

Determination of Chemical Shifts in Si2p Core-Level Spectra for Silicon-Hydrogen Bonds on Chemically-Cleaned Si(100) and Si(111) Surfaces

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The energy positions of the various Si-H_x chemical states in the Si2p core-level spectrum of H-terminated Si surfaces mostly prepared by UHV cleaning and atomic hydrogen exposure have been studied by synchrotron radiation, although the extent of chemical shifts are still controversial. Hricovini et al.¹⁾ measured a chemical shift of 140 meV with respect to the bulk Si2p_{3/2} peak for the Si-H component on Si(111) surfaces. Yamamoto et al.²⁾ studied H-terminated Si(100) and obtained chemical shifts of 300 and 500 meV for the Si-H and Si-H₂ bonds, respectively. Karlsson et al.³⁾ recently assigned an energy shift of 193 meV for Si-H bonds on H-terminated Si(111) surfaces.

In this paper we have determined the chemical shifts of Si-H and Si-H₂ bonds on chemically-cleaned Si(100) and Si(111) surfaces by employing high-resolution XPS measurements (Scienta ESCA-300 instrument with monochromatized AlK α radiation). The core-level spectra were acquired at a take-off angle of 5° in order to enhance the signal from the surface. The p-type Si(111) and Si(100) substrates were first cleaned in an SC1 solution at 80°C for 10 min. Then the H-terminated surfaces were obtained through three different treatments for 5 min: a) Si(111) with 40 % NH₄F, b) Si(111) with 4.5 % HF, and c) Si(100) with 1 % HF. All treatments were followed by a short rinsing in deionized water and loaded into the XPS chamber by disconnecting the various vacuum gages. This loading procedure resulted in a significant reduction of total surface contamination of C, O and F to less than 6 at%. The Si2p core-level peak has been deconvoluted into the Si2p_{3/2} and Si2p_{1/2} components with a 0.61 eV spin-orbit splitting and an intensity ratio of 0.5. Shirley background subtraction, Voigt line shape for bulk peaks and Gaussian shape for Si-H_x peaks have been employed for the deconvolution. Also, the Si2p_{3/2} and Si2p_{1/2} peaks showed an asymmetric component as reported in other studies.³⁾

The influence of crystallographic orientations and different HF-based solutions on the actual H-termination of the surface is displayed in Fig. 1. The NH₄F-treated, atomically-flat Si(111) surface exhibits stronger signal around the Si 2p_{3/2} component while 4.5% HF-treated Si(111) and 1% HF-treated Si(100) show increased signal around and above the Si2p_{1/2} component. These variations can be explained by the fact that NH₄F-treated Si(111) exhibits almost exclusive monohydride termination while the other surfaces also show dihydride and trihydride termination as confirmed by FT-IR-ATR (Attenuated Total Reflection) studies.⁴⁾ The deconvolution of the Si2p spectra shown in Figs. 2, 3 and 4 indicates that the H-termination of the NH₄F-treated Si(111) surface is dominated by the Si-H

component whereas the HF-treated Si(111) and Si(100) surfaces exhibit both Si-H and Si-H₂ components. Note that the Si-H₂ component of Si(100) is as intense as the Si-H one.

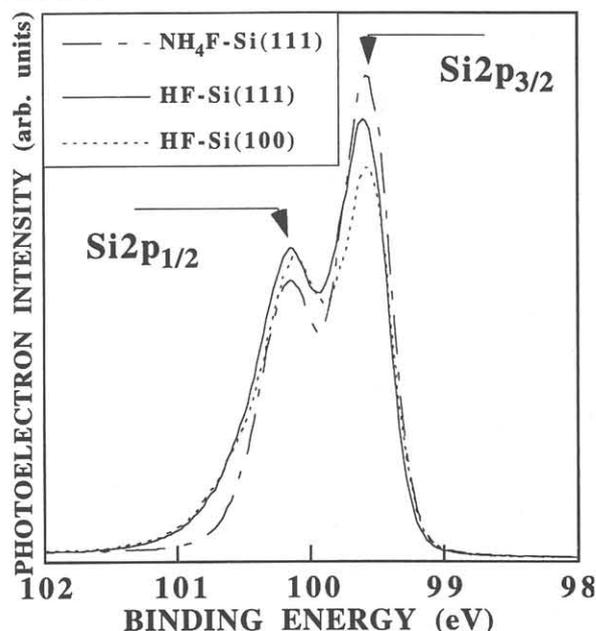


Fig. 1 : Si2p core-level spectra obtained from differently H-terminated Si(111) and Si(100) surfaces.

This is consistent with the results of previous FT-IR-ATR studies in which the HF-treated Si(111) surface show an equally strong Si-H₂ peak together with Si-H and the Si(100) surface exhibits a predominant Si-H₂ peak together with trihydride and monohydride.^{4,5)} This crystallographic orientation dependence has enabled us to evaluate the chemical shifts for monohydride and dihydride to be 250 and 480 meV, respectively, in close agreement with those found in Refs. 2 and 3. In addition, we have observed two very small contributions (peaks labeled as A) with an estimated chemical shift equal or higher than 710 meV which might be induced by extra asymmetric phonon broadening³⁾ or otherwise by the presence of Si-H₃ as also detected in previous infrared studies,^{4,5)} although in this case a precise evaluation of the chemical shift is not possible due to the very small signal. As indicated in Table I, the respective FWHMs of the Si-H_x species are broadened as x increases from 1 to 2, similar to what was observed for the different oxidation states of Si. In addition, the relative concentrations of the Si2p signal originating from bulk Si, Si-H, Si-H₂, and asymmetric phonon broadening A or Si-H₃ for the different surfaces are summarized in

Table I as well. The ratio of Si-H to Si-H₂ termination decreases as the Si(111) becomes rougher and also when comparing Si(111) to Si(100) surfaces.

In summary, the chemical shift of the monohydride and dihydride chemical bonds in the Si2p core-level spectrum has been determined by comparing various H-terminated Si surfaces.

References

- 1) K. Hricovini, R. Günther, P. Thiry, A. Taleb, Ibrahimi, G. Indlekofer, J. E. Bonnet, P. Dumas, Y. Petroff, X. Blase, X. Zhu, S. G. Louie, Y. J. Chabal, and P. A. Thiry, *Phys. Rev. Lett.* **70**, 1992 (1993).
- 2) K. Yamamoto and M. Hasegawa, *J. Vac. Sci. Technol. B* **12**, 2493 (1994).
- 3) C. J. Karlsson, F. Owman, E. Landemark, Y.-C. Chao, P. Mårtensson, and R. I. G. Uhrberg, *Phys. Rev. Lett.* **72**, 4145 (1994).
- 4) T. Yasaka, K. Kanda, K. Sawara, S. Miyazaki, and M. Hirose, *Jpn. J. Appl. Phys.* **30**, 3567 (1991).
- 5) M. Hiroshima, T. Yasaka, S. Miyazaki, and M. Hirose, *Jpn. J. Appl. Phys.* **33**, 395 (1994).

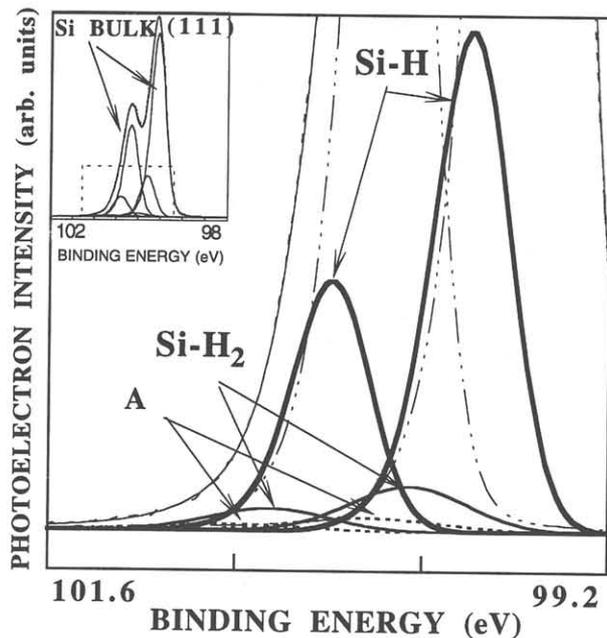


Fig. 2 : Si2p core-level spectrum obtained from a NH₄F-treated Si(111) surface expanded in the Si-H_x energy range.

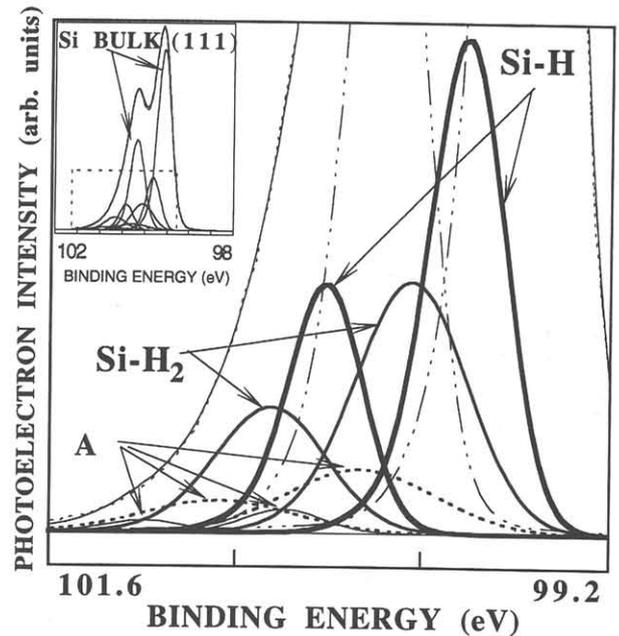


Fig. 3 : Si2p core-level spectrum obtained from a HF-treated Si(111) surface expanded in the Si-H_x energy range.

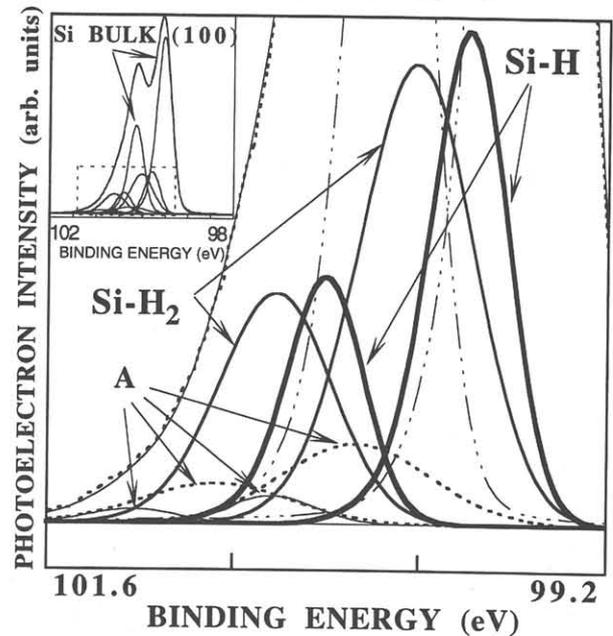


Fig. 4 : Si2p core-level spectrum obtained from a HF-treated Si(100) surface expanded in the Si-H_x energy range.

Table I : Energy shifts (relative to bulk Si 2p_{3/2}), FWHM, and intensity relative percentage for each Si-H_x and phonon broadening peak.

	Energy (meV)	FWHM (meV)	NH ₄ F-Si(111)	HF-Si(111)	HF-Si(100)
Bulk Si	0	380±10	79.8 %	64.1 %	62.0 %
Si-H	250±20	380±20	17.0	18.0	14.2
Si-H ₂	480±20	560±30	2.3	13.4	19.4
A or Si-H ₃	710±50	750±50	0.9	4.5	4.4