Core-Level Spectroscopy of the Clean Si(001) Surface: Charge Transfer within Asymmetric Dimers of the 2×1 and $c(4\times 2)$ Reconstructions

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Extremely well-resolved Si 2*p* core-level spectra have been obtained from the clean Si(001) surface. Spectra from the cold $c(4\times 2)$ and the RT 2×1 surfaces are very similar, implying that the local structure of the two reconstructions is the same. Shifted components originating from both up and down atoms of asymmetric dimers, as well as second-layer atoms, are identified. The split of ~0.55 eV between the two dimer-atom components points to a substantial charge transfer within the dimers. We find no support for the recently proposed crystal-field splitting of the surface components.

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The Si(001) surface is generally accepted to consist of dimers that constitute the basic 2×1 building block of the reconstructed surface. Normally, a 2×1 periodicity is observed at room temperature, but higher-order reconstructions have also been reported [1]. The dimerization of the surface comprises substantial subsurface distortions extending several layers into the bulk [2,3]. Despite the fact that Si(001) is one of the most extensively studied semiconductor surfaces both experimentally and theoretically, it is still a question under debate whether the dimers are symmetric or asymmetric, covalent or ionic. For example, the clearly visible surface component shifted ~0.5 eV towards lower binding energy in surface sensitive Si 2*p* core-level spectra has been interpreted in two different ways resulting in conflicting conclusions. The shifted component has been interpreted as either due to $\frac{1}{2}$ monolayer (ML) of surface atoms corresponding to the up atoms of ionic, asymmetric, dimers (leaving the down-atom component close to the bulk component) [4–6] or due to 1 ML corresponding to covalent dimer atoms [7,8].

In the late seventies Chadi [9] found from energy-minimization calculations that buckling of the dimers lowers the total energy and gives surface electronic bands in better agreement with photoemission data. The formation of the asymmetric dimers results in a charge transfer from the down to the up atom of the dimer. These results were later confirmed by several theoretical calculations and got support from many experimental techniques [1,2]. From calculations based on the asymmetric dimer geometry, Ihm *et al.* [10] found that the 2×1 reconstruction is not the ground state of the Si(001) surface and that higher-order reconstructions, resulting from different arrangements of asymmetric dimers, should occur. An order-disorder phase transition leading to the disappearance of higher-order diffraction spots was predicted to take place at roughly 250 K. Recently Tabata, Aruga, and Murata [11] in a low-energy electron diffraction (LEED) experiment observed this kind of order-disorder phase transition from $c(4\times 2)$ (corresponding to an antiferromagnetic order of asymmetric dimers) to 2×1 at about 200 K.

The dimers appear in scanning tunneling microscopy (STM) images as symmetric protrusions with some minor amount of asymmetric protrusions mainly present close to defects and step edges [12–14]. Based on these observations (and the core-level study with the covalent dimer interpretation [7]) a few calculations supporting a lower total energy for symmetric or only slightly buckled dimers have been presented [15]. Ideas of asymmetric dimers that dynamically flip with a high frequency and thus would look symmetric in the time averaged STM images have also been proposed [12,14,16]. In a very recent, low-temperature, STM study the number of observed asymmetric dimers increased after cooling to 120 K [14].

The core-level spectra obtained in this study from the cold $c(4\times 2)$ and the RT 2×1 surfaces are very similar which shows that the local structure for the two phases must be the same. This fact must be accounted for in any model trying to explain the atomic structures of these surfaces. In particular, no realistic model exists that can explain the quarter order spots of the $c(4\times 2)$ reconstruction without asymmetric dimers. In addition, our Si 2*p* spectra contain two shifted surface components assigned to the outermost surface layer. The large energy split of ~0.55 eV between the two components is explained in terms of charge transfer, which implies that the dimers have an ionic character and are asymmetric. A picture of the 2×1 surface consisting mainly of symmetric dimers is therefore not consistent with the results of this work.

The experiments were performed at the MAX synchrotron radiation facility in Lund, Sweden. All core-level spectra shown in this paper were obtained using a modified SX700 plane grating monochromator and a large hemispherical electron energy analyzer. The angle between the incident photon beam and the direction of the analyzed photoelectrons was 40°. The total energy resolution was for all the investigated photon energies < 70 meV and the angular resolution of the analyzer was ±8°. An *n*-type (P doped, $\rho = 2\ \Omega\,\mathrm{cm}$) Si(001) crystal was preoxidized using an etching method [17] and cleaned *in situ* by resistive heating up to ~950 °C, which gave rise to a sharp two-domain 2×1 LEED pattern. A sharp two-domain $c(4\times 2)$ LEED pattern with well-defined quarter order spots and low background was obtained after cooling the sample to ~120 K. The quality of a Si(001) surface can vary considerably, as can be seen by comparing the defect density obtained in different STM studies [12–14]. It is therefore essential for the interpretation of the core-level data to check the quality of the prepared surface in some way. For this purpose the 2×1 and $c(4\times2)$ surfaces were also studied in another experimental setup, which allowed us to record both angle-resolved valence band spectra, at low photon energies (21.2 eV), and Si $2p$ spectra, at 130 eV, with a slightly lower resolution. We could from this additional study verify that the appearance of the Si $2p$ spectra presented here corresponds to surfaces which exhibit sharp and intense surface state peaks in excellent agreement with published valence band spectra [18,19].

The uppermost Si $2p$ core-level spectrum in Fig. 1 was recorded at RT from a 2×1 reconstructed sample. A photon energy of 130 eV and an emission angle of 60° were used in order to obtain high surface sensitivity. Also shown in Fig. 1 are the corresponding spectrum obtained from the cold $c(4\times2)$ surface together with normal emission spectra taken at photon energies ranging from 114 to 150 eV, giving a variation in the surface sensitivity. A rigid shift of 0.73 eV towards higher binding energies, due to the surface photovoltage effect [20], and a drastic decrease in the spectral linewidth can be observed after cooling the sample.

Without any data processing the $c(4\times2)$ spectra in Fig. 1 reveal the presence of several shifted components contributing to the line shape. Most evident is the component S giving rise to the well-resolved peak to the right, while the presence of S' is most clearly revealed by its $2p_{1/2}$ component which gives rise to a shoulder in the spectra (dashed line in Fig. 1). A third weaker component C is partly filling up the valley between B and S. As the surface sensitivity is enhanced, especially S, but also the S' component, shows a clear increase in intensity. At the same time, the maximum of the main peak moves towards the left, suggesting the presence of one more surface sensitive component, SS, shifted only slightly towards higher binding energies.

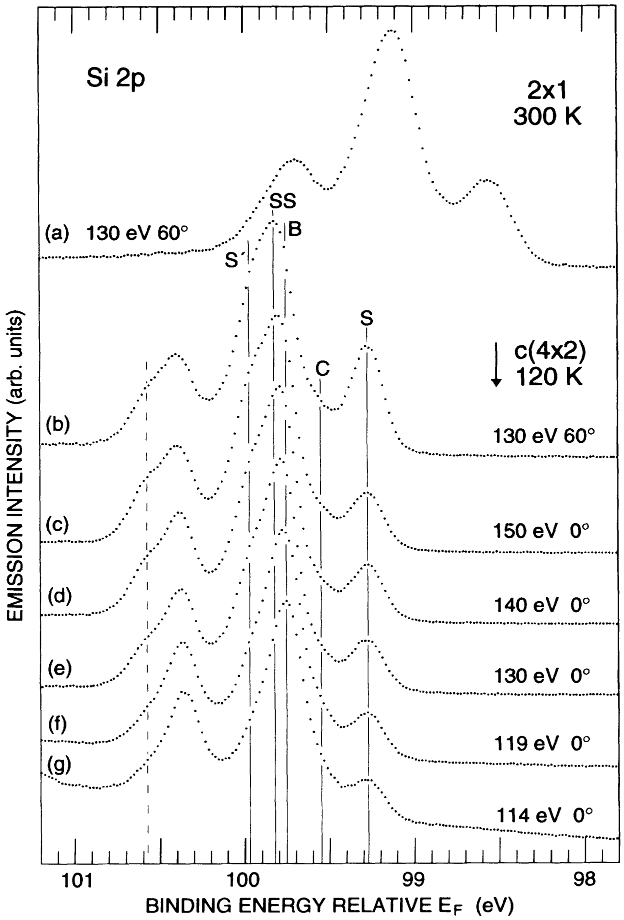

FIG. 1. Si $2p$ core-level spectra obtained from (a) Si(001)2×1 at RT and (b)–(f) Si(001)$c(4\times2)$ at 120 K at photon energies from 114 to 150 eV. Spectra (c)–(g) were measured in normal emission, $\theta_e=0°$ while (a) and (b) were measured at $\theta_e=60°$ in the [011] azimuthal direction. The Si $2p_{3/2}$ energy positions of the five components (solid lines) as well as the Si $2p_{1/2}$ energy position of the S' component (dashed line) are indicated. The S, C, SS, and S' lines are located 0.48, 0.20, −0.06, and −0.22 eV relative to the B line, respectively.

More quantitative information is obtained by a least-squares fitting procedure [21], in which the spectra are decomposed into components consisting of spin-orbit split Voigt functions. When first trying to decompose the spectra into four components, the bulk component B moved in energy as the surface sensitivity varied. The movement of B could be avoided by introducing the fifth component (SS), shifted slightly (62 meV) towards higher binding energies, with roughly the same intensity as the S component. Only after the introduction of the SS component was it possible to obtain decompositions into components with the same energy shifts for all spectra. Figure 2 shows the result after the curve fitting with five components, for two different $c(4\times2)$ spectra and one 2×1 spectrum, recorded with 130 eV. The energy shifts for S, C, SS, and S' are, for the $c(4\times2)$ spectra, −485, −205, 62, and 220 meV in normal emission, and −488, −195, 62, and 219 meV for the more surface sensitive spectrum recorded with 60° emission angle. For the 2×1 spectrum recorded in normal emission the corresponding shifts are −500, −230, 62, and 225 meV. The values of the parameters describing the width of the model function are often critical for getting a correct result of the fit. The linewidth of the well-resolved S component could in our spectra be determined accurately and was then used for all the shifted components. For the bulk components a slightly smaller Gaussian width gave better fits for most of the spectra. The Gaussian widths of the surface components (bulk component) were for $c(4\times2)$, 180 (160) meV, and for 2×1, 250 (215) meV, full width at half maximum (FWHM). A Lorentzian width of 85 meV (FWHM) and a spin-orbit split of 602 meV were used. For ease of comparison all the widths were held constant for all spectra from the same sample. The inten-

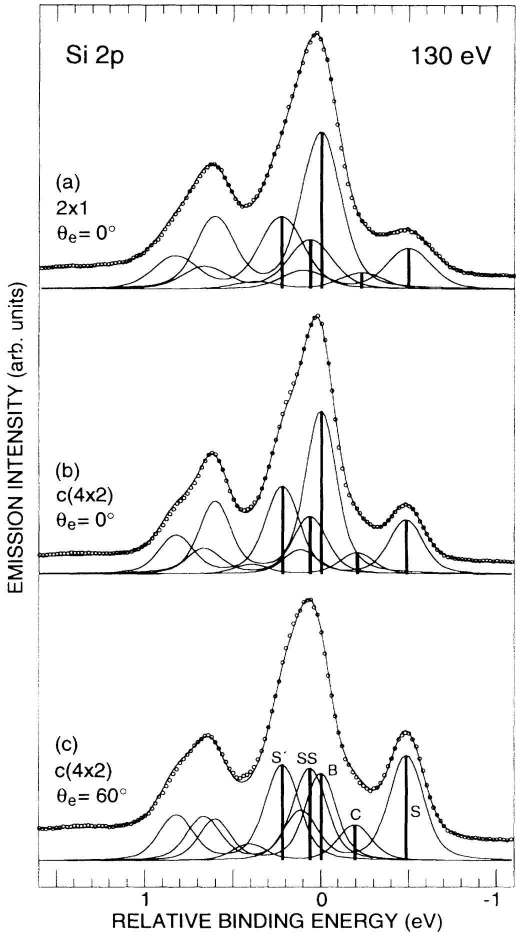

FIG. 2. Decomposition of the Si $2p$ photoelectron spectra from (a) the 2×1 surface and (b),(c) the $c(4\times2)$ reconstructed surface. The spectra were recorded with a photon energy of 130 eV at (a),(b) 0° and (c) 60° emission angle. An integrating background was used in the fitting procedure of these spectra.

sities of the shifted components obtained from fits of $c(4\times2)$ spectra recorded at different photon energies and emission angles are plotted in Fig. 3.

The S component, which exhibits the largest energy shift, is like in previous studies identified as a contribution from dimer atoms. The SS component shows a very similar intensity behavior to that of S, while the S' component has a larger intensity than both S and SS in all but the most surface sensitive spectra. From these observations and the fact that the shifted components exist for a $c(4\times2)$ surface, it is quite natural to adopt the asymmetric dimer model and to assign S to the up atoms, SS to the down atoms, and S' to the second-layer atoms. The energy difference between SS and S reflects the charge redistribution from the down to the up atom when forming the asymmetric dimer. The assignment of S to the up atoms ($\frac{1}{2}$ ML) gives an escape depth λ of 3.9 Å for photoelectrons excited with 130-eV photon energy, which is in good accordance with values reported in other core-level studies of Si surfaces [6,22,23]. The intensities

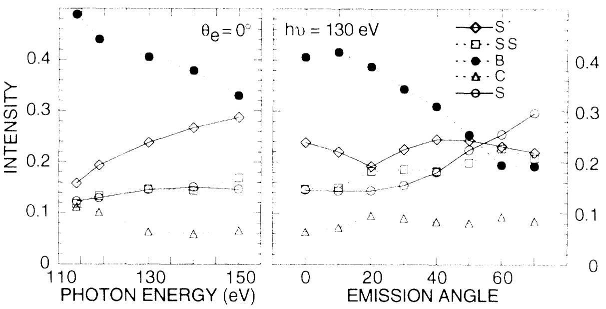

FIG. 3. Fraction of total intensity for the decomposed components obtained from fits of the $c(4\times2)$ spectra recorded at normal emission with different photon energies and at 130-eV photon energy for different emission angles. The energy shifts for the S, C, SS, and S' components were -483 ± 8, -200 ± 5, 61 ± 1, and 220 ± 5 meV relative to the B component in all fits.

for the underlying layers can easily be estimated from the escape depth values. The intensity from S' corresponds quite well to the intensity expected for 1 ML of atoms in the second layer [in a $c(4\times2)$ geometry all second-layer atoms are identical]. A perfect correspondence cannot be expected, as the intensities of the components are affected by photoelectron diffraction and uncertainties introduced in the fitting procedure. The C component shows a decreasing intensity when the photon energy is changed to get higher surface sensitivity. This suggests that C originates from subsurface layers (in fact, emission from half the third layer would give an emission corresponding fairly well to C). A contribution from surface defects to the intensity of the C component cannot be totally excluded.

Very recently two Letters have been published dealing with surface-induced shifts in the Si $2p$ core level of the Si(001) surface [5,8]. The large linewidth of the Si $2p$ core level in both these studies was assumed to be due to fundamental reasons, such as phonon broadening, inherent to the silicon surface. Our data clearly demonstrate that, with high instrumental resolution combined with a well-ordered surface with low defect density, the width of the Si $2p$ spectrum can be reduced much further. In the Letter by Wertheim *et al.* [5] the Si $2p$ core level was studied at 77 K with high instrumental energy resolution. Despite this the presented spectra were very broad. It is also remarkable that no phase transition to $c(4\times2)$ was reported. Deconvolution of the spectra with a Gaussian function was used to circumvent the problem with the large linewidth. The procedure resulted in two S components, shifted towards lower binding energies, with equal intensities and split by 190 meV. A highly asymmetric S' component shifted towards higher binding energy was also reported. The existence of the two S components was explained by crystal-field splitting of the up-atom core level of the asymmetric dimers. We do not find any support for a crystal-field split of the S component. Our S component is on the contrary extremely narrow and the C component cannot be interpreted in terms of a split part of S. The C component has a much lower intensity and a different intensity dependence compared to the S component as can be seen in Fig. 3. The S' component was in the study by Wertheim *et al.* explained as due to the down atoms. The assignment was based on the assumption that the core ionization of the down atoms would cause excitations to the empty surface state band, located mainly at these atoms, which could in principle explain the large asymmetry (represented by a Doniach-Šunjić line shape). This kind of large asymmetry is not seen in our spectra and we conclude that it is not a significant feature in spectra from a clean and well-ordered Si(001) surface.

In the other Letter Lin, Miller, and Chiang [8] studied the initial growth of Ge on the Si(001) surface and could in this experiment observe an S' component close to the bulk line, shifted towards higher binding energy. From the intensity behavior of the S' component, i.e., the decay during the growth of Ge, they could identify this component as due to second-layer Si atoms. This experimental observation is in agreement with our interpretations and is taken as further support for our assignment of S' as due to second-layer atoms. Lin, Miller, and Chiang were only able to resolve one more shifted component (S), which was then assumed to correspond to 1 ML of covalent dimer atoms in agreement with an earlier study by the same group, where the core-level emission from the surface atoms of the Si(111)7×7 and Si(001)2×1 surfaces was compared [7]. There is, however, a disunity about the result of this comparison. With the shifted component $S2$ of the 7×7 surface assigned to the rest atoms, instead of adatoms as in Ref. [7], the comparison would instead lead to 0.5 ML of surface atoms contributing to the S component of the 2×1 surface (as discussed in Ref. 49 of Ref. [6]). The rest-atom interpretation of the 7×7 surface is supported by several groups [6,23,24] and is consistent with the presence of charge transfer from the adatom to the rest-atom dangling bonds [25]. An interpretation of our data in terms of covalent dimers, i.e., with the S component corresponding to 1 ML of surface atoms, is not consistent with the presence of the SS component. Moreover, it would give a mean free path of 8.9 Å for photoelectrons excited with 130-eV photon energy which is in serious disagreement with other reported values [6,22,23].

In conclusion, we have shown that the low-temperature $c(4\times2)$ and the RT 2×1 reconstructions of the Si(001) surface must have the same local structure consisting of asymmetric dimers with a large charge transfer from the down to the up atom. This supports the picture of the $c(4\times2)$ to 2×1 phase transition as a loss of long-range order among the antiferromagnetically ordered buckled dimers [10,11,18]. Underlying layers are shown to have a great influence on the spectral line shape and a component originating from the second-layer atoms is identified.

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