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Surface Core-Level Photoelectron Diffraction from Si Dimers at the Si(001)-(2×1) Surface

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Intensity variations of the dimer derived surface shifted Si $2p$ core level from single domain Si(001)-(2×1) have been measured as a function of azimuthal angle. Comparisons to multiple scattering calculations show that such measurements provide a method for determining the structural origins of surface shifted core levels. In addition, a structural analysis illustrates the sensitivity of this method to the detailed structure around the emitting atoms. In this case, a determination of the surface geometry indicates that the dimer bond is tilted 19.0° with respect to the surface.

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Surface core-level shifts (SCLS's) observed in high resolution photoemission experiments provide a wealth of information concerning the electronic and atomic structure of surfaces. In principle, every surface and subsurface atomic species at a clean surface which has a chemical environment different from that of the bulk atoms will produce a separate peak in a given core-level spectrum. Clean Si and Ge surfaces, for instance, often exhibit complex reconstructions with their core-level spectra containing several SCLS's [1–10]. However, photoemission is not inherently a structural technique and, controversy over the structural origins of the observed SCLS's has been more the rule than the exception [3,9,10]. Clearly, a knowledge of the structural origin of a given SCLS is a prerequisite for drawing any conclusions from the core-level spectra.

In the last few years, this debate has been particularly strong concerning the origins of the peaks observed in the Si $2p$ spectrum of the Si(001)-(2×1) dimer reconstructed surface, and thus there has been much discussion of the consequences of the different peak assignment possibilities. Specifically, this debate has centered on the degree of charge asymmetry or bond ionicity of the dimer bond [5–10]. Surface sensitive photoemission measurements of the Si $2p$ core level show that several peaks are present, one of which is visible as a separate, well-defined peak with ~ 0.5 eV lower binding energy compared to the bulk signal [5,6,8–10]. Although it has generally been acknowledged that this low binding energy component is due to the dimer atoms, analyses of such spectra have been divided between two opposing views. Some authors have concluded that this SCLS originates from both atoms of an essentially covalent dimer bond [5,6], while others have taken the very different view that this peak is due to the up atoms only of a strongly buckled dimer with a bond of significant ionic character [7–10]. In this case, the dimer down atom emission would occur at higher binding energy, closer to the bulk signal. This controversy underscores the

difficulty and also the importance of making the correct structural assignment to SCLS's.

The problem of associating particular SCLS's to their corresponding atomic species can be solved by combining high resolution photoemission with photoelectron diffraction (PD). In a photoemission experiment from a crystalline surface, the outgoing electron wave field is diffracted by atoms in the vicinity of the emitting atom. This PD is manifested as oscillations in the photocurrent from a given core level as a function of angle or energy and contains structural information of short range (~ 5 – 20 Å) around the emitting atom. By modeling this PD using a suitable scattering formalism, photoemission is thus transformed into a structural technique [4,11–13]. By monitoring the PD from a SCLS it is possible to do two things not easily accessible by other means: (1) determine the structural origins of SCLS's appearing in high resolution photoemission measurements from clean surfaces; (2) determine the three-dimensional geometry around the surface atoms which gives rise to the observed SCLS's. In this Letter, we report azimuthal scanned PD experiments from the Si $2p$ low binding energy surface shifted core level of single domain Si(001)-(2×1). Comparisons with fully convergent multiple scattering calculations show clearly that this peak is due to the up atoms only of buckled dimers containing a bond of significant ionicity. In addition, an R factor analysis of a comprehensive geometry search shows a clear minimum for a dimer bond of 19.0° with respect to the surface plane. Agreement between theory and experiment is excellent for this geometry, and the calculated curves show a high sensitivity to changes in the structural parameters indicating that such experiments can determine the atomic arrangement around such surface species with a high degree of accuracy.

The experiments reported here were performed at the MAX I storage ring of the MAX-laboratory synchrotron radiation facility in Lund, Sweden on beam line 41. This beam line is equipped with a toroidal grating monochroma-

tor (TGM), an angle resolving hemispherical analyzer, and a high precision manipulator for rotations in both the polar and azimuthal angles. For the data presented here, the photon energy was 130 eV yielding Si $2p$ photoelectrons of ~ 26 eV kinetic energy with respect to the vacuum level. The total energy resolution used was 100 meV and the angular acceptance of the analyzer was $\pm 2^\circ$. A well-oriented ($\pm 0.1^\circ$) preoxidized n -type Si(001) wafer was used for creating a single domain (2×1) surface. After mounting the wafer on the sample holder, the orientation of the surface normal relative to the azimuthal rotation axis was corrected so that these directions coincided to within $\leq 0.08^\circ$ over the full azimuthal range of 180° . The surface was cleaned *in situ* using standard procedures [14] resulting in a high quality double domain surface as judged from the low energy electron diffraction (LEED) pattern, the sharpness of the surface state peaks taken at a photon energy of 30 eV, and the shape of the Si $2p$ core level taken at a photon energy of 130 eV. Such a surface consists of (2×1) and (1×2) domains in equal quantities with the dimer rows of one domain running perpendicular to the dimer rows of the other. In order to simplify the interpretation of the PD patterns, a single domain surface was prepared by Si evaporation and annealing as described in Ref. [14]. The resulting surface consisted of (2×1) and (1×2) domains in a ratio of 80:20 as judged by the relative intensities of the LEED spots.

The azimuthal scanned PD measurements were made by rotating the sample about the surface normal and recording the Si $2p$ photoemission spectrum every 3° over an azimuthal range of 180° . The electron emission angle was 45° . During the measurements, the pressure remained $< 2 \times 10^{-10}$ mbar. Even so, the sample was flashed to 990°C every 2 h to ensure that the surface remained free of contaminants. According to the procedure established by the high resolution Si $2p$ photoemission results of Landmark *et al.* [9], each spectrum was decomposed into five spin-orbit split Voigt functions using a least-squares fitting procedure. For all spectra in the PD scan, the best fit SCLS values never varied more than 20 meV from the values of -500 , -230 , 62, and 225 meV relative to the bulk peak obtained in Ref. [9] for the (2×1) surface. A Lorentzian full width at half maximum of 100 ± 10 meV was obtained for all spectra and a value of 602 meV used for the spin-orbit splitting. It should be noted, however, that the integrated intensity obtained for the well-resolved low binding energy SCLS, which is the quantity of interest here, is not sensitive to small changes in the fitting parameters of the other peaks. By varying the fitting parameters, it was estimated that the error in obtaining this quantity was $< 2\%$ for all spectra.

At the top of Fig. 1 are shown two Si $2p$ photoemission spectra from the Si(001)-(2×1) room temperature surface corresponding to two points in the azimuthal scans. The dots are the experimental data, and the solid lines are the results of the fitting procedure. The dimer derived SCLS peak S is also shown in both cases. Although

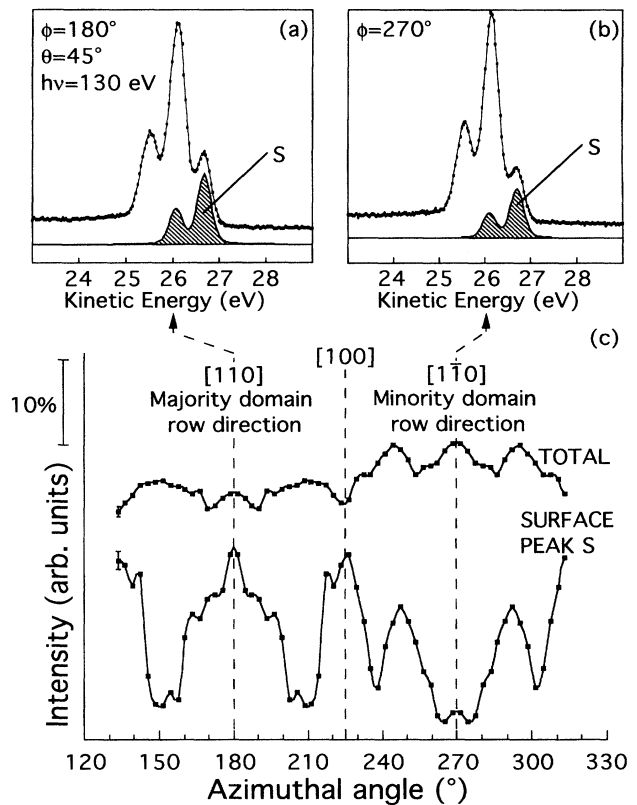


FIG. 1. (a) Si $2p$ photoemission spectrum from single domain Si(001)-(2×1). The azimuthal direction is parallel to the majority domain rows. (b) The same spectrum with the azimuthal direction parallel to the minority domain rows. In both spectra the dimer derived SCLS (peak S) is shown. (c) Azimuthal photoelectron diffraction curves for the total Si $2p$ and peak S signals.

the only difference between the two spectra is a 90° rotation in azimuth, the raw data show clear differences in peak shape. In particular, the relative intensity of peak S is significantly lower in 1(b). This is a diffraction effect and reflects the fact that the atoms giving rise to peak S have a different structural environment than the atoms giving rise to the rest of the Si $2p$ signal. Thus the electron wave field originating from the peak S atoms is diffracted differently resulting in a different intensity behavior as a function of angle. Figure 1(c) shows the total Si $2p$ and peak S integrated intensities as functions of the azimuthal angle after an integrated background subtraction and normalization with respect to the background. Both curves show mirror symmetries around the $[110]$ and $[\bar{1}\bar{1}0]$ directions but not around the $[100]$ direction which corresponds to 225° on the angle scale. These symmetries reveal the single domain nature of the surface: A surface with (2×1) and (1×2) domains in equal quantities would exhibit mirror symmetries around the $\langle 100 \rangle$ directions as well as the $\langle 110 \rangle$ directions. For a surface in which one domain is predominant over the other, how-

ever, the symmetry around the $\langle 100 \rangle$ directions is broken. The fact that the two diffraction curves show the symmetry of a surface in which the domain ratio is not 50:50 thus indicates the sensitivity of these measurements to the dimer geometry.

In order to establish the structural origin of peak S and to determine the three-dimensional atomic structure around the atoms giving rise to the peak S signal, fully convergent multiple scattering calculations were performed for a wide range of dimer structures and comparisons made to the experimental data. The theoretical approach to these calculations, which is described elsewhere [13,15], includes multiple scattering paths to infinite order. The starting point for the geometry search was based on a structure determination for the $c(4 \times 2)$ surface reported by Northrup who performed total-energy calculations within the local-density approximation [17]. In this work, the author found the lowest energy surface to consist of alternating buckled dimers with a bond length of 2.29 Å and a bond angle $\omega = 17.7^\circ$ with respect to the surface plane. Using this geometry, we performed calculations assuming three possibilities for the structural origin of peak S : (1) peak S originates from both atoms of the dimer; (2) peak S originates from the up atom only of the dimer; (3) peak S originates from the down atom only of the dimer. Possibility (1) would indicate that the two atoms of the dimer are electronically equivalent and the dimer bond covalent in agreement with the conclusions of Refs. [5,6]. Possibility (2) would indicate that the up atom is significantly more negative than the down atom (with the down atom photoemission signal occurring somewhere to higher binding energy) and that the dimer bond is ionic in character in agreement with the conclusions of Refs. [7–10]. Possibility (3) has never been proposed but the calculations were performed in order to illustrate how sensitive such measurements are to the structural origins of a given SCLS. Of the three possibilities, only the calculations assuming that peak S originates from the up atom showed good agreement with the experiment. The geometry was then optimized by varying the vertical and lateral positions of the up and down atoms over all physically reasonable values and also by varying slightly the subsurface atomic positions. Figure 2 shows a comparison of theoretical (solid lines) and experimental (dots) PD curves for the up atom only assignment for peak S for a range of dimer bond angles. As can be seen, agreement is excellent for a bond angle of 19.0° with respect to the surface plane. The calculated curve at this angle represents the optimized geometry for the two dimer atoms and the four subsurface atoms to which they are bound. The optimized dimer bond length was found to be 2.25 Å, yielding a dimer bond angle and length very close to the values found in Ref. [17]. Small displacements of the subsurface atoms very close to the values in Ref. [17] were also found. It should be noted that for all calculations, the domain ratio was varied between 100:0 (pure single domain) and 50:50 (pure double domain) and the best fit for the optimized geometry was found for a ratio of 70:30,

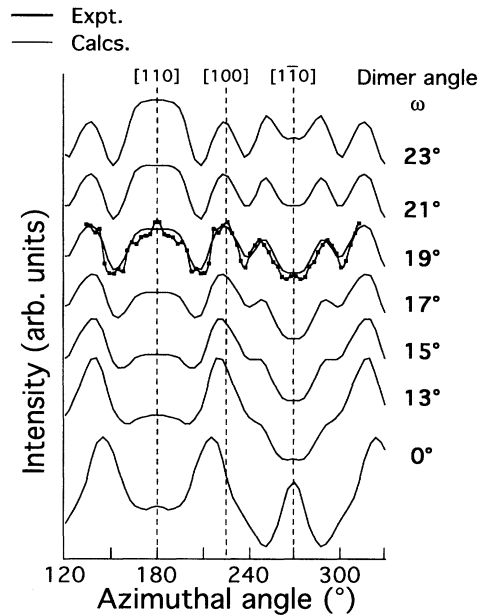


FIG. 2. The peak S photoelectron diffraction data (dots) compared to multiple scattering calculations for emission from the up atom only of the surface dimer for a range of dimer bond angles (solid lines). The bottom curve represents a symmetric dimer bond.

gratifyingly close to the experimentally determined value. These calculations show a high degree of sensitivity to changes in dimer bond angle. Note, in particular, that a prediction assuming a symmetric dimer geometry (bottom curve) is very different from the asymmetric dimer calculations. In fact, all of the structural parameters of the dimer atoms showed a similar sensitivity. This is a consequence of the fact that the scattering factor at low kinetic energies has significant amplitude at all scattering angles. Thus a change in any structural parameter will show changes in the calculated curves and such measurements are necessarily sensitive to the short range three-dimensional structure around the emitting atoms.

Figure 3 reports a further comparison of theory with experiment in the form of R factors as functions of dimer bond angle for the three structural assignment possibilities discussed above. The R factor is a simple sum of differences between experiment and calculations which has been used in previous PD studies [18]. For the up atom only assignment for peak S , the R factor shows a clear minimum for $\omega = 19.0^\circ$. The other two curves represent identical geometries but assuming that peak S originates from both atoms of the dimer and the down atom only of the dimer, respectively. Over the range of geometries represented here, it is clear that for all cases, the up atom only calculations give far better agreement with experiment. In fact, for all geometries in the vicinity of the optimized one, a simple inspection of the calculated curves shows large differences among the three structural assignment possi-

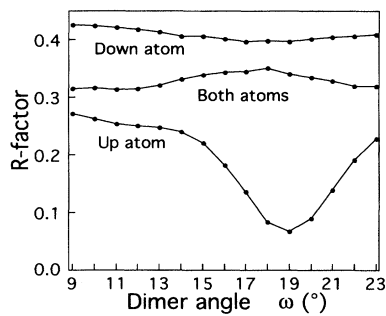


FIG. 3. R -factor comparisons of theory vs the peak S photoelectron diffraction data for a range of ω , the dimer bond angle with respect to the surface plane. The lowest curve assumes that peak S is derived from the up atom only of the dimer while the other two curves assume that peak S originates both from atoms of the dimer and from the down atom only of the dimer, respectively.

bilities and it is immediately obvious that peak S cannot originate from equivalent atoms of a covalently bonded dimer and must instead be due to emission from the up atoms only of an asymmetric ionic dimer bond. It should be noted that the appearance of a large proportion of symmetric dimers in scanning tunneling microscopy (STM) images of this surface [19] is not in conflict with the results presented here. It is believed that the asymmetric dimers flip with the up and down atoms trading positions and that the STM images show a time average of this situation resulting in a symmetric appearance [20]. On the other hand, PD occurs on a time scale which is fast compared to the dimer flip thus providing "snapshots" of the surface. The existence of significant diffraction from peak S and the measurement of a large bond angle thus indicate that the dimers spend most of their time in the asymmetric position but does not preclude the possibility of dimer flips.

In summary, a knowledge of the structural origins of the SCLS's appearing in high resolution photoemission spectra from clean surfaces is essential for understanding the fundamental relationship between surface electronic and atomic structures. By measuring the intensity variations of the low binding energy SCLS from the Si $2p$ core level of single domain Si(001)-(2 × 1) and comparing the results with multiple scattering calculations, we have been able to determine unequivocally that this surface shifted component is due to the up atoms only of asymmetric dimers at the surface. The dimer atoms are thus electronically inequivalent with the bond between them being significantly ionic in character. This type of measurement should be applicable to other surfaces in which the structural origins of the SCLS's are unknown or in question. In addition, a geometry optimization based on comparisons with calculations exhibits very high sensitivity to the three-dimensional geometry around the dimer up atom. Excellent agreement with experiment was found for a dimer angle of 19.0° with respect to the surface plane and a bond length of 2.25 Å. The isotropic nature of the scattering factor at low electron

kinetic energies and the fact that such measurements isolate the signal from a single surface species indicate that photoelectron diffraction from surface core-level shifted peaks constitutes a particularly sensitive method for obtaining bond angles and bond lengths at complex surfaces.

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