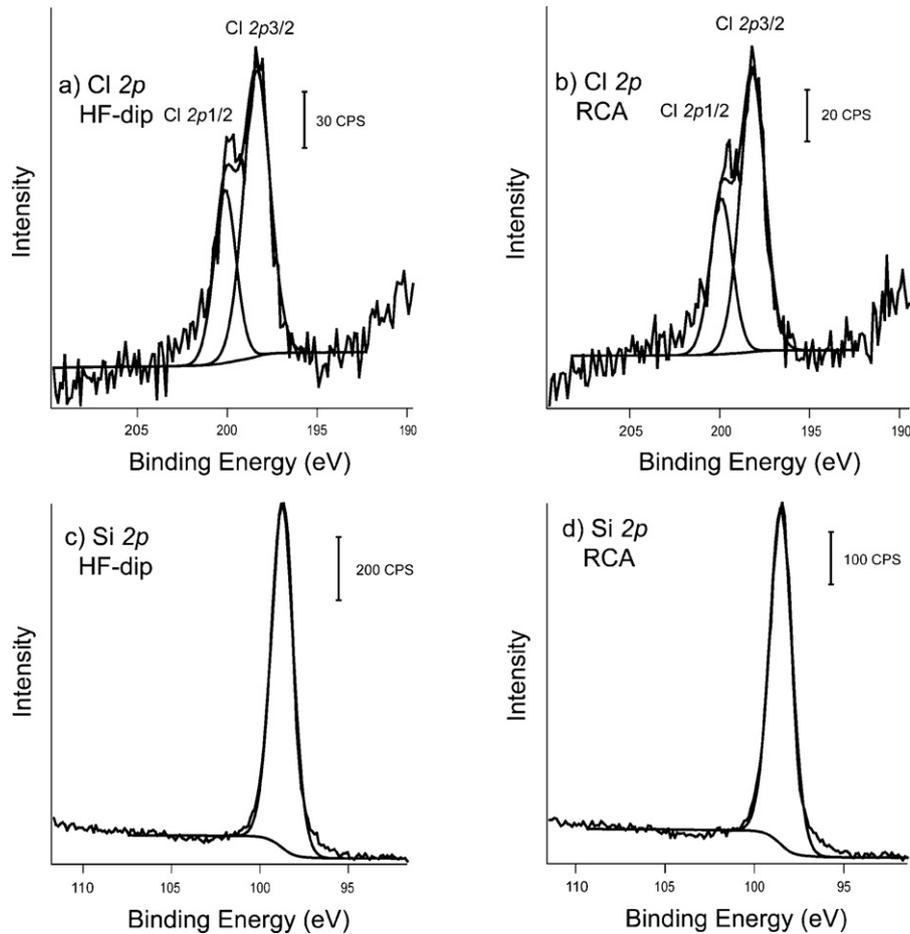


Fig. 6. XPS investigation of Cl-Si(1 1 1) surfaces produced by HF-dip ((a) Cl 2p edge and (c) Si 2p edge) and RCA ((b) Cl 2p edge and (d) Si 2p edge) surface preparation procedures.

method used to prepare H-terminated silicon single crystal as a starting point.

Acknowledgments

This work was partially supported by the National Science Foundation (CHE-0650123 and CHE-1057374). We gratefully acknowledge the help of Professor Douglass F. Taber (Department of Chemistry and Biochemistry, University of Delaware) for his help with surface chlorination experiments.

References

- [1] R.L. Opila, D.W. Hess, *J. Electrochem. Soc.* 150 (2003) S1–S10.
- [2] W. Kern, *J. Electrochem. Soc.* 137 (1990) 1887–1892.
- [3] Q.Y. Tong, E. Schmidt, U. Gosele, M. Reiche, *Appl. Phys. Lett.* 64 (1994) 625–627.
- [4] G.J. Pietsch, *Appl. Phys. A* 60 (1995) 347–363.
- [5] K.A. Shaw, Z.L. Zhang, N.C. MacDonald, *Sens. Actuators A* 40 (1994) 63–70.
- [6] M. Tabe, *Appl. Phys. Lett.* 45 (1984) 1073–1075.
- [7] D.J. Michalak, S.R. Amy, D. Aureau, M. Dai, A. Esteve, Y.J. Chabal, *Nat. Mater.* 9 (2010) 266–271.
- [8] H. Ubara, T. Imura, A. Hiraki, *Solid State Commun.* 50 (1984) 673–675.
- [9] M.F. Faggin, S.K. Green, I.T. Clark, K.T. Queeney, M.A. Hines, *J. Am. Chem. Soc.* 128 (2006) 11455–11462.
- [10] M. Kulkarni, S.K. Green, C. Shea, K.T. Queeney, *J. Phys. Chem. C* 113 (2009) 10206–10214.
- [11] H. Ogawa, K. Ishikawa, C. Inomata, S. Fujimura, *J. Appl. Phys.* 79 (1996) 472–477.
- [12] N. Araki, *Jpn. J. Appl. Phys.* 48 (2009) 011201.
- [13] X. Zhang, E. Garfunkel, Y.J. Chabal, S.B. Christman, E.E. Chaban, *Appl. Phys. Lett.* 79 (2001) 4051–4053.
- [14] A. Bansal, X.L. Li, I. Laueremann, N.S. Lewis, S.I. Yi, W.H. Weinberg, *J. Am. Chem. Soc.* 118 (1996) 7225–7226.
- [15] M.R. Linford, C.E.D. Chidsey, *J. Am. Chem. Soc.* 115 (1993) 12631–12632.
- [16] M.R. Linford, P. Fenter, P.M. Eisenberger, C.E.D. Chidsey, *J. Am. Chem. Soc.* 117 (1995) 3145–3155.
- [17] S. Ciampi, J.B. Harper, J.J. Gooding, *Chem. Soc. Rev.* 39 (2010) 2158–2183.
- [18] T.K. Mischki, G.P. Lopinski, D.D.M. Wayner, *Langmuir* 25 (2009) 5626–5630.
- [19] I.V. Antonova, R.A. Soots, V.A. Seleznev, V.Y. Prints, *Semiconductors* 41 (2007) 991–997.
- [20] I.V. Antonova, R.A. Soots, M.B. Guliaev, V.Y. Prinz, M.S. Kagan, J. Kolodzey, *Appl. Phys. Lett.* 91 (2007) 102116.
- [21] A. Bansal, X.L. Li, S.I. Yi, W.H. Weinberg, N.S. Lewis, *J. Phys. Chem. B* 105 (2001) 10266–10277.
- [22] M.K. Weldon, V.E. Marsico, Y.J. Chabal, D.R. Hamann, S.B. Christman, E.E. Chaban, *Surf. Sci.* 368 (1996) 163–178.
- [23] M.F. Juarez, E.M. Patrito, P. Paredes-Olivera, *J. Phys. Chem. C* 113 (2009) 681–690.
- [24] A.B. Sieval, R. Opitz, H.P.A. Maas, M.G. Schoeman, G. Meijer, F.J. Vergeldt, H. Zuilhof, E.J.R. Sudholter, *Langmuir* 16 (2000) 10359–10368.
- [25] R. Mendelsohn, J.W. Brauner, A. Gericke, *Annu. Rev. Phys. Chem.* 46 (1995) 305–334.
- [26] C. Miramond, D. Vuillaume, *J. Appl. Phys.* 96 (2004) 1529–1536.
- [27] T. Ishizaki, N. Saito, L. SunHyung, K. Ishida, O. Takai, *Langmuir* 22 (2006) 9962–9966.
- [28] H. Angermann, J. Rappich, I. Sieber, K. Hubener, J. Hauschild, *Anal. Bioanal. Chem.* 390 (2008) 1463–1470.
- [29] J.A. Haber, N.S. Lewis, *J. Phys. Chem. B* 106 (2002) 3639–3656.
- [30] L.J. Webb, E.J. Nemanick, J.S. Biteen, D.W. Knapp, D.J. Michalak, M.C. Traub, A.S.Y. Chan, B.S. Brunschwig, N.S. Lewis, *J. Phys. Chem. B* 109 (2005) 3930–3937.