

Correlation of surface core levels and structural building blocks for the Si(111)-7×7 reconstruction through high-resolution core-level spectroscopy

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The Si(111)-7×7 reconstruction is investigated by high-resolution core-level spectroscopy. A detailed line-shape analysis of spectra recorded over a wide photon energy range demonstrates the presence of four surface-derived components in the Si 2*p* line. These are attributed to the structural building blocks of the (7×7) structure through their relative intensities, evaluated for different photon energies in order to take photoelectron-diffraction effects into account, and on the basis of temperature-dependent changes in line shape that occur in the (7×7)-(1×1) phase transition at around 1130 K.

The Si(111)-7×7 reconstruction is probably the most frequently studied semiconductor surface; as such, it is important to understand the relationship between the geometric and electronic structure of its building blocks. In order to understand the electronic structure, photoelectron spectroscopic investigations of the silicon 2*p* core-level spectrum, and the occurrence of surface-core-level (SCL) emission, have been studied by several authors (see, for example, Refs. 1–6). It is hence surprising that the origin of the SCL shifts is still a subject of controversy. Here we demonstrate by high-resolution core-level photoemission that, apart from the two surface lines that were previously found, additional core-level shifts exist. By comparing our low-temperature (100 K) data with spectra that were recorded above the temperature of the (7×7)-(1×1) phase transition, and through an evaluation of SCL intensities over a range of photon energies, we arrive at a consistent assignment of the SCL peaks to the different moieties of the (7×7) structure.

The Si 2*p* core level of the Si(111)-7×7 has been investigated using the BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H.) beamline HEPGM3 and a hemispherical electron-energy analyzer (ESCALAB by Fisons Ltd., G.B.), resulting in an overall instrumental resolution of between 40 and 60 meV in the energy range from 108 to 190 eV as determined from the Xe 4*d* gas-phase photoemission.^{7,8} The photoelectron spectra were measured with an angular acceptance of 15° in normal emission. Samples were *p*-doped wafers (Wacker Chemitronics, 5–10 Ω cm) oriented within 0.5° of the (111) direction, and were cleaned using a careful degassing and flashing procedure.⁹ The preparation technique was checked using a scanning tunneling microscope, and routinely results in a defect density of less than $\frac{1}{100}$ of a monolayer, mostly due to missing adatoms. In order to avoid sample contamination, the sample preparation procedure was repeated every 60–90 min. The pressure in the vacuum system was $1\text{--}2 \times 10^{-10}$ mbar during data acquisition and below 1×10^{-9} mbar during the flashing procedure. For experiments at elevated temperatures our computer-controlled chopping system was employed.^{10,11}

A representative set of spectra, for photon energies from 108 to 153 eV is shown in Fig. 1. The bottom trace shows the bulk-sensitive spectrum measured at a photon energy of 108 eV. Here, the well-resolved 2*p*_{3/2}-2*p*_{1/2} doublet from bulk silicon atoms is evident. Spectra at 120 and 131 eV demonstrate how the main intensity shifts into the surface emission, rendering the bulk peaks (identified from their narrow line-width) less dominant. Even though the so-called “universal curve” of electron mean free paths¹² would suggest that no decrease of surface sensitivity should occur when going to slightly higher photon energies, the top spectrum ($h\nu=153$ eV) shows that the bulk peaks are certainly more prominent here than at 131 eV; this observation is explained below. Due to the high signal-to-noise ratio several surface-related features can be located directly by visual inspection; they are

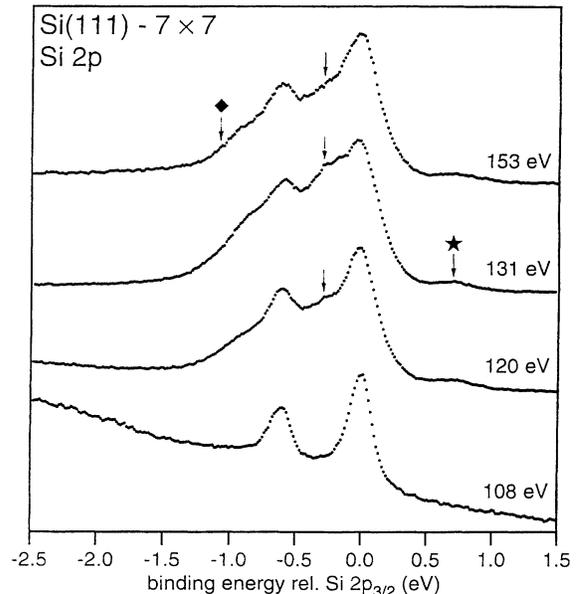


FIG. 1. Photoelectron spectra of the Si(111)-7×7 Si 2*p* core level at different photon energies as indicated. Arrows, diamond, and asterisk indicate features in the spectra that are enhanced under conditions of increased surface sensitivity.

marked by arrows. There is a clearly visible peak at high kinetic energies (asterisk), named S_2 by previous investigators. The filling up of the "valley" in between the main spin-orbit split peaks (arrow) is caused by another SCL named S_1 . However, the shoulder on the low-kinetic-energy side of the peak with an inflection visible in the top spectrum (diamond) cannot be attributed to emission from S_1 as will be shown below. We are thus led to postulate a different, third component (S_3) at this stage.

In order to more quantitatively evaluate the contributions to the Si $2p$ spectrum, the spectra were analyzed by means of a least-squares-fitting procedure¹⁰ based on the Levenberg-Marquardt algorithm. Lorentzian peaks numerically convoluted by a Gaussian (for the description of instrumental resolution and phonon broadening) are used to model the photoemission lines. Asymmetric (Doniach-Sunjić) shapes were also tried, since the Si(111)-(7×7) surface exhibits a metallic character,^{13,14} but did not result in reasonable line-shape analyses. As a result of this procedure, four representative spectra are shown, together with results of the line-shape analysis, in Fig. 2, normalized to equal intensity of the bulk peak. The data are represented by dots, while the fits to the data are given by the solid line; components used for the fit are indicated below each spectrum.

Even the model function consisting of three SCL's and one bulk component has serious deficiencies, as can be seen by direct inspection from the surface-sensitive spectra. The curvature of the high-kinetic-energy side of the main peak structure cannot be modeled by a Gauss-Lorentz line shape. Trying to fix this deficiency by inserting a different component at this position [arrow on 117-eV spectrum in Fig. 2(a)] increases the quality of the fit for individual spectra, but introduces two severe problems when describing the entire set of data for a photon-energy range of 80 eV. First, the Gaussian width would have to be increased by more than 100 meV for a photon-energy increase from 115 to 120 eV, which is not due to instrumental broadening as determined from gas-phase photoemission.⁸ Second, the position of the S_1 component would have to shift by more than 50 meV as the photon energy is changed; these are clearly unphysical assumptions. These observations led to the introduction of a fourth surface component S_4 at or very close (± 20 meV) to the bulk line. Using this position of S_4 , all spectra are well described using a small set of parameters: a Lorentzian broadening derived from bulk-sensitive spectra, identical spin-orbit splitting for all components, and a constant Gaussian broadening (although different for bulk [$\sigma_b = (144 \pm 10)$ meV] and surface [$\sigma_s = (360 \pm 10)$ meV] lines). The branching ratio was allowed to vary in order to account for the different photoionization cross sections close to threshold, but tends to the statistical value for photon energies above 120 eV.

There is a certain amount of interplay between the Lorentzian broadening γ of the bulk line and the Gaussian-dominated intensity of the S_4 component; the value of (60 ± 20) meV for γ determined from our line-shape analysis is well within the range of the recent high-resolution data for Si,^{15,16} but is considerably smaller than the values given by previous studies of Si(111)-(7×7).^{4,6,17} The higher value can be reproduced if S_4 is omitted from the model function for the fit of a bulk-sensitive spectrum. The mystery of a seemingly surface-orientation-dependent lifetime broadening

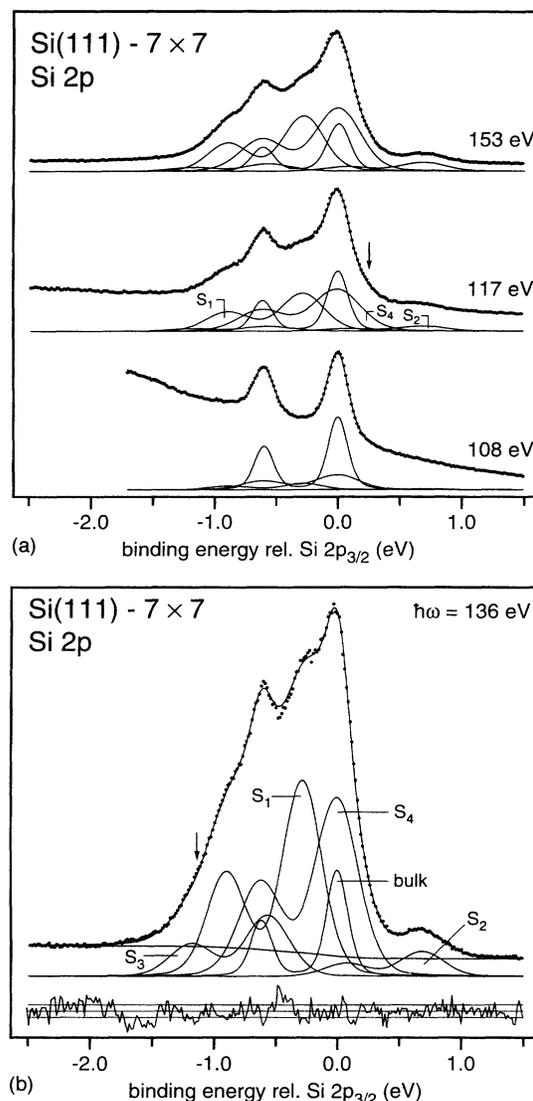


FIG. 2. (a) Si $2p$ spectra of the Si(111)-(7×7) surface, recorded at 108, 117, and 153 eV, with the corresponding line-shape analysis indicated underneath each spectrum. The arrow in the center spectrum indicates the region where significant deviation from the Lorentzian shape of the bulk component due to the influence of the surface component S_4 is observed. (b) Enlarged version of a surface-sensitive spectrum taken at a photon energy of 136 eV, with surface and bulk components and background contribution. Below the spectrum, the residuum of the fit is indicated, where upper and lower lines indicate deviations from the data curve within statistical error.

of the Si $2p$ line can thus be traced to the use of an incomplete model function. The peak S_1 on the high-binding-energy side of the bulk line is shifted by (280 ± 10) meV with respect to the bulk emission, and the second clearly visible component is S_2 , shifted by $-(690 \pm 10)$ meV. The component at the high-binding-energy side of the spectrum, S_3 , is shifted by (560 ± 10) meV. From the higher-energy spectra it is obvious that an inelastic background contribution occurs in the spectra; this was modeled by a steplike (Shirley¹⁸) background proportional to the area of the peak, plus a third-order polynomial, which is included in Fig. 2(b).

Modeling the background by using a spectrum recorded at higher or lower photon energies such as proposed by Himpfel¹⁹ works for low kinetic energies but a step function has to be additionally introduced at higher kinetic energies [cf. top spectrum of Fig. 2(a)]. The deficiencies of the line-shape analysis obvious from the residuum can be traced to (a) the description of the background and (b) to the constraints put on σ_s and γ_s . A detailed account of the different procedures to model the background by Shirley¹⁸ or Tougaard models²⁰ is presented elsewhere.²¹

It has recently been suggested²² that more than four lines are necessary in order to describe the Si 2*p* spectrum from Si(111)-(7×7). Using an instrumental resolution of 40 meV we do not require more than four surface components; there is no clear evidence for additional peaks in the spectra. In this regard it is important to analyze a wide range of photon energies in order to obtain direct signatures of different contributions, through a variation of surface sensitivity and the intensity variations due to interference discussed below.

Investigations of surface core-level shifts have received a new stimulus through the development of high-photon-flux and high-resolution synchrotron-radiation beamlines.^{15,16} The study of Landmark *et al.* resulted in the observation of several other SCL's for the Si(100), and has been used as a test for improved calculations of photoelectron spectra including final-state effects.²³ For the present case of the Si(111)-7×7 reconstruction, only two SCL's have been reported so far,^{3,4,6,24,25} although there are more structural elements in the reconstruction. One 7×7 unit cell contains, in the first bilayer, 12 adatoms, 6 rest atoms, 18 dimer atoms, 36 so-called pedestal atoms (atoms bonded directly to adatoms), 18 atoms bonded to the layer of rest atoms, and 12 atoms immediately below adatoms.²⁶ The origin of the two SCL components (S_1 and S_2) known so far in terms of structural building blocks of the (7×7) structure has been under debate. While some groups assign S_2 to rest atoms, based on calculations of charge transfer from the rest atoms to the adatoms²⁷ and an initial-state picture, others, including a recent photoemission extended-fine-structure study,²⁵ assign it to the adatoms.

We have chosen two ways in order to obtain an interpretation of the four SCL peaks found in this paper in terms of the structural building blocks. The first is based on electron mean free paths and relative peak intensities. However, these are not based on data from one particular electron kinetic energy, since Carlisle *et al.* have recently shown²⁵ that peak intensities exhibit large oscillations with photon energy, which they interpret in terms of interference effects similar to extended x-ray-absorption fine structure. Our intensities exhibit oscillations that are quite similar to those of Carlisle *et al.* for S_2 , with amplitudes of about 30–50 %;²¹ these give rise to the strengthening of the bulk emission peaks in the top spectrum of Fig. 1, for example. Thus a reliable estimate of relative intensities is obtained only by averaging over a wider photon-energy range. We achieve this by starting at a photon energy (125 eV) below which a strong decrease of surface sensitivity occurs, and including maxima and minima in the intensity curve over a range of 60-eV photon energy. The relative intensities were then compared with results from a model calculation based on the exponential attenuation of signals as a function of distance from the surface. Taking into

account the electron mean free path from Himpfel *et al.* for silicon at 130 eV, $\lambda=3.3$ Å,²⁸ and other literature data,¹⁵ the low intensity (cf. Fig. 2) of the bulk component (identified from its narrow line shape) shows that its signal is attenuated by about two double layers of silicon. Our model then calculates the intensity of emission for each of the building blocks of the (7×7) structure from the number of atoms involved and their distance to the surface. The experimentally obtained intensities are reproduced best when we use the following assignment: (a) the 36 atoms bonded to the adatoms plus 18 atoms bonded to the rest atoms, i.e., 54 atoms in all to the component S_1 ; (b) the 6 rest atoms to S_2 ; (c) the 12 adatoms to S_3 , and the first bulklike layer consisting of 98 atoms, 18 atoms from dimers and 12 atoms underneath adatoms, i.e., in total 128 atoms to S_4 . It is possible that the width of S_4 , attributed to almost bulklike atoms, is due to some extent to overlapping peaks, which cannot be separated. Using this peak assignment, we can calculate the approximate number of emitters for each component based on the layer-attenuation model. We find 54 emitters for S_1 , 8 for S_2 , 12 for S_3 , and, finally, 135 emitters for S_4 . The model properly reproduces the distribution of emitting atoms among the different SCL peaks, except for a discrepancy with the number of rest atoms. This may be traced to the fact that we assume the adatom layer will not attenuate the emission from the underlying layers because of their small concentration. It is a reassuring feature that this

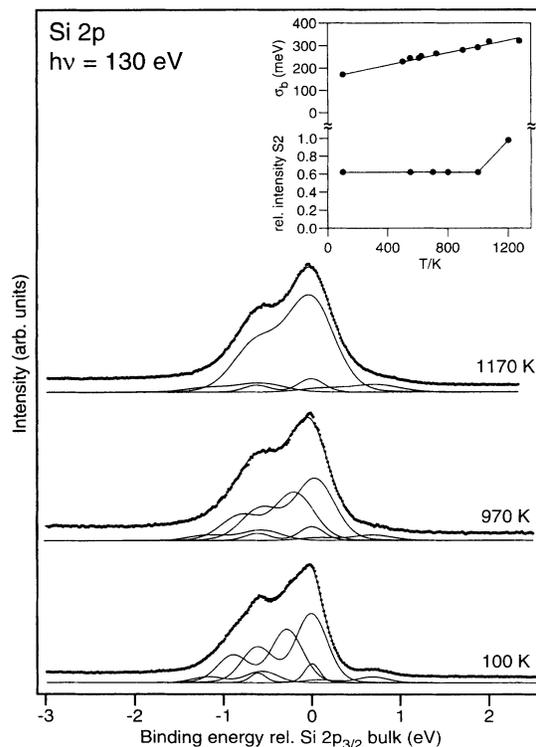


FIG. 3. Si 2*p* spectra recorded at a photon energy of 130 eV and a substrate temperature of 100 and 970 K, below the (7×7)-(1×1) phase transition, and 1170 K, above the transition. Note the persistence of emission from S_2 above the temperature of the phase transition. The insets show the temperature-induced broadening of the bulk Si 2*p* line and the intensity of the S_2 component as a function of temperature.

model gives a best fit for $\lambda = 3.3 \text{ \AA}$; the agreement between calculated and experimental intensities deteriorates rapidly for λ values 0.2 \AA higher or lower.

The second argument for SCL assignment is derived from spectra recorded below and above the (7×7) - (1×1) phase transition at around 1130 K.²⁹ From a comparison with laser-annealed (1×1) surfaces, the (1×1) phase can be viewed as a disordered (2×2) structure, which contains the essential building blocks for the (7×7) structure, i.e., one adatom and one rest atom.³⁰ This means that the relation of rest atoms to adatoms increases from $\frac{6}{12}$ in the (7×7) structure to 1 above the phase transition. Spectra recorded at 100, 970, and 1170 K, i.e., below and above the phase transition, are shown in Fig. 3. In order to model the high-temperature spectra, which are affected by phonon broadening, we have restricted the number of free parameters by deriving the Gaussian width for the bulk line from data recorded with high-bulk sensitivity²¹ (see inset), and by fixing the relative intensity of surface components for T below the transition temperature. While σ_s remained a free parameter, it was found that its temperature dependence closely matched that of σ_b . As evident from the line-shape analyses shown in Fig. 3, the spectrum above the transition temperature can only be modeled by assuming that S_1 actually coincides with S_4 at the bulk peak energy; S_1 actually is found to shift by about 80 meV over the temperature range from 100 to 970 K. The fact that S_1 and S_4 coincide above the phase transition is most likely related to the loss of (7×7) structural elements, making the second layer more bulklike; the lack of information about the structure of the (1×1) phase does not permit a more de-

tailed interpretation. The important message from the phase-transition data is, however, that the intensity of S_2 increases by about a factor of 2 above the phase transition as shown by the diagram in the inset of Fig. 3. Since this is what one would expect from the rest atoms, we take this as direct proof for an assignment of S_2 to the rest atoms, in support of the relative intensity evaluation above.

The above assignment is in line with expectations from an initial-state picture of charge transfer: emission from the adatoms, which give up charge, has the highest binding energy, while that from the rest atoms, which are thought to receive this charge, has the lowest binding energy. Emission from the layer of atoms that act as an intermediary in the charge-transfer process (S_1) is shifted by a small amount to higher binding energies, while the first bulklike layer emission coincides with the bulk line, but with a higher Gaussian width, most likely through enhanced phonon broadening. This interpretation neglects final-state effects,²³ which for Si(100) may induce shifts of up to 0.5 eV, with a strong site dependence of the amount of final-state screening. Since final-state screening depends on the availability of empty states above the Fermi edge derived from the atoms in question, the only species for which this model would apply are the adatoms that have states near E_F . The other building blocks have surface states that are well below E_F (Ref. 27) and their Si $2p$ binding energies therefore will not be affected by final-state effects.

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