Reinvestigation of the Si 2p photoemission line shape from a clean Si(001) $c(4\times 2)$ surface

H. Koh, J. W. Kim, W. H. Choi, and H. W. Yeom*

Atomic-scale Surface Science Research Center and Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Korea

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We have reinvestigated the Si 2p photoemission spectra of a clean Si(001) $c(4 \times 2)$ surface with an apparently higher resolution than previous studies. A systematic and extensive line-shape analysis of the spectra taken at various photon energies and emission angles indicates that the Si 2p spectra are composed of seven different components. With regard to the recent debate on the Si 2p component of the down-dimer atoms, we conclude that even with the present resolution the corresponding surface core-level shift (SCLS) cannot be determined accurately but is in the range of 30-130 meV between the bulk and the second-layer components. One of the two newly identified components, with a SCLS of 1.4 eV, is interpreted as a surface loss structure due to the interband transition between surface-state bands.

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Atomic and electronic structures of clean Si surfaces have been studied extensively over the past two decades both theoretically and experimentally with a great variety of techniques due to their fundamental and crucial importance for various adsorption, reaction, and growth phenomena on Si surfaces. One of the most important surface structures on Si is the reconstruction of Si(001) with a $p(2 \times 1)$ [at room temperature (RT)] or a $c(4 \times 2)$ ordering (below 200 K).¹ These surface structures are basically understood from the dimerization of Si surface atoms, which are buckled asymmetrically with a strong charge transfer from the dangling bond electron of one dimer atom buckled down (the socalled down-dimer atom) to the other buckled up (the updimer atom).² The surface Si dimers favor an antiferomagnetically buckled configuration of $c(4 \times 2)$ in the ground state but dynamically flip above 200 K to form an apparent $p(2 \times 1)$ order. In the course of establishing the existence of the buckled dimers, the surface band structure measured by angle-resolved photoemission combined with theoretical band calculations,³⁻⁵ the scanning tunneling microscopy images at low temperature,^{7,8} and the high-resolution Si 2pphotoemission spectra had played their own crucial roles.⁶

The Si 2p surface core-level shift measurements have been one of the major analytical techniques for the study of not only the clean Si surface reconstructions but also various adsorbates and initial growth or reaction systems on Si, providing crucial information on the bonding states and the adsorption geometries. In this technique the core-level binding energy shifts of different surface atoms are detected, which reflect the valence charge distribution affected by chemical bond formation and structural or electronic changes on the surface atoms as well. From early studies, it has been known that the Si 2p spectra of the Si(001) surface are composed of at least three components, the bulk component and two (sub)surface-related components with SCLS's of about -0.5and 0.2–0.4 eV.⁹ The origins of these two components, however, had been under debate for a long time. Later, Landemark *et al.*⁶ identified two more components at about -0.2and 0.06 eV with a significantly improved resolution, providing a consistent interpretation of the major surface-related components within the asymmetric dimer structure. That is, the origins of the surface components with SCLS's of -0.5, 0.06, and 0.2 eV are interpreted as the up-dimer, the downdimer, and the second-layer atoms, respectively.⁶ This interpretation scheme has been adopted by many other authors and was supported by an *ab initio* calculation¹⁰ and a photoelectron diffraction experiment.¹¹ However, recently Pi, Cheng, and Hong proposed a different decomposition scheme, where the component due to down-dimer atoms (denoted as S_d hereafter) is introduced at a higher binding energy than the second-layer component (S'),¹² or even at a lower binding energy than the bulk component (B).¹³ This discrepancy stems from the fact that the S_d is too close to Bby less than 100 meV, while the apparent full width at half maximum of Si 2p is about 200 meV and also partly from the quantitative difference in the SCLS values for S_d between theory¹⁰ and the previous experiment.⁶

In this Brief Report, we present an extensive set of highresolution Si 2p spectra obtained at 90 K, which exhibit an improved resolution over previous reports. These spectra are systematically and carefully analyzed especially to establish a reliable SCLS value for the S_d component. Several different spectral features are also identified and their origins are discussed.

The photoemission experiments were performed on an 8A1 undulator beam line at Pohang Light Source using a high-resolution electron analyzer (SES-200, Gamma Data, Sweden). The overall instrumental energy resolution, defined by photon beam and electron analyzer, is better than 40 meV and the acceptance angle of the analyzer is $\pm 8^{\circ}$. A clean $Si(001)c(4 \times 2)$ surface was obtained by repeated flashing of a P-doped Si(001) wafer up to 1470 K followed by a slow cooling down to 90 K at a pressure below 2×10^{-10} Torr. All the measurements were performed at 90 K in order to reduce the thermal broadening of the spectra. For comparison, a well-ordered Bi-terminated Si(001) $2 \times n$ surface was prepared by depositing Bi of about 1 monolayer (ML) using a Knudsen cell and subsequent annealing at 500 K. The Bi termination removes the dimer reconstruction of the surface Si atoms, which are instead brought into a bulklike configuration.14

Figure 1 shows the Si 2p spectra taken at various photon energies and emission angles. The spectrum of a Biterminated Si surface is displayed together (the bottom spec-



FIG. 1. Si 2p core-level spectra obtained from the clean Si(001) $c(4\times2)$ surface and the Bi-terminated surface (the spectrum at bottom) at 90 K. The photon energies and emission angles (along the [110] azimuthal direction) are given for each spectrum. The obvious spectral features are indicated by arrows and denoted as *L*, *D*, *S'*, *B* (the bulk component), *C*, and *S_u* (see text for detailed explanation).

trum), which consists almost of a single spin-orbit doublet *B*, the bulk component. As the photon energy increases from 114 to 150 eV, the photoelectron kinetic energy increases and the escape depth decreases. Then the intensities of the surface-related components are enhanced and the components are most well resolved at a photon energy of 145 eV (dots and solid line in Fig. 1). There, the raw spectrum clearly reveals at least six different spectral features, which are marked by the arrows and denoted as S_u , C, B, S', D, and L. Note that none of these features could be explained by the spin-orbit splitting of another feature except for D. The energy position of D closely overlaps with the $2p_{1/2}$ component of C. However, the apparent intensity of D is similar to that of C, which cannot be fully accounted for only by the $2p_{1/2}$ component of C. This point will be made clearer below. The presence of the structure at 1.4 eV (L) is not evident in Fig. 1 due to its small intensity. However, its presence and its doublet line shape are clear in the enlarged spectra in Fig. 2 [see the insets in Figs. 2(c) and 2(d)]. As shown in Figs. 1 and 2, these spectral features are almost completely removed by the Bi termination, further supporting the fact that they are related to the Si surface dimerization.



FIG. 2. Decompositions of the Si 2p spectra taken at a photon energy $(h\nu)$ of 145 eV and an emission angle (θ_e) of 0° with different SCLS's for S_d of (a) $E_d = 150$, (b) 80, and (c) 10 meV. Open circles represent the raw data, and solid lines are the fitting results, fitted components, and integral backgrounds. The data in the insets of (c) and (d) are magnified vertically 9.5 times.

So far, there is a consensus on the origins of only three components: (i) the dominant bulk component, *B*, is obvious; (ii) the well-separated peak at a SCLS of -0.5 eV, S_{μ} , comes from the up-dimer atoms on the top layer; (iii) the peak at 0.2 eV, S', originates from the Si atoms in the second layer.⁶ Although the presence of C has been established, its origin is uncertain.^{6,15} The two extra components D and L, which only few previous studies observed, will be discussed further below. In addition to these components, the seventh component, one from down-dimer atoms, S_d , should be included, which represents half of the top-layer Si atoms.² However, the S_d component does not appear as any obvious spectral feature in the raw spectra (see Fig. 1). Instead, its presence may be suggested in an indirect way: As guided by the vertical lines in Fig. 1, the energy positions of the maximum intensity peaks clearly shift systematically toward a higher binding energy as the surface sensitivity increases. This implies that there is a hidden surface component that is very close to *B* and is located at a higher binding energy.⁶

In order to determine the SCLS of S_d as precisely as possible, we first applied the standard least-squares fitting procedure to the most well-resolved spectrum taken at a photon energy of 145 eV and an emission angle of 0°. The raw spectrum is fitted by seven spin-orbit-split Voigt functions (S_u , C, B, S_d , S', D, and L), as explained above, with a branching ratio of 0.5 and an integral background. Several constraints are applied initially to reduce the ambiguity of the fitting procedure. (i) The same Lorentzian full width at half maximum (LW) of 50 meV is used for all seven components since there is no obvious physical reason for a different LW.⁶ This value of 50 meV itself is determined reliably by the best fit of the lower-binding-energy tail of the S_{μ} component, the only place where the line shape of a single component shows up without any overlap from other spectral features.¹⁶ This LW value agrees well with the result of a gas-phase Si 2p measurement reporting 45 meV (Ref. 17) although a somewhat larger [85 meV (Refs. 6 and 18)] or a smaller [35 meV (Ref. 19)] value of LW have been used in previous studies. (ii) Considering the same amount of the upand down-dimer atoms on the topmost layer, the same intensity and Gaussian full width at half maximum (GW) are used for the S_u and S_d components. The value of GW was determined to be 185 meV from the S_u component as in the case of LW. (iii) The energy separation between B and S_u , that is, the SCLS of S_{μ} , is fixed to -0.496 eV, as determined precisely from a bulk-sensitive spectrum (114 eV and 0° in Fig. 1). Otherwise the energy position of the bulk component Bvaries unexpectedly in the fitting procedure caused by the interference from S and S_d (see Fig. 2). Then the curve fittings were done with varying the SCLS of S_d systematically and then the energies, intensities, and GW's of other components are determined accordingly.

The results of such curve fittings are displayed in Figs. 2(a)-2(c) for several selective SCLS's of S_d (E_d). The energy positions of S_d are marked by the arrows. We note that the raw spectrum is almost equally well fitted for different E_d 's, making a precise determination of the SCLS of S_d by the goodness of the fits almost impossible. When S_d shifts to a lower-binding-energy side, the major noticeable changes are that the intensity and GW of S' increase and those of Bdecrease as expected. That is, the three components, B, S', and S_d , are too close and interfere too much to be fitted out unambiguously. The trends of the intensities and GW's of Band S' are examined quantitatively in Figs. 3(a) and 3(b). When E_d is smaller than 20 meV, the intensity of S' is larger than twice that of S_d (0.17 in the fractional intensity) and its GW is also larger than that of S_d (0.185 eV). These values are physically unreasonable because (i) the intensity of the second-layer component should be less than twice the intensity of S_d (i.e., the total intensity of the first-layer components) and (ii) a smaller GW is expected for a deeper layer due to the increased connectivity and thus the reduced photon broadening. These arguments set a lower limit of E_d at 20 meV [the dashed lines in Figs. 3(a) and 3(b)]. Therefore, we exclude the previous decomposition scheme of Pi, Cheng, and Hong which suggested a negative SCLS of S_d , i.e., S_d at a lower binding energy than B^{13} . That decomposition is qualitatively contradictory to the spectral behavior shown in Fig. 1 since the maximum peak position, which results from the convolution of B and S_d , shifts to a higher binding energy as the surface sensitivity increases, indicating a surface peak (S_d) at a higher binding energy than B.

The behavior of the intensity and width of S_d shown in Figs. 3(a) and 3(b) further indicates that the reasonable range



FIG. 3. (a) Fractional intensities (intensities normalized by the total integrated intensity) and (b) Gaussian widths of the bulk (squares) and the second layer (circles) components obtained from the fittings of the Si 2*p* spectrum taken at $h\nu = 140 \text{ eV}$ (as in Fig. 2) with various SCLS's of the down-dimer component (S_d). (c), (d) Fractional intensity of each component in bulk- ($\theta_e = 0^\circ$) and surface-sensitive ($\theta_e = 60^\circ$) configurations at various photon energies for the whole spectra shown in Fig. 1.

of E_d is roughly 40–140 meV. We then applied a thorough and extensive curve-fitting procedure to the whole set of Si 2p spectra shown in Fig. 1, varying E_d with and without the constraint of the same intensity for the S_d and S_u components in order to take into account of the possible photoelectron diffraction effect.¹¹ Through comparing the goodness of fits (the sums of the goodness of fits for each spectrum), it is found that the reasonable energy range of E_d is from 30 to 130 meV. Although not conclusive enough, the best fits of whole spectra are obtained for $E_d = 55$ meV when keeping the constraint of the same intensity for up- and down-dimer components. This value is fully consistent to the previous report of 62 meV by Landemark et al.⁶ Some of these fitting results are shown in Fig. 4. The LW of 50 meV is used for the whole spectra as explained above. The branching ratio is fixed to 0.5, which is decided by the multiplicity of $2p_{3/2}$ and $2p_{1/2}$. The same spin-orbit splitting of 615 meV is applied to all seven components. The SCLS's for S_u , C, S_d , S', D, and L are determined to be -0.496, -0.207, 0.055, 0.225, 0.366, and 1.400 eV, respectively. The GW's of S_{μ} (S_{d}), C, B, S', D, and L are 0.185, 0.150, 0.145, 0.160, 0.180, and 0.400 eV, respectively. Note that the physically rigorous conditions for the curve-fitting analysis above is that the SCLS, LW, and GW of each component should not be changed to fit the whole spectra taken at various photon energies and angles. The constraint of the same intensity for the S_{μ} and S_{d} components and the same branching ratio of 0.5 for all components are not rigorous, since the intensity and the branching



FIG. 4. Optimized decompositions of four selective Si 2p spectra with seven components. The SCLS of down-dimer component (S_d) is set to 55 meV. The SCLS's of S_u , C, S_d , S', D, and L are -0.496, 0.207, 0.055, 0.225, 0.366, and 1.400 eV, respectively, and the GW's of S_u (S_d), C, B, S', D, and L are 0.185, 0.150, 0.145, 0.160, 0.180, and 0.400 eV, respectively. See text for the details.

ratio of each component can be modulated due to the different matrix element or the photoelectron diffraction effect.^{11,20} Therefore, small modulations within 10% can be allowed for the intensity of S_d and the branching ratio of each component, which slightly enhances the goodness of the fits without significantly affecting the above conclusions. However, in the latter case there are too many variable fitting parameters increasing the arbitrariness of the fitting.

The fractional intensities of the components at various photon energies are displayed in Figs. 3(c) and 3(d). Comparing the normal emission spectra with the spectra taken at an emission angle of 60°, the noticeable changes are the increase of S_u and the decrease of the bulk component *B* for the surface-sensitive configuration. This is what is expected naturally. The fractional intensities of other components do not change as much as that of S_u with emission angle. Hence, it is clear that the components S', C, and D are not

- *Author to whom all correspondence should be addressed. Electronic address: yeom@phya.yonsei.ac.kr
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related to the Si atoms on the topmost layer and they should be related with subsurface layers. This excludes the suggestion of the symmetric dimers as the origin of the *C* component¹² and favors the suggestion that one half of the third layer is the origin of C.⁶ In the above decomposition the component *D* is clear and essential. This component was also noticed in a recent high-resolution measurement similar to the present one.²¹ The *D* component may come from vacancy-type defects but the small intensity prevents assigning its origin unambiguously.

The L component (see the insets of Fig. 2), which exists in the clean surface spectra but not in the Bi-terminated surface spectrum, is interpreted as a surface loss structure due to the interband transition between two near-gap surface-state bands. Its SCLS of 1.4 eV agrees well with both the experimental results of electron-energy-loss spectroscopy and optical spectroscopy measurements and the theoretical prediction of 1.5 eV.^{22,23} Although Landemark et al.⁶ did not consider the spectral feature at this energy range, Pi, Cheng, and Hong¹² recently introduced a tiny two-peak structure at the high-binding-energy side, which is similar to L. They, however, interpreted the two high-binding-energy peaks as the surface and bulk loss features, respectively. This interpretation is not consistent with the fact that the Si 2p spectrum from the Bi-terminated surface in Fig. 2 exhibits no bulkrelated loss structure. Instead, the peak separation and intensity ratio of the two peaks of the feature L indicates a spinorbit doublet.

In summary, we report high-resolution Si 2p photoelectron spectra from the clean Si(001) $c(4 \times 2)$ surface taken at various photon energies and emission angles, and compare them with the spectrum from the Bi-terminated surface. The clean Si 2p spectra are shown to be composed of seven different components including a small surface loss structure at 1.4 eV. The SCLS of down-dimer atoms cannot be determined precisely due to its proximity with the bulk component but is proved to be in the range of 30-130 meV between the bulk and the second layer components.

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