

## Si 2p Core-Level Spectroscopy of the Si(111)-(1 × 1):H and Si(111)-(1 × 1):D Surfaces: Vibrational Effects and Phonon Broadening

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Very sharp photoemission spectra have been obtained from the Si(111)-(1 × 1):H and Si(111)-(1 × 1):D surfaces prepared by a simple well-defined *in situ* method. Both the Si 2p core-level spectra and the valence band spectra are essentially identical to spectra reported for the chemically prepared (1 × 1):H surface. We can conclusively exclude contributions from Si-H(D) stretching vibrational losses to the Si 2p core-level spectra, contrary to a recent suggestion. The line shape of the component originating from the surface Si atoms is found to be asymmetric, which we assign to asymmetric phonon broadening.

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The unreconstructed Si(111)-(1 × 1):H monohydride surface is of great fundamental importance due to the simple atomic structure. The study of substrate-adsorbate interactions, e.g., vibrational effects, is simplified since the experimental data are more straightforward to interpret and comparisons with theory are easier. The importance of a well-ordered (1 × 1):H surface for experimental observations of new physical phenomena is clearly demonstrated by the large number of studies of the (1 × 1):H surface prepared by the wet chemical etching method [1–3]. This method involves chemical etching in buffered HF solutions and careful introduction into the ultrahigh vacuum (UHV) chamber. In this study we have instead utilized a simple well-defined *in situ* method to obtain the (1 × 1):H surface [4]: atomic hydrogen exposure of the Si(111)-(7 × 7) surface at a temperature around 400 °C. This method enables a direct comparison of identically prepared hydrogen and deuterium terminated 1 × 1 surfaces, which has not been possible with the chemical etching method [5].

Intense Si-H stretching vibrational losses (295 meV) have been observed in Si 2p core-level spectra from SiH<sub>4</sub> molecules [6,7]. It was suggested that ion-state vibrational effects must be considered also in the analysis of core-level spectra of hydrogen chemisorbed Si surfaces since the vibrational energy loss is similar to observed shifts in the Si 2p core level for these surfaces [7]. In a very recent photoemission study of the Si(111)-(1 × 1):H surface prepared by chemical etching, two of the surface components were assigned to Si-H stretching and bending vibrational losses [2]. To conclusively determine whether Si-H vibrational losses contribute or not to the Si 2p core-level spectra we make use of the fact that the different masses of hydrogen and deuterium should result in different vibrational energies.

In this Letter, we report Si 2p core-level spectroscopy and angle-resolved photoemission of the (1 × 1):H and (1 × 1):D surfaces and scanning tunneling microscopy (STM) measurements on the (1 × 1):H surface. The photoemission spectra from the (1 × 1):H and (1 × 1):D surfaces are virtually identical and also very similar to the

spectra recently reported for the (1 × 1):H surface, prepared by wet chemical etching, by Hricovini *et al.* [2]. The Si 2p core-level spectra consist mainly of two well-resolved components originating from the bulk and the surface. The surface component is assigned to the hydrogen terminated topmost Si layer. The analysis of the Si 2p core-level spectra results in two important conclusions with implications also for other systems: (i) there is no significant Si-H(D) stretching vibrational contribution and (ii) the line shape of the component originating from the surface Si atoms deviates substantially from the Voigt line shape in that it is asymmetric, which we attribute to asymmetric phonon broadening. This interpretation explains why several components of different origins, some of which were unexplained, had to be used in Ref. [2].

The Si 2p core-level spectra were recorded at beam line 22 at the Max synchrotron radiation facility in Lund, Sweden. This beam line is comprised of an SX-700 type of monochromator and a large hemispherical analyzer (radius 200 mm). The total energy resolution was better than 70 meV and the angular resolution was ±8° for all Si 2p core-level spectra presented in this paper. The angle between the incident photon beam and the analyzed photoelectrons was 40°. The angle-resolved valence band spectra were recorded at beam line 41, which consists of a TGM monochromator and an angle resolving hemispherical analyzer. The total energy resolution was ≈150 meV and the angular resolution was ±2° for the valence band spectra. All spectra in this Letter were recorded along the [10 $\bar{1}$ ] bulk azimuthal direction. The Si(111) samples used for the photoemission experiments were lightly *n* doped (Sb, 3 Ω cm). The STM measurements were performed in a third UHV setup using heavily *n* doped (As, 5 mΩ cm) samples. The (1 × 1):H(D) surfaces for the photoemission experiments were obtained by hydrogen (deuterium) exposure (10 000 L, where 1 L = 1 Langmuir = 10<sup>-6</sup> torr s) of the clean 7 × 7 surface at a temperature of 400 °C, while the sample was facing a hot tungsten filament (1700 °C). The (1 × 1):H surface imaged in Fig. 1 was obtained by a hydrogen exposure of

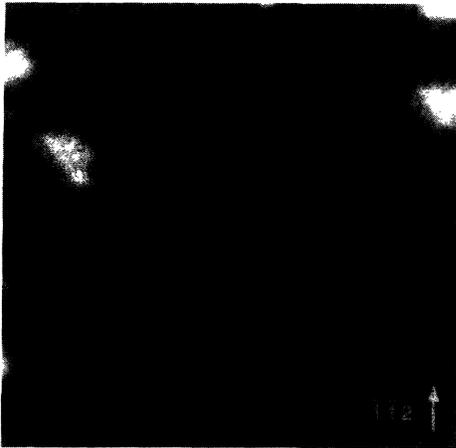


FIG. 1. Constant-current STM image,  $135 \text{ \AA} \times 135 \text{ \AA}$ , of the Si(111)-(1  $\times$  1):H surface (+2.5 V on the tip, 0.1 nA). The corrugation corresponding to the (1  $\times$  1):H surface is seen on almost the entire surface. Approximately 5% of the surface area is stacking faulted (triangular areas) and less than 2% of the surface atoms are pointlike defects, mainly missing hydrogen atoms and trihydride species. About 7% of the surface area is covered by islands, some of which exhibit hydrogen terminated 1  $\times$  1 structure. Note that the apparently large lateral extent of some of the pointlike defects partly is due to the finite size of the tip. In order to make the atomic corrugation visible on all levels of the surface, the image has been processed using statistical differencing.

5000 L at 380 °C. The *in situ* method results in sharp 1  $\times$  1 low-energy electron diffraction (LEED) patterns, occasionally with hardly noticeable streaks along the lines joining the 1  $\times$  1 spots. A detailed STM study of (1  $\times$  1):H surfaces prepared by this method is presented in Ref. [4].

The STM image in Fig. 1 clearly shows that the 7  $\times$  7 reconstruction has transformed to the (1  $\times$  1):H surface: over essentially the entire surface the atomic corrugation corresponding to the 1  $\times$  1:H surface can be seen. There are also some structural defects on the surface. The effect of these on the surface state band structure is minor as evidenced by the angle-resolved valence band spectra shown in Fig. 2. The two sharp peaks marked *a* and *a'* are due to the Si-H bond and the Si-Si backbond, respectively. The peak due to the backbond surface state (*a'*) has been considered as a sign of the quality of the surface since it is not seen on the ("7  $\times$  1"):H reconstruction (induced by moderate H exposures of the 7  $\times$  7 reconstruction [8]). It was first observed by Landmark, Karlsson, and Uhrberg [9] in the study of the (1  $\times$  1):H surface obtained by hydrogen exposure of the ( $\sqrt{3} \times \sqrt{3}$ ):In surface. Recently, Hricovini *et al.* [2] reproduced it on the (1  $\times$  1):H surface, prepared by chemical etching. It was suggested that the small widths obtained for *a* and *a'*, 330 and 280 meV full width half maximum [FWHM], respectively, were due to the long-range order and high degree of perfection of the chemically prepared (1  $\times$  1):H surface [2]. We obtain 330 and 310 meV (FWHM) for *a* and *a'* in the 17.5 eV spectrum (Fig 2), respectively, i.e., essentially the same widths as for the chemically prepared (1  $\times$  1):H surface. Tak-

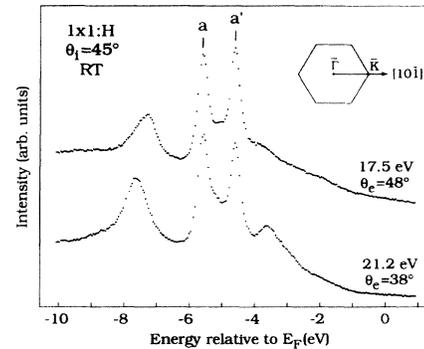


FIG. 2. Angle-resolved valence band spectra recorded with 17.5 and 21.2 eV for emission angles such that the Si-Si backbond surface state (*a'*) was probed close to the  $\bar{K}$  point in the 1  $\times$  1 surface Brillouin zone (shown as an inset). The structure *a* originates from the Si-H bonds.

ing the different energy resolutions into account, 150 meV for our study and 25 meV for Ref. [2], we obtain slightly smaller widths for our *in situ* prepared surface.

Figures 3 and 4 show a set of Si 2*p* core-level spectra recorded on the Si(111)-(1  $\times$  1):H surface (at  $T = 120 \text{ K}$ ) with different photon energies and emission angles, giving a variation of the surface sensitivity. The most bulk sensitive spectrum is shown in the bottom panel of Fig. 3, while the most surface sensitive is shown in Fig. 4. The corresponding spectrum of the (1  $\times$  1):D surface is included in Fig. 4, for comparison. It is clear from these spectra that they consist mainly of two components: the bulk component *B* and the surface component *S*. There is, however, a need for four more small components (*A1*, *A2*, *A3*, and *D*) to achieve a high-quality fit of the most surface sensitive spectra (Fig. 4). Note, however, that the *A1*–*A3* components are not interpreted as normal surface components (discussed further below).

The following section describes the fitting procedure used in our detailed analysis of the data. Figures 3 and 4 clearly demonstrate that we have used an accurate procedure resulting in consistent high-quality fits of spectra recorded with different photon energies and emission angles. The spectra were fitted using a nonlinear least squares method with components consisting of convolutions of Gaussian and Lorentzian functions (Voigt functions). As is obvious from the spectra in Fig. 4 they consist of two main components, corresponding to the two peaks that are clearly resolved. The Gaussian width obtained from the fitting for these components, *B* and *S*, is 160 meV. It is not possible to change this value by more than  $\approx 20 \text{ meV}$ ; a smaller value just results in the need for introducing several more components. This Gaussian width was then used for all surface components. The Gaussian width for the bulk component was, however, allowed to vary since the width of the bulk component is larger in surface sensitive spectra (presumably due to small unresolved shifts for the near surface layers that are included in the bulk component) [10]. Results

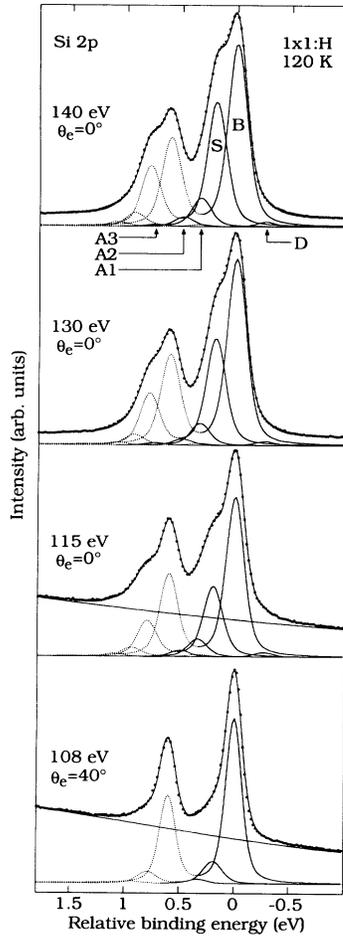


FIG. 3. Si  $2p$  spectra (raw data) recorded with various photon energies on the  $1 \times 1$ :H surface and their decompositions. The fitted background to the two lowermost spectra is also shown. The two topmost spectra were fitted with an integrated background (not shown). The energy shifts for the  $S$ ,  $A1$ ,  $A2$ ,  $A3$ , and  $D$  surface components are 193, 335, 495, 745, and  $-264$  meV, respectively. Note that the  $A1$ ,  $A2$ , and  $A3$  components are not interpreted as normal surface components. They have to be included in order to obtain a high-quality fit of the most surface sensitive spectra using Voigt functions.

from gas phase Si  $2p$  core-level spectroscopy of  $\text{SiH}_4$  give a Lorentzian width of 45 meV [6], while a value of 35 meV for the Lorentzian width was used in the study of the chemically prepared  $(1 \times 1)$ :H surface [2]. We have, however, used a Lorentzian width of  $80 \pm 5$  meV simply because it gave better fits of the most surface sensitive spectra. The spectra in this study can be fitted with a Lorentzian width of 35 meV without altering any conclusion in this paper. The spin-orbit splitting was 602 meV and the branching ratio between the  $2p_{1/2}$  and the  $2p_{3/2}$  peaks was  $0.51 \pm 0.03$  for all spectra. These values were determined from both the fitting procedure and by minimizing the oscillations of the low energy tail of the spectra when subtracting the  $2p_{1/2}$  contribution. With the above-described procedure and values it was possible to achieve

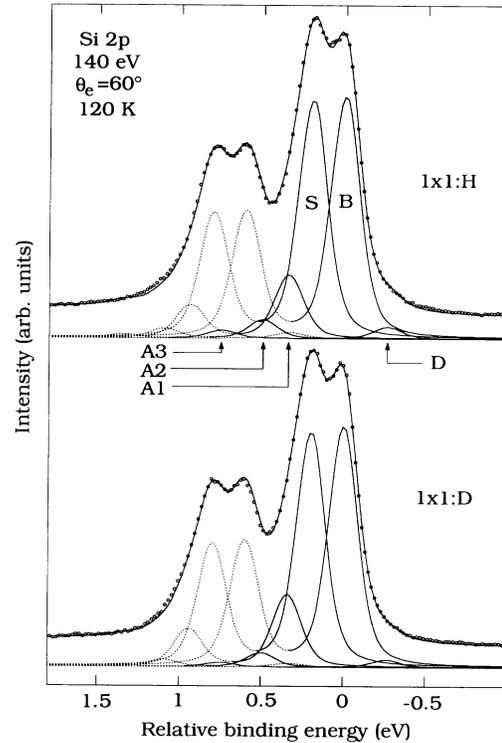


FIG. 4. Si  $2p$  spectra (raw data) recorded with 140 eV at an emission angle of  $60^\circ$  on the  $1 \times 1$ :H and  $1 \times 1$ :D surfaces. The spectra were fitted with an integrated background. Note that the spectra and their decompositions are virtually identical.

high-quality fits of all spectra with a variation of the surface core-level shifts within  $\pm 5$  meV.

Two of the surface components in the Si  $2p$  core-level spectra recorded on the chemically prepared  $(1 \times 1)$ :H surface have been attributed to discrete Si-H vibrational losses [2]. This assignment was based on the gas phase Si  $2p$  core-level spectroscopy studies which identified intense Si-H stretching vibrational losses [6, 7]. Figure 4 compares surface sensitive Si  $2p$  core-level spectra recorded on the  $1 \times 1$ :H and  $1 \times 1$ :D surfaces together with decompositions of the spectra. Note that these surfaces have been prepared with identical experimental parameters. Independent of the details of the decompositions one can conclude that the spectra consist of virtually identical sets of components. Since there would be a difference in the energies (by a factor of  $\sqrt{2}$  assuming a linear harmonic oscillator) of the vibrational losses for H and D due to their different masses, one expects any vibrationally related component to show the corresponding energy shift. This isotope effect is indeed observed for gas phase  $\text{SiH}_4$  and  $\text{SiD}_4$ , giving a factor of 1.39 between the stretching vibrational energies (295 meV for H and 212 meV for D) [7]. Since there is virtually no difference between the decompositions of the  $1 \times 1$ :H and  $1 \times 1$ :D spectra, we can conclude that there are no Si-H(D) stretching vibrational losses in the Si  $2p$

core-level spectra of the  $1 \times 1:H$  and  $1 \times 1:D$  surfaces, contrary to the findings in Ref. [2].

Why are six components needed to fit a Si  $2p$  core-level spectrum from such a simple surface? In a simple picture one expects that the Si  $2p$  core-level spectra should consist of a bulk component and a surface component due to the Si atoms binding to the H atoms, and indeed, the spectra are composed of two main components ( $B$  and  $S$ ). The inclusion of the  $A1$ ,  $A2$ ,  $A3$ , and  $D$  components is, however, necessary to achieve a wholly satisfactory fit. There are in principle two conceivable simple explanations to the  $A1$ – $A3$  and  $D$  components: defects and different layers beneath the topmost Si layer. It is not possible to exclude that there is some contribution from defects to these components. However, the high degree of similarity between the Si  $2p$  spectra obtained in this study and the Si  $2p$  spectra recorded on the chemically prepared  $1 \times 1:H$  surface provides information about the extent of this contribution. The number of defects on the chemically prepared surface is reported to be very small [11] and they should also be of a different type compared to the defects on the surfaces we have studied. Despite these differences concerning the defects, the spectra are very similar, which indicates that the contribution from the defects is small [12]. Another conceivable contribution to the four minor components is emission from some of the layers beneath the topmost Si layer. This explanation is, however, not likely since the atoms in these layers are located in a very bulklike environment and therefore should not exhibit shifts that are as large as the shifts for the  $A1$ ,  $A2$ , and  $A3$  components. Neither of the two explanations described above seems plausible. Besides the  $D$  component, which may be due to defects, we propose that the occurrence of  $A1$ – $A3$  is due to asymmetric phonon broadening [13].

Applying the Franck-Condon model to a diatomic molecule results in a more or less asymmetric Franck-Condon envelope. In analogy, the Franck-Condon model applied to a solid, using harmonic potentials with phonon states closely and equally spaced in energy, results in a phonon broadening which has a varying degree of asymmetry. If the difference between the equilibrium nuclear coordinates for the initial and final states is large, the phonon broadening approaches a Gaussian in the limit of a large number of phonons [14]. The phonon broadening is normally considered to be Gaussian. It has been concluded from theoretical studies that the excitations of phonons in the final state in photoemission can give rise to a Gaussian phonon broadening [15]. However, if the difference in the equilibrium coordinates for the initial and final states is small, the resulting line shape can be significantly asymmetric. For gas phase Si  $2p$  core-level spectroscopy of  $\text{SiH}_4$ , the difference is small since the adiabatic peak (transitions from  $\nu = 0$  to  $\nu' = 0$ ) is the strongest [7]. This gas phase observation is an example where the decreasing intensity with increasing  $\nu'$  represents an asymmetry case. Based on the above discussion, we propose that  $A1$ – $A3$  mainly originate

from asymmetric phonon broadening of the surface component ( $S$ ). This asymmetry could be detected due to the very high resolution in this experiment. The need for  $A1$ – $A3$  is thus merely an artifact of the use of symmetric Voigt functions.

In conclusion, we have clearly demonstrated that Si-H(D) stretching vibrational losses are not significant in the Si  $2p$  core-level spectra from Si(111)-(1  $\times$  1):H(D) surfaces. Our interpretation of the core-level spectra is straightforward, i.e., they consist of a bulk component and a surface component as expected for the simple  $1 \times 1:H$  surface. The surface component is found to be asymmetric which we propose is due to asymmetric phonon broadening. The quality of the photoemission spectra of the Si(111) $1 \times 1:H$  surface, prepared by the simple well-defined *in situ* method, is equally high as those recorded on the chemically prepared  $1 \times 1:H$  surface.

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- [10] The Gaussian widths for the bulk component were 130, 145, 160, and 160 meV for the spectra recorded with a photon energy of 108, 115, 130, and 140 eV, respectively.
- [11] P. Jakob *et al.*, *Surf. Sci.* **285**, 251 (1993).
- [12] Many of the defects on the surfaces we have studied are expected to contribute to the  $S$  component. To exactly predict the effects of the defects on the binding energies is, however, very difficult.
- [13] Asymmetry due to metallic screening of the core hole, which gives rise to the asymmetric Doniach-Šunjić (DS) line shape, is not expected since the  $1 \times 1:H(D)$  surface is semiconducting with no surface states in the fundamental band gap. The DS line shape has been used earlier for the Si(100)-(2  $\times$  1) surface; however, we recently showed that it was incorrect [E. Landemark *et al.*, *Phys. Rev. Lett.* **69**, 1588 (1992)].
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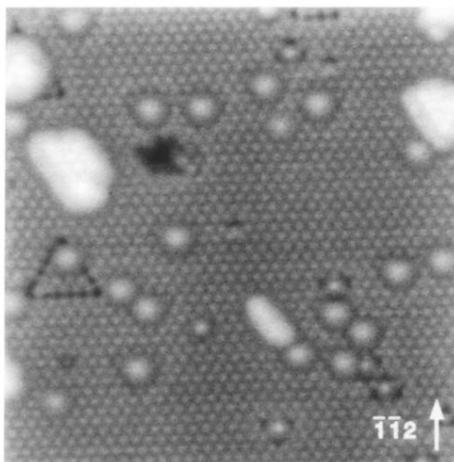


FIG. 1. Constant-current STM image,  $135 \text{ \AA} \times 135 \text{ \AA}$ , of the Si(111)-(1  $\times$  1):H surface (+2.5 V on the tip, 0.1 nA). The corrugation corresponding to the (1  $\times$  1):H surface is seen on almost the entire surface. Approximately 5% of the surface area is stacking faulted (triangular areas) and less than 2% of the surface atoms are pointlike defects, mainly missing hydrogen atoms and trihydride species. About 7% of the surface area is covered by islands, some of which exhibit hydrogen terminated 1  $\times$  1 structure. Note that the apparently large lateral extent of some of the pointlike defects partly is due to the finite size of the tip. In order to make the atomic corrugation visible on all levels of the surface, the image has been processed using statistical differencing.