Combined use of AFM and FTIR in the analysis of the hydrogen termination of Si(100) surfaces

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The preparation of hydrogen terminated Si(100) surfaces of high quality is of paramount relevance in many areas of fundamental and technological research. These surfaces must display both a sub-nanometric residual roughness and a uniform, controlled chemical termination. Both points are somewhat critical when surfaces are prepared using wet-chemistry procedures. We show how a combined use of Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) provides a rationale to surface protocols. Specifically, the effect of combined low-concentrated HF solutions, annealing, and ultrasonic cleaning on Si(100) surfaces was systematically analyzed. Through the present tutorial mini-review on FTIR and AFM of H-terminated surface, we will get to discuss about the interplay between hydrogen coverage and surface roughness at different length scales. On these bases, optimal processing conditions are found to hydrogenate Si(100) surfaces.

Keywords: AFM microscopy; FTIR spectroscopy; silicon; surfaces; etching

1. Introduction

A large body of literature is currently available concerning silicon surface preparation methods [1] as well as techniques to characterize them as of their morphology [2-4] or of their chemistry [5]. However, less is known about the interplay between the two issues. Methods leading to atomically flat surfaces are not necessarily able to provide homogeneous surface termination — and vice versa.

The making of atomically flat, homogeneously terminated Si surfaces is actually of fundamental importance in many diverse situations. In the field of very-large-scale-integration microelectronics, surface flatness at the (sub)nanometric scale impacts on the control of critical features of field-effect devices, especially in view of the transition to the 22-nm technology node. For nanotechnological applications, the integration of molecules into nanoelectronic devices calls for an even stricter command on surface morphology and chemistry in a non-conflicting way. However, even less extreme applications, such as optoelectronics and sensors, display the importance of mastering the chemical termination and the residual roughness of surfaces.

The aim of this paper is to show an example of good practice aimed at the preparation of a homogeneous and flat surface through the concurrent assessment of an appropriate chemical procedure and the implementation of a suitable analytical toolbox. We will focus on the problem of the termination of Si (100) surfaces with hydrogen atoms, which is also in itself a case study of major relevance in many respects, because it is the common route for the initialization of the (100) surface before any other type of treatment, both in academic research and in device-quality processing.

While vacuum techniques are currently available and used to get flat and homogeneously H-terminated Si (100) surfaces – and almost ideal Si (111) surfaces can be obtained both by wet and vacuum techniques – no assessed method exists to obtain clean, smooth and homogeneous Si (100) surfaces by wet chemistry. The preparation procedure that will be reported is purposefully based on a small number of well assessed, apparently simple elemental processes. It will be shown how a simple permutation in the processing sequence has effects on the final surface quality. As of the analytical toolbox, we will show how two rather widely available characterization techniques, atomic force microscopy (AFM) and Fourier-transform infrared (FTIR) spectroscopy, when systematically combined, may be sufficient to guide the setup of an optimal procedure of surface qualification. More specifically, we will study the variation of the dose of surface silicon hydrides (SiH₄) through the surveying of the integral absorbance of the associated infrared band. The variation of the surface roughness through the monitoring of the mean squared deviation from the planarity of the surface (σ), provided by AFM investigation.

It is important to note that the application of the IR spectroscopy to the surfaces is made difficult by the fact that the calibration of the signals would require a surface of reference of extremely problematic realization. At the end we will indicate which procedure gives the highest dose of SiH₄. Nonetheless, the quantification of the integral absorbances from IR investigation requires the coupling with an independent, intrinsically quantitative, techniques as x-ray photoelectron spectroscopy [6,7].

In view of the assignment of vibrational bands to Si surface species, it may be convenient to anticipate some information about the main terminating groups commonly found at Si surfaces. In principle, all terminating groups should be assigned to a well defined crystallographic orientation of the pertinent surface. This is however possible and convenient only for a few of them. In this set, hydrogen-terminated Si dimers [(SiH)₂, Fig. 1-a] and dihydrogen-
terminated Si monomers (SiH₂, Fig. 1-b) populate H(2×1)-Si(100) and H(1×1)-Si(100) surfaces, respectively. Instead, other species such as SiH and SiH₃ (Fig. 1-c and -d), although formally pertaining to regular H(1×1)-Si(111) facets, are often present on silicon surfaces as defective sites belonging to steps and edges at corrugated or otherwise featured surfaces. In addition to Si-H species, silanols [Si(OH)ₙ (n = 1, 2, 3)], Fig. 1-e) are often encountered onto silicon surfaces of any orientation that were exposed to water, being an alternative to siloxo groups (Si–O–Si, Fig. 1-f) as oxidized terminations of Si surfaces. Finally, oxidation is also responsible for the formation of oxygen-backbonded silicon hydrides [(–O)ₙSi–Hₙ], such as (–O)₃Si–H in Fig. 1-g. For a more detailed description of terminating species at Si surfaces the reader may refer to Refs. 8–13.

Figure 1: Cluster representation of the main functional groups involving hydrogen and oxygen at silicon surfaces. See text for details.

2. Experimental

2.1 Surface Cleaning

Electronic grade p-type Si(1 0 0), 14 ÷ 22 Ω cm, both side polished, was used throughout this study. All reagents were electronic grade (Sigma Aldrich). Unless otherwise specified, bidistilled water, conductivity < 5×10⁻⁸ Ω⁻¹ cm¹, was used as solvent and rinsing agent. The prisms for FTIR (fully described in Sect. 2.4) and the 1×1 cm² samples for AFM were processed simultaneously.

Preliminary to the specific process of final hydrogen termination, all samples were submitted to the following cleaning process:
1. degreasing using a surfactant in water;
2. 10-min immersion in water at 95 °C;
3. two 10-min sonications (frequency of 45 kHz ± 5%) in water at 60 °C;
4. 30-min piranha etch (2 parts of H₂SO₄, 98% vol., and 1 part of H₂O₂, 33% vol.) at 95 °C (CAUTION! Piranha solution can be explosive if H₂O₂ concentration exceeds 50% in volume, and the etching process can anyway bring solution to a violent boiling.);
5. two 10-min sonications in water at 60 °C;
6. 10-min ammonia peroxide mixture (APM) etch (1 part of H₂O₂, 33% vol., 1 part of NH₄OH, 33% vol., and 5 parts of water) at 80 °C;
7. removal of the formed oxide layer by dilute (2% vol.) HF etching (DHF);
8. further 10-min APM etch at 60 °C under sonication;
9. removal of the formed oxide layer by DHF;
10. further 10-min APM etch at 80 °C;
11. 10-min piranha etch at 95 °C;
12. final 10-min sonication in water at 60 °C.

Between any oxidative step and the subsequent dipping in DHF the samples were rinsed in water for 30 s. This methodology is somehow different from the most common RCA cleaning. We set it up specifically for this study, since (i) AFM measurements are extremely influenced by any particulate sitting onto the surface, and (ii) organic contamination lying on surface reduces the surface reactivity. Ultrasounds are efficient in removing particles by
mechanical action, while APM is efficient for their chemical removal, by including them into the oxide layer which is simultaneously formed and etched. Particles originate from the boxes containing the Si wafers and the bottles containing the chemicals, the laboratory environment, and are further generated during the polishing step. Then, the piranha solution is much more efficient than any organic solvent for the removal of organic contaminations.

2.2 Hydrogen-terminating processes

Each couple of samples (one for FTIR, one for AFM) was then submitted to different specific H-terminating processes. They are summarized in Table 1. At this point, the bidistilled water for rinsing and solutions is also O₂-free. Dissolved oxygen was stripped away from water by bubbling high-purity Ar (5.5) for 7 h. We made use of the following steps:

- **HF-last**: an etching carried out in a 0.5% vol. solution of HF obtained by dilution of commercial HF in O₂-free water;
- **oxidative annealing (OA)**: an annealing in dry, high-purity O₂ (5.0) flow at 1050 °C for 2 h, leading to the formation of a 110-nm thick oxide layer;
- **argon annealing (AA)**: an annealing in dry, high-purity Ar flow at 1050 °C for 30 min, aimed at promoting the plastic reflowing of the surface.

<table>
<thead>
<tr>
<th>#</th>
<th>Processing sequence</th>
<th>( A_{\text{int}} ) (nm) before</th>
<th>( A_{\text{int}} ) (nm) after</th>
<th>( \sigma )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HF-last, rinsing in O₂-free water</td>
<td>&lt; 1.15 ± 0.02</td>
<td>&lt; 1.03 ± 0.02</td>
<td>0.96</td>
<td>0.46</td>
</tr>
<tr>
<td>2</td>
<td>OA, AA, HF-last, rinsing in O₂-free water</td>
<td>&lt; 1.06 ± 0.01</td>
<td>&lt; 0.93 ± 0.02</td>
<td>0.27</td>
<td>0.17</td>
</tr>
<tr>
<td>3</td>
<td>OA, AA, HF-last under sonication, sonication</td>
<td>&lt; 1.06 ± 0.01</td>
<td>1.14 ± 0.01</td>
<td>0.53</td>
<td>0.25</td>
</tr>
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</table>

2.3 AFM analysis

AFM measurements were performed in tapping mode in air with a Nanoscope V MultiMode (Digital Instruments) using silicon tips (Veeco RTESP, force constant 40 N/m, resonance frequency 250 kHz). AFM images were analysed with the Veeco Nanoscope 7.30 software version and corrected with zero order filter. Surface roughness was quantified through the mean squared deviation from the planarity of the explored surface, calculated on 1×1 µm² scan areas. The results are listed in Table 1.

2.4 Vibrational spectroscopy

The vibrational study of the surfaces was performed in attenuated total reflection mode and multiple internal reflection geometry (ATR-MIR). It is one of the methods to exalt the signal of the surface (where about \( 10^{15} \) absorbents cm² are present) over the bulk signal (where about \( 10^{25} \) absorbents cm² are present). Actually, imagining equal the dose of surface absorbents and the projected dose of bulk absorbents, the ATR mode is more sensitive than the transmission mode [14]. Moreover, MIR geometry allows the surface to be probed by the evanescent wave several times. At 2000 cm⁻¹ (i.e. a wavelength of 5 µm) the evanescent wave in the Si-air system explores around 5 µm beyond the surface. Since this work focuses about the combined use of infrared spectroscopy and AFM, it is important to note that, with respect to the IR range used here (25 ± 2.2 µm), the analyzed silicon surfaces are always optically flat, so that the condition of total internal reflection (internal angle of incidence above the critical angle, which for Si-air is around 17°) occurs at each reflection independently of local corrugation, which are surveyed by AFM and never exceed the nm length-scale.

The samples were shaped into prisms (55 × 10 × 0.6 mm³) polishing the sides. The short sides were beveled at 45° so that the radiation exiting the interferometer is focused at normal incidence onto one of the two bevels, propagates through the wafer (about 110 internal reflections occurred in our prisms), and finally exits from the other bevel and is collected by a HgCdTe (MCT) detector cooled with liquid nitrogen. The samples were placed in the spectrophotometer sample-chamber under dry-N₂ immediately after the end of the process of H-termination. Instead, the interferograms were collected after purging in dry N₂ (for around 7 h), in order to decrease the amount of water (both in the optical path and physisorbed on the surface).

All the absorbance spectra presented in this work were obtained with a Bio-RAD FTS-6000, from the integration of 1024 interferograms \( (I) \) with a resolution of 4 cm⁻¹, and then ratioing it against the reference \( (I_0) \). The choice of a good reference was complicated by the fact that in this investigation the optical reflecting element coincides with the sample under study. In order to prepare a suitable reference, we chose to treat the prisms in Ar at 450 °C for 2 h, once collected...
the single beam of the H-terminated surface. These very mild conditions should change minimally the morphology of the surface, while a very thin layer containing Si, C, O and some residual hydrogen was formed on surface. The as-prepared surface was eligible as reference, thanks to the small number of weak absorption peaks that it presents in the entire infrared range, especially in the SiH₄ stretching region of our interest.

Subtracting the reference to the sample, the absorbance spectra do not contain any information about the bulk, but only on the differences in the chemical population of sample and reference. In order to calculate the integral area of the SiH₄ band ($A_{int}$), a baseline must be traced. The line of zero is a source of systematic uncertainty in the value of the integral area. Thus, $A_{int}$ was calculated after the subtraction of (1) an automatically-traced baseline, (2) a semi-automatically-traced baseline, and (3) a straight line. For all the samples, these three different lines of zero were calculated between 1900 and 2500 cm⁻¹, while the integrals were calculated between 2000 and 2200 cm⁻¹. Since clearly no statistical uncertainty can be computed in this case, the error bar is set here as max $|A_{intr} - <A_{int}|$, where $A_{intr}$ (i = 1, 2, 3) is the integral absorbance computed according to procedures (1) – (3) and $<A_{int}>$ is its average. The results are listed in Table 1, as obtained on all the samples before and after sonication.

3. Results

The absorbance spectrum of sample # 1 before sonication is reported in Fig. 2. It displays all the typical absorption bands of the H-terminated silicon surfaces analyzed in this work in the spectral region 1500 – 4500 cm⁻¹. The spectral region below 1500 cm⁻¹ is not accessible because of the strong lattice absorption [15]. Therefore, all the SiH₄ and SiO₄ bending modes are cut-off.

The following features are noted:

(a) a broadband covering the interval 3000 ± 3650 cm⁻¹, attributed to O–H stretching modes, both belonging to physisorbed water and surface silanols [15, 16];

(b) a very strong band in the region 2780 ± 3030 cm⁻¹, associated with C–H stretching modes (if not otherwise specified, all the assignments were made according to [17]);

(c) a very weak doublet at 2362 and 2337 cm⁻¹, characteristic of CO₂ and attributed to an uneven N₂-purging of the sample compartment during sample and reference measurement;

(d) a region between 2180 and 2300 cm⁻¹ related to the (–O)ₚ₋ₐ(Si–H)ₚ stretching modes [18];

(e) a band in the interval 2000 ± 2150 cm⁻¹, associated with Si(–H)ₚ stretching modes [19];

(f) an absorption at 1735 cm⁻¹ associated to carbonyl stretching;

(g) a peak at 1650 cm⁻¹ due to the scissor mode H–O–H assigned to liquid-like water [20].

Although this work is dedicated to the study of the H-terminated surface, before analyzing the SiH₄ band we briefly discuss on the other species on the surface. Features b and f cannot be associated with other species than organic contaminants [21]. The intensity of these bands indicates a rather high level of surface contamination. What is more important is the presence of features a and d, because they are evidence that the surface is partially oxidized even after the etching in HF solution. The study of the IR bands related to surface partial oxidation, although of paramount importance for the full understanding of the etching process, is made difficult by several reasons. First, both the regions of the silicon hydrides with oxygen in backbond and silanols are affected by the fact that they exist even on the reference surface. This results in complex waving baselines, which prevents any reliable calculation of the associated integral areas. Then, the O–H stretching band is extremely broad and structureless, containing contributions also from water molecules interacting with silanols through hydrogen bonds. Evidence can be put forward [6] showing that (i) the absorption around 3300 cm⁻¹ is likely to be mainly due to silanols, while that around 3450 cm⁻¹ is related with water molecules, (ii) further signals contribute to the band, but they cannot reliably be singled out because of the extreme broadness of all the signals therein, (iii) the proportion between water molecules and silanols (since the IR spectra are collected under dry N₂) should not exceed 4 to 1 [22]. Finally, although feature g depends only on physisorbed water, and the amount of physisorbed water is in principle proportional to the dose of surface silanols, it is a too indirect evidence to be of concrete usefulness in the study of surface residual oxidation.

Before evaluating how the SiH₄ band changes process by process, some very general considerations are needed. In principle, the combined analysis of the second derivative of the band and its spectral decomposition would allow the contributions of different hydride structures (mono-, di- and trihydrides, with all their different symmetries) to be discriminated [23]. The minima of the second derivative of the SiH₄ band provide the number of the peaks composed in the band. Then, the number of constituting peaks and Gaussian line shapes are imposed, leaving the other parameters (peak frequency, full width at half maximum, and integral area) free to float. Actually, the band is so poorly structured (Fig. 3) that it can be decomposed with no more than 5 broad peaks (15 ± 25 cm⁻¹), although the asymmetries in the minima of the second derivative suggest the presence of other signals (as it can be appreciated in Fig. 3). Therefore, the decomposition is not univocal and depends on the initialization of the parameters. Each of these peaks is too broad to be attributed to one specific chemical configuration, as it has been done for more ordered surfaces [8-13, 23]. In this view we find more convenient to separate the whole SiH₄ (2000 ± 2150 cm⁻¹) into three parts: we assign the spectral region
below 2090 cm\(^{-1}\) to monohydrides (SiH), the region between 2090 and 2120 cm\(^{-1}\) to dihydrides (SiH\(_2\)), and the region between 2120 and 2145 cm\(^{-1}\) to trihydrides (SiH\(_3\)). The part of the band at wavenumbers higher than 2120 cm\(^{-1}\) also contains signals from the hydrides with only one or two oxygen atoms in backbond, depending on the number of hydrogen.

Although the second derivative is helpful to single out the peaks under a structureless band as the SiH\(_n\) bands in our spectra, it can be a powerful tool in providing information about the homogeneity of the surface. Actually, the depth of a minimum in the second derivative is inversely proportional to the width of the related peak. The IR peak width increases as the heterogeneity of the neighborhood within few bonds from the absorbing structure. Thus, providing that we are comparing normalized bands related to same structures, the intensity range of the second derivative is connected with surface heterogeneity [23]. Independent of the processing, all the analyzed surfaces showed a normalized SiH\(_n\) band whose second derivative is in the range of \(10^{-4}\) cm\(^2\), \textit{i.e.} that of the randomly heterogeneous surfaces [24].

![Figure 2: Infrared spectrum of the hydrogen-terminated Si(100) before sonication in O\(_2\)-free water (sample #1).](image1)

![Figure 3: Detail of the SiH\(_n\) band of the hydrogen-terminated Si(100) before sonication in O\(_2\)-free water (sample #1). Being a logarithm of the ratio between two intensities, absorbance is a pure number. Instead, the second derivative of IR absorbance bands is measured in cm\(^2\).](image2)
Sample #1, which underwent only to a treatment in HF-last, has been taken as the starting point for the present investigation. Then, we systematically added one different step to the processing, setting to exclude it in the forthcoming treatment if useless. Actually, the treatment in O₂-free water was reported to flatten the H-Si(1 1 1) [25, 26], and, on the other hand, the use of low-concentrated HF solutions for the H-termination of Si(1 0 0) was already demonstrated to improve its quality [6]. Thus, we assumed that a low-concentrated HF solution using O₂-free water (HF-last) provided flat, non-oxidized, H-Si(100).

Sample #1 demonstrates the effect of the sonication in O₂-free water after the etching in HF-last. AFM measurements carried out before and after sonication show a decrease of σ of a factor 2. On the other side, due to the high temperatures locally generated by ultrasounds, sonication is likely to favor the diffusion of oxygen into the surface, leading to (i) an increase of the intensity of the signals due to silanols and hydrides with oxygen in backbond, and (ii) a depression of the non-backbonded SiHₙ species (-10% of the initial value).

Figure 4: 1×1 µm² AFM images of the surface of sample # 1 (a and c), # 2 (b and d), # 3 (e), and # 4 (f). Images c-f were collected after sonication in O₂-free water for 10 min, whereas image a and b were collected before sonication. Color bar applies to all images.

The actual effect of the sonication carried out after HF-last is confirmed by sample #2. Indeed, as for sample #1, this treatment promotes the removal of small islands present on the surface (Fig. 4a vs c for sample #1, and b vs d for sample #2). Sample #2 also demonstrates the efficiency of the thermal processing OA + AA inserted before the HF-last. Actually, the σ measured on sample #2 is the lowest we obtained. The dose of SiHₙ decreased slightly (10%), but the silanols band is far less intense than in sample #1 (Fig. 5).

Figure 5: Comparison between the spectrum of the H-Si(100) undergone only HF-last (sample #1) and the spectrum of the H-Si(100) undergone thermal treatment OA + AA before HF-last (sample #2), after sonication in O₂-free water.
In the logic of this sequence of experiments, the thermal treatment has been maintained in the preparation of sample #3, but the HF-last treatment is carried out under sonication. Although with other etching solutions [27] ultrasounds were reported to reduce surface roughness and improve etching uniformity, in our case this treatment leads to a large increase of roughness, noticeable in the image reported in Fig. 4-e, where protrusions and hollows appear. The corresponding IR spectrum (Fig. 6) shows a large amount of silanol groups, a particularly waving baseline in the region of \((-\text{O})_2\text{Si}(-\text{H})_n\), and an increase of the $A_{\text{int}}$ by about 10% with respect to sample #2.

![Figure 6](image)

**Figure 6**: Comparison between the spectrum of the H-Si(100) undergone thermal treatment OA + AA before HF-last (sample #2) and the spectrum of the H-Si(100) undergone thermal treatment OA + AA and HF-last under ultrasounds (sample #3), after sonication in O$_2$-free water.

Along the same line, in sample #4 we perform the HF-last without sonication, but we added a thermal treatment in Ar also before the standard OA + AA. The idea is to check if, acting the oxidation on a surface already planarized, the flatness of the final surface is improved. Actually, the $\sigma$ is higher than in sample #2, although surface areas analysed are uniform, without islands and hollows (Fig. 4-f). The IR spectrum, instead, shows a surface with a negligible signal of hydrides with oxygen in backbond, SiOH and physisorbed water (Fig. 7). The integral absorbance of the SiH$_n$ band increases of about the 20% with respect to sample #2.

![Figure 7](image)

**Figure 7**: Comparison between the spectrum of the H-Si(100) undergone thermal treatment OA + AA before HF-last (sample #2) and the spectrum of the H-Si(100) undergone thermal treatment AA + OA + AA before HF-last (sample #4), after sonication in O$_2$-free water.
4. Discussion and Conclusions

Beyond the specific assessment of the optimal conditions of surface preparation, probably the most interesting result stemming from the compared analysis of the FTIR spectra and the AFM data is that both the concept of surface roughness and of chemical homogeneity must undergo a deeper scrutiny before being of any practical usability in this type of contexts. The surface is investigated at three different levels by combination of FTIR and AFM:

- **global**, the complete spectrum provides a sort of picture of the chemical state of the surface averaged over the entire sample (squared centimetres);
- **local**, σ provides an image of its morphology averaged over areas of squared microns;
- **glocal**, the second derivative of the SiH\textsubscript{n} band provides information about the homogeneity of very local neighborhood (squared nanometers), but averaged over the entire sample.

If a direct relation between AFM and IR results can be possible in very ordered and homogeneous surfaces [28], any unifying interpretation must be asserted with a lot of precaution in case of randomly heterogeneous surfaces. First, IR information is always intrinsically statistic, while AFM information would required the acquisition of several images of the same size (and also several of different sizes) to setup a reliable statistics for a randomly heterogeneous surface. Then, particulate may increase the value of σ in a way which is not related to the behaviour of surface species. Finally, the rich variety of terminating groups at the surface is such that σ should be correlated with the sum of the \(A_{\text{int}}\) of all the absorbent surface species—what is not always possible.

Sonication in O\textsubscript{2}-free water after H-terminating process improves the surface quality because particle are removed, but it increases surface oxidation by exalting reactivity of water. In this case, the changes in σ and \(A_{\text{int}}\) are not correlated.

We suggest that the thermal treatment OA + AA before H-terminating process does flatten the surface. In this case the lower dose of SiH\textsubscript{n} with respect to sample #1 (\(A_{\text{int}}\ #1 > A_{\text{int}}\ #2\), both before and after sonication) does correlate with a less corrugated real surface (σ #1 > σ #2, both before and after sonication). Actually, the amounts of all the surface species per unit of geometric area have decreased (Fig. 5) since the real surface has diminished.

Performing HF-blast under sonication goes exactly in the opposite direction. Non uniform surface oxidation is promoted, but etching of the just formed oxide occurs simultaneously, thus giving a highly corrugated surface. In this case, the high value of σ does not depend on particles. Such a corrugated surface is populated by hydrides (\(A_{\text{int}}\ #3 > A_{\text{int}}\ #2\), large amounts of silanols and hydrides with oxygen in backbond. Looking at the second derivative, some new minima appear in the region of O\textsubscript{4a}SiH\textsubscript{n}, and the very waving baseline in the same region confirms the formation of important amount of such species.

What happens to the surface when an annealing in argon precede the thermal treatment OA + AA deserves a particular interest. The slightly higher corrugation with respect to the sample prepared with standard OA + AA process (σ #4 > σ #2) goes with an infrared spectrum devoid of the recurring absorptions due to surface oxidized structures. The surface seems to be covered only by silicon hydrides, as evidenced by the increase of the 20% in the \(A_{\text{int}}\) with respect to sample #2. Nonetheless, the relevance of this result is slightly limited by considering that the absorbance spectrum is the difference between the sample and the reference. Actually, the values of \(A_{\text{int}}\) reported in Table 1 for samples #1 - #3 are an overestimation of the surface silicon hydrides, since the contribution of the silicon hydrides with few oxygen atoms in backbond cannot be singled out and subtracted. Instead, the calculated \(A_{\text{int}}\) for sample #4 is likely to be due only to SiH\textsubscript{n}, provided that the amount of SiOH, easily detectable, is below the sensitivity of the technique. Therefore, we believe that 20% is a underestimated of the difference in the hydride population on samples #2 and #4.

From the point of view of surface roughness and dose of surface hydrides, we are now able to discriminate the effects of each single process. Rather than pointing out the best methodology out of the others, we can conclude that the surface quality (the most flat, or the most homogeneous in H terminations, or that bearing the highest dose of OH terminations) can be actually tailored depending on the application of the final surface — no “best surface” existing.

The second derivative, although global in the sense that it pictures the heterogeneity state of the entire surface, is local in the sense that it is determined by neighborhoods within a few bond lengths. The second derivatives of the studied samples show some differences in the number and position of their minima. For example, as already said, for sample #3 it shows some additional minima in the O\textsubscript{4a}SiH\textsubscript{n} region with respect the other samples, disclosing the higher surface oxidation degree. However, since the second derivatives of all the samples substantially fall in the same range of values, the H-Si(100) surface is not improved at its nanoscale by any of the treatment performed in this investigation.
References


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