

Atomic origins of the surface components in the Si 2*p* core-level spectra of the Si(111)7×7 surface

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The 7×7 surface has been studied with Si 2*p* core-level spectroscopy using an experimental resolution better than 70 meV at a temperature of 120 K. The spectra are much more well resolved than earlier reports and provide considerably more information. They consist of a bulk component and five surface components, three of which appear as peaks or shoulders in the spectra. We find that the component that is shifted 0.70 eV to lower binding energies (S_2) is due to the rest atoms. The contribution from the adatoms is revealed by a component, twice as large as S_2 , shifted 0.53 eV to higher binding energies.

The atomic origin of the surface components in the core-level spectra of clean semiconductor surfaces has been the subject of an ongoing debate for many years. The debate has also concerned many basic matters, e.g., charge transfer and atomic structure as well as the very understanding of the mechanisms which cause the surface core-level shifts. Especially, core-level spectroscopy of the Si(111)7×7 and Si(100)2×1 surfaces has been discussed extensively.¹⁻⁷ Recently, however, the core-level spectroscopy study by Landemark *et al.*⁶ in combination with the theoretical study by Pehlke and Scheffler⁷ established the origins of the different surface components in the spectra from Si(100)2×1. In the case of the 7×7 surface there still exist two alternative interpretations of the spectra: the essential difference being a factor of 2 of the escape depth. The conclusions drawn from the two interpretations are very different with respect to the issues mentioned above.

The Si 2*p* core-level spectra of the Si(111)7×7 surface have earlier been decomposed into three components: a bulk component, a surface component shifted ≈ 0.3 – 0.4 eV to higher binding energies (S_1), and a surface component shifted ≈ 0.7 – 0.8 eV to lower binding energies (S_2).^{2,4,5} Two different kinds of surface atoms have been suggested to give rise to S_2 : the twelve adatoms or the six rest atoms (plus possibly one corner hole atom). S_1 has been assigned to the atoms binding to the adatoms plus either the rest atoms or the adatoms depending on the assignment of S_2 . The presence of the nine dimers in the 7×7 unit cell and the stacking fault in one-half of the unit cell have been argued to be responsible for the fairly large widths of the components.²

The main argument for assigning S_2 to the rest atoms is a charge transfer resulting in a completely filled surface-state band located mainly on the rest atoms and a partially occupied surface-state band corresponding to the adatom dangling bonds.⁸ Assuming that the remaining valence electron configuration is similar to that of the bulk, this charge transfer should result in a valence charge which is larger (smaller) on the rest atoms (adatoms) compared to the bulk atoms. This change in charge would, neglecting final-state contributions, result in a lower (higher) ionization energy for the Si 2*p* core electrons of the rest atoms (adatoms) compared to the bulk atoms. In the alternative interpretation, the S_2 com-

ponent is instead assigned to the adatoms⁴ which, initially, was based on the different bonding geometry for the adatoms compared to other surface atoms as observed in scanning tunneling microscope (STM) images. Recently, a photoemission extended x-ray absorption fine structure (EXAFS) analysis resulted in the adatom assignment of S_2 .⁵ It has been argued that the contradiction of this assignment with the charge transfer is due to final-state effects. The intensity of S_2 has been used as an argument for both the rest-atom and adatom assignment.^{2,4}

In this paper we report Si 2*p* core-level spectra recorded on the Si(111)7×7 surface at a temperature of 120 K utilizing a total-energy resolution of better than 70 meV. These spectra provide considerably more information compared to earlier reports. By mere visual inspection of the spectra we can identify three surface components. The energy shifts and the widths of the components used to fit the spectra are constrained to a large extent by the raw data which allow for comparatively accurate determinations of the intensities of the components. Based on the intensities and the mutual relations between the intensities of the components we assign S_2 to the rest atoms and a surface component (S_3) twice as large as S_2 and shifted 0.53 eV to higher binding energies is assigned to the adatoms. These assignments are consistent with the charge transfer that occurs on the surface. Further, a component (S_1) due to the atoms binding to the adatoms and a component (S_4) which possibly could originate from the dimers are identified.

The measurements were performed at beam line 22, comprised of an SX-700 plane grating monochromator and a large hemispherical analyzer (radius 200 mm), at the MAX synchrotron radiation facility in Lund, Sweden. The total energy resolution was better than 70 meV and the angular acceptance was $\pm 8^\circ$ for all Si 2*p* core-level spectra presented in this paper. The angle between the incident photon beam and the analyzed photoelectrons was 40° . All spectra in this paper were recorded along the [101] bulk azimuthal direction. The Si(111) sample (Sb doped, 3 Ω cm) was cleaned and preoxidized⁹ before insertion into the ultrahigh vacuum chamber. The chemical oxide was removed by direct-current heating of the sample to 850 $^\circ$ C for several minutes. The resulting 7×7 surface exhibited a sharp 7×7 low-energy electron diffraction pattern.

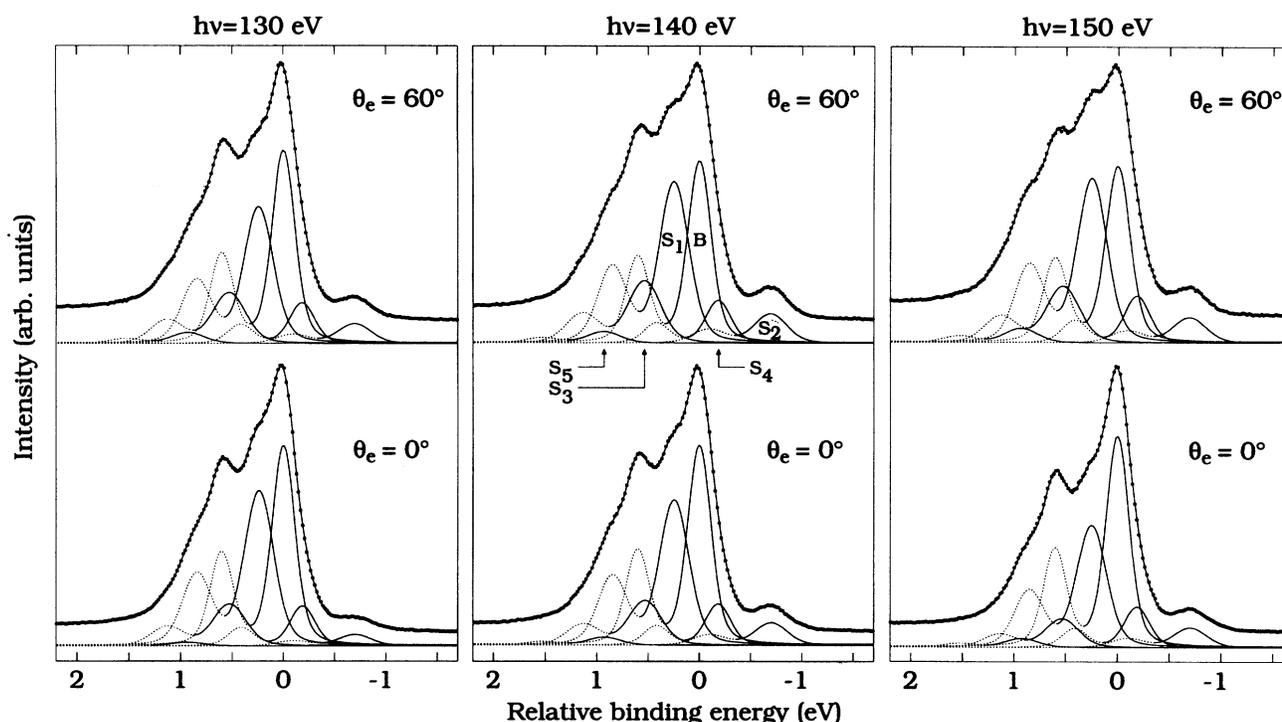


FIG. 1. Surface-sensitive Si $2p$ core-level spectra recorded on the 7×7 surface for various photon energies and emission angles at a temperature of 120 K and their decompositions. The spectra were fitted with an integrated background (not shown). The energy shifts for the S_1 , S_2 , S_3 , S_4 , and S_5 surface components are 244, -698 , 530, -183 , and 930 meV, respectively. The solid curves through the data show the resulting fits. Each spin-orbit-split component is indicated by a solid curve ($p_{3/2}$) and a dashed curve ($p_{1/2}$).

Figure 1 shows six surface-sensitive Si $2p$ core-level spectra together with the results from a curve-fitting procedure (described below). The spectra alone immediately show the existence of three surface components. The S_1 and the S_2 surface components are readily seen in all spectra. They are most intense in the spectra recorded with photon energies of 140 and 150 eV at an emission angle (θ_e) of 60° . The existence of the S_3 surface component is evidenced by the shoulder (due to the $p_{1/2}$ peak of S_3) at ≈ 1.2 eV relative binding energy in the spectrum recorded with a photon energy of 130 eV at $\theta_e = 60^\circ$. The presence of a fourth surface component (S_4) is seen best in the more bulk-sensitive Si $2p$ core-level spectrum shown in Fig. 2, in which S_4 fills up the valley between the bulk component (B) and S_2 . The need for the S_5 surface component is due to the tail at low binding energies of the spectrum recorded with a photon energy of 140 eV (and 150 eV) at $\theta_e = 60^\circ$.

In order to extract more quantitative information about the energy shifts and the intensities for the different components we employed a curve-fitting procedure utilizing Voigt line shapes to represent each spin-orbit-split component.¹⁰ An accurate determination of the intensities and energy shifts of the components demands precise knowledge about the widths of the components. It turned out that the widths of the five largest components were controlled to a large degree by the shape of the spectra. We used a Lorentzian width of 85 meV for all components [this value has earlier successfully been used for a Si(111) 1×1 :H surface,¹¹ which exhibits the most narrow Si $2p$ core-level spectra] and determined the

Gaussian width as follows. The Gaussian width of S_2 (330 meV) was determined by the best fit of the corresponding peak in the spectrum recorded with a photon energy of 140 eV at $\theta_e = 60^\circ$ (Fig. 1). The Gaussian widths of S_1 (290 meV) and S_4 (240 meV) were determined from the spectra recorded with photon energies of 115 eV (Fig. 2) and 120 eV (not shown) for which the width of the bulk component is constrained by the main peak. Using these Gaussian widths, the best fits were obtained with the same width for S_3 as the

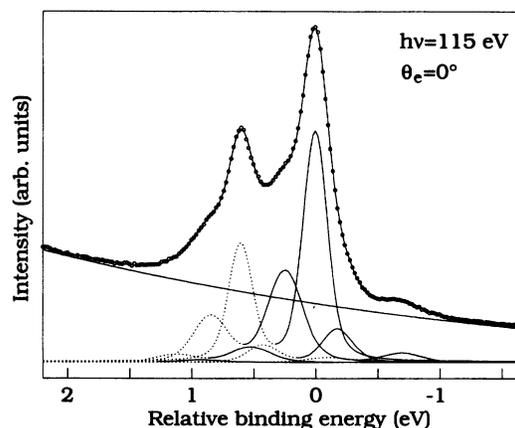


FIG. 2. Si $2p$ core-level spectrum recorded on the 7×7 surface with a photon energy of 115 eV at $\theta_e = 0^\circ$ at a temperature of 120 K. The spectrum was fitted with an exponential background.

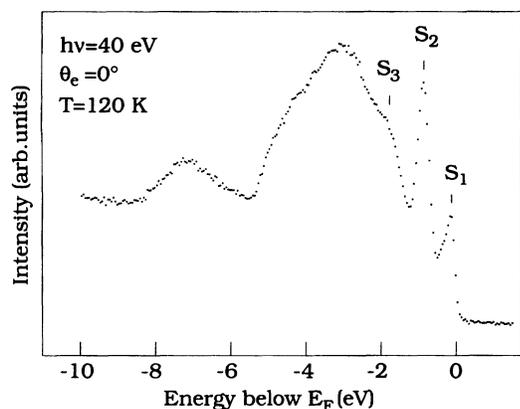


FIG. 3. Valence-band spectrum showing the characteristic surface states S_1 , S_2 , and S_3 corresponding to the adatom dangling bonds, rest-atom dangling bonds, and the adatom back bonds, respectively.

width of S_2 . The Gaussian widths for the bulk component varied slightly (185–220 meV) with photon energy.¹² Inclusion of the small S_5 surface component (with a Gaussian width of 330 meV) resulted in high-quality fits of all spectra, also for those recorded with other photon energies and emission angles not shown here, with a variation of the surface core-level shifts within ± 5 meV. This consistency of the fits, due to the high quality of the raw data, makes the determined shifts and intensities reliable.

Three important facts are immediately obtained from the curve fitting: (i) the intensity of S_3 is roughly twice that of S_2 , (ii) the intensity of S_1 is roughly three times that of S_3 , (iii) the relative intensity of S_4 (I_{S_4}/I_{tot}) varies very little between the different spectra (see Figs. 1 and 2), indicating that S_4 originates from a layer below the outermost one. These mutual intensity relations and the individual intensities of the components (discussed below) lead to a simple and straightforward interpretation of the spectra: S_2 is due to the rest atoms, S_3 originates from the adatoms (which are twice as many as the rest atoms), S_1 is due to the atoms binding to the adatoms (which are three times more than the adatoms), and finally S_4 originates from either the dimer atoms, which are located in the lower half (second layer) of the first double layer, or from second-layer atoms in one half of the unit cell (unfaulted or faulted half).

A simple explanation of the small S_5 component would be contamination, e.g., carbon or oxygen. We could, however, detect neither carbon nor oxygen using photon energies which should result in the largest cross sections for the 1s core level of these elements. Also the valence-band spectrum in Fig. 3, which exhibits strong surface-state emission, shows that contamination is a very unlikely origin for S_5 . Another conceivable explanation would be asymmetry of the adatom component S_3 due to metallic screening of the core holes (the 7×7 surface is metallic due to the partially occupied adatom dangling-bond band) or some other deviation from the Voigt line shape of some component. Yet another guess would be defects. However, S_5 is very small and represents an unresolved component and it is thus hard to make a positive assignment.

Recently, large oscillations of the intensity ratio between

the S_2 and the B components as a function of photon energy were reported by Carlisle *et al.*⁵ These oscillations are not consistent with a smoothly varying escape depth and they thus demonstrate the need for considering many spectra recorded with different photon energies when estimating the number of surface atoms contributing to a certain component. In cases where assignments have been made unambiguously, the obtained escape depths are in the range 2–4 Å, for photoelectrons excited with photon energies of 130–150 eV. These cases include, e.g., Si(100) 2×1 and $c(4\times 2)$,⁶ Si(111) 1×1 :H,¹¹ Si(111) $\sqrt{3}\times\sqrt{3}$:In,¹³ and Si(111) 1×1 :As.^{14,15} Correct assignments of the surface components for the 7×7 surface should be consistent with an average escape depth in this range. In fact, the values of the intensity ratios for the S_2 and B components, presented by Carlisle *et al.*⁵ (Fig. 2 in that paper), result in an average escape depth of ≈ 3.1 Å (for photoelectrons excited with the most surface-sensitive photon energies 130–150 eV) for an assignment of S_2 to the six rest atoms,¹⁶ which is in good agreement with those obtained from the other surfaces.

For the normal emission spectra recorded with photon energies of 130–150 eV presented in this paper, the assignments stated above for S_1 – S_4 result in escape depths of the photoelectrons between 2 and 4 Å. There is one exception though; the assignment of S_2 in the 130-eV spectrum to the rest atoms gives an escape depth of 5.6 Å. However, S_2 assigned to the adatoms gives an escape depth of 12 Å for the photoelectrons excited with a photon energy of 130 eV, which is in strong contradiction to any other reported value.

The Si $2p$ core-level spectra reported by Carlisle *et al.*⁵ were recorded with photon energies in the range 108–320 eV. They used the oscillations of the intensities of their B , S_1 , and S_2 components for an EXAFS analysis, resulting in the adatom assignment of the S_2 component. Note, however, that it is clear from our spectra presented here that their decompositions are erroneous and thus the EXAFS analysis is likely to lead to spurious conclusions. It is also important to point out that the intensities of the components are affected significantly by photoelectron diffraction.

These photoelectron diffraction effects as well as the uncertainty in the escape depth introduce an uncertainty in our assignments of the components since they are based on the intensities of the different components. In addition, the experimentally determined intensity of a component can suffer from errors due to uncertainties in the width and the line shape. Detached from its context, the assignment of, e.g., S_1 to the atoms binding to the adatoms may therefore seem somewhat uncertain and indeed we cannot exclude that S_1 has some other smaller contribution, e.g., one half of the second layer. However, our assignments give escape depths in the proper range and they are consistent with the mutual intensity relations among the different components. Our assignments of S_2 and S_3 are also consistent with the charge transfer between the adatom dangling bonds and the dangling bonds of the rest atoms. The charge transfer was inferred from a theoretical study of the electronic structure of a 2×2 adatom structure, which exists on the terraces of the 7×7 unit cell.⁸ Moreover, the charge transfer is corroborated by another theoretical study,¹⁷ by STM,¹⁸ and by angle-resolved photoelectron spectroscopy.¹⁹ Recently, an *ab initio* total-energy calculation of the 7×7 structure concluded that

charge transfer occurs.²⁰ As mentioned earlier, this charge transfer should, in an initial-state picture, lead to a lower (higher) ionization energy for the Si 2*p* core electrons in the rest atoms (adatoms) compared to the bulk atoms.

In general, there are also final-state contributions to the shift since the screening of the core hole by the valence electrons in the final state may be different in the bulk and at the surface. Recently, a theoretical study inferred that the screening of the core holes on the Si(100) surface is site sensitive.⁷ The screening of the down atom of the asymmetric dimer was found to be more effective than the screening for the bulk atoms. This result was depicted to originate from the filling of a dangling-bond state by electrons from the Fermi level after the ionization. This state, which is located on the down atom, is initially empty. This extreme example of screening (complete filling of an empty dangling-bond state) resulted in a final-state contribution to the surface core-level shift of ≈ 0.5 eV. Turning to the 7×7 surface: the S_2 surface component in the spectra of the 7×7 surface is located 0.70 eV above the bulk component. If the atoms giving rise to S_2 would experience the same extreme screening as the down atoms on the Si(100) surface they would, in an

initial-state picture, be located 0.2 eV above the bulk component. Thus, still under the assumption of extreme screening effects as for the down atoms on Si(100) 2×1 , the S_2 component would have to be assigned to the rest atoms which in an initial-state picture should have a shift to lower binding energies.

To summarize, high-quality Si 2*p* core-level spectra recorded on the 7×7 surface are presented. They are decomposed using five surface components, three of which are manifested by peaks or shoulders in the spectra. The component shifted 0.70 eV to lower binding energies (S_2) is assigned to the rest atoms. The component shifted 0.53 eV to higher binding energies, twice as large as S_2 , is assigned to the adatoms. These are the only assignments consistent with the observed intensities of the components. Further, our high-resolution spectra clearly demonstrate that analysis based on the intensities or intensity oscillations of the components used in earlier reported spectra can lead to erroneous conclusions.

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