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Possibility of charge transfer between dimer atoms on Si(100)-(2×1)

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A precision determination of the number of dimer atoms on the Si(100)-(2×1) surface which contribute to the 2*p* core-level shift as measured by high-resolution photoemission is performed by an *in situ* comparison with Si(111)-(7×7). By correlating distinct features of the Si(111)-(7×7) spectrum with the known structural features of the (7×7) surface, the number of surface atoms which contribute to the Si(100)-(2×1) 2*p* core shift is 0.92 ± 0.07 monolayers. Implications regarding the symmetry of the valence charge distribution about the dimers are addressed.

We present an application of photoemission spectroscopy to a precision determination of the number of surface atoms of a semiconductor crystal which contribute to a surface core-level energy shift. The system under study is the technologically important Si(100)-(2×1) surface, which remains a topic of considerable controversy despite its extensive experimental and theoretical history. A recent scanning-tunneling-microscopy (STM) study of Si(100)-(2×1) has confirmed the dimer nature of the surface, revealing that both buckled and nonbuckled dimers are present in approximately equal numbers.[1] The topographs supplied in this study also reveal the existence of a significant defect density of about (10–20)%, most of which is due to missing dimers. Photoemission spectroscopy of the Si 2*p* core level has indicated the existence of one surface-shifted core-level component which is approximately 0.52 eV toward lower binding energies relative to the bulk component.[2,3] Although the Si 2*p* core shift is known to originate from the surface layer, there is still a question as to which of the three types of dimer atoms (two for the buckled dimer and one for the nonbuckled dimer) contribute to the core-level shift. Since any atomic charge transfer will result in a change in potential and hence a corresponding core-level binding-energy shift,[4] a careful evaluation of the core-level spectra may reveal significant insights concerning the symmetry of the total valence-charge distribution about the dimer atoms. This is a basic issue in connection with the mechanisms behind the reconstruction and the surface electronic properties in general, which have been investigated theoretically by several groups.[5–9] Chadi concluded from a tight-binding energy-minimization calculation that a charge transfer of 0.36*e* occurs between the two atoms in a buckled dimer.[5] Based on a chemical-bond theory, Pauling and Herman proposed a buckled dimer model involving a Si^+-Si^- ionic pair with sp^2 and s^2p^3 bonding configurations.[8] But recently, the large charge transfer in connection with the buckling was called into question by Schluter, who discussed the importance of the intra-atomic repulsion which would resist any tendency for charge transfer.[9] The present work confirms that the charge transfer is indeed much smaller than 0.36*e*, and therefore the dimer bond, buckled or nonbuckled, is covalent in nature.

In photoemission, the usual method to quantify the number of atoms giving rise to a particular core shift relies on a standard layer attenuation model involving the phenomenological electron escape depth, which is generally uncertain and depends sensitively on the sample-to-analyzer collection geometry.[4,10] Because of fundamental difficulties in reproducing experimental (analyzer collection) geometries, various studies have led to different values for the escape depths. For the closely related Ge(100)-(2×1) surface, for example, the uncertainty in the escape depth has led to reports for the number of surface atoms giving rise to the core shift ranging from about $\frac{1}{2}$ atomic layer to 1 full atomic layer.[4,11,12] This is a problem for surfaces like Si(100)-(2×1) and Ge(100)-(2×1), which exhibit more than one type of a reconstruction unit in addition to possible intrinsic surface defects (which are likely to occur near domain boundaries), and the connection between different types of surface atoms and the core shifts cannot be easily established.

The present technique does not use the layer attenuation model and is free from employing an estimated escape depth. The technique relies on the use of a well-characterized reference sample, in this case Si(111)-(7×7), for which a surface structural feature and the corresponding surface-shifted core-level component can be accurately correlated. STM and transmission electron diffraction have shown convincingly that the surface structure of Si(111)-(7×7) is described accurately by the Takayanagi dimer-adatom-stacking-fault model.[13–16] The structure consists of 12 adatoms per surface unit cell occupying the outermost surface layer, a second reconstructed layer with a stacking fault in one half of the unit cell and a corner hole vacancy per unit cell. Because the 12 adatoms are in a distinctly different atomic environment than the rest of the system, a distinct surface core-level shift associated with the adatom sites is expected and is observed.[2–4,17] Since large-area STM scans of Si(111)-(7×7) show the surface structure to be generally flawless without any appreciable defects, the photoemission intensity of the adatom core-level component serves as an excellent intensity reference. Thus, by an *in situ* comparison of Si(100)-(2×1) and Si(111)-(7×7) 2*p* core-level spectra with identical experimental geometries, it will be pos-

sible to accurately determine the number of atoms contributing to the Si(100)-(2×1) surface core-level shift. Furthermore, since there are uncertainties introduced by the limited experimental precision in the photoemission technique as well as questions about sample reproducibility, many different samples are employed to assess the statistical average and uncertainty in the measured dimer contribution.

The photoemission experiments were carried out with synchrotron radiation from the University of Illinois beam line on the 1-GeV storage ring at the Synchrotron Radiation Center of the University of Wisconsin-Madison at Stoughton, Wisconsin. Light from the ring was dispersed by an extended range grasshopper monochromator, which was designed and constructed by F. C. Brown and his co-workers. The photoelectrons were analyzed with a Leybold-Heraeus EA-10 hemispherical electrostatic analyzer. The overall instrumental resolution was about 0.2 eV. The *n*-type Si(100) and Si(111) samples were cleaned by thermal annealing at 1100 and 1250 ± 100 °C, respectively, in the vacuum chamber [note that the thermal annealing technique was also used in the STM study to generate the Si(100)-(2×1) surface.] The samples were allowed to cool down to temperatures between 50 and 100 °C before the photoemission measurement. All of the 40 samples used in this study were checked by high-energy electron diffraction (HEED) which revealed a sharp two-domain (2×1) pattern for Si(100) and a sharp (7×7) pattern for Si(111); in all cases, the background was extremely low. HEED was performed only after the photoemission measurement, to avoid possible carbidization of the surface.

A photon energy of 150 eV was used for all samples, corresponding to a surface-sensitive condition for Si.[2-4] Two typical spectra (dots) are shown in Fig. 1, one for Si(100)-(2×1) and the other for Si(111)-(7×7). Bulk sensitive spectra taken with a photon energy of 108 eV, not shown here, can be found in earlier publications.[2-4,17] Previous studies of these surfaces employing a nonlinear least-squares-fitting procedure have shown that the line shapes contain surface and bulk contributions. The decomposition into various components as well as the overall fit to the line shape are indicated in Fig. 1 by the various curves. The Si(100)-(2×1) surface shows a surface component (labeled *S* in the figure) in addition to the bulk component (labeled *B*), while the spectrum for Si(111)-(7×7) shows two surface components (labeled *S*1 and *S*2). The details of the line-shape analysis and the basis for assignment of the various peaks can be found in previous publications and will not be repeated here.[2-4,17] In all cases, each component exhibits a spin-orbit splitting of 0.61 eV. The abscissa in Fig. 1 (the relative binding energy) is referred to the bulk contribution of the Si $2p_{3/2}$ core.

The same analysis was performed for 20 Si(100)-(2×1) samples and 20 Si(111)-(7×7) samples which were positioned in exactly the same geometry during an experimental period of several days. The experimental sequence involved several Si(100) samples followed by several Si(111) samples, etc. The weights (fraction of total intensity) of the *S* component for Si(100)-(2×1) and the *S*2 component for Si(111)-(7×7) are plotted for each sample shown in Fig. 2. The fairly small data scattering implies a high degree of reproducibility of the surfaces. The average values of the weights for the *S* and *S*2 components are 0.163 and 0.050, respectively. An error bar, indicating a length of two standard deviations for each average is shown in Fig. 2.

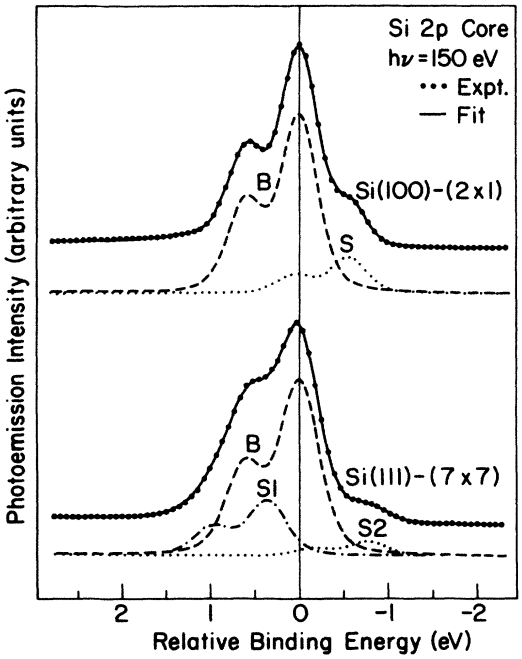

FIG. 1. Si 2*p* core-level spectra taken with a photon energy of 150 eV for the Si(100)-(2×1) and Si(111)-(7×7) surfaces in the same analyzer collection geometry. The solid curves running through the data points (dots) are the fits to the data. The other curves show the decomposition of the spectra into bulk (*B*) and surface (*S*, *S*1, and *S*2) contributions. The binding energy is referred to the bulk Si $2p_{3/2}$ components.

The *S*2 component for Si(111)-(7×7), with a fairly large binding-energy shift relative to the *B* component, is known to be derived from the adatoms.[17] Its intensity should correspond to 12 atoms per (111)-(7×7) surface unit cell. From the direct comparison of emission intensity shown in Fig. 2, it is now possible to determine the number of atoms per unit cell which contribute to the *S* component emission of the Si(100) surface. For a fixed photon flux, photon energy, and sample geometry, the integrated core-level intensity must be a fixed constant for different crystallographic surfaces of a given material, since diffraction effects are negligibly small for an angle-integrated photoemission geometry used in this experiment.[10] Thus, the number of Si(100)-(2×1) surface atoms in terms of (100) monolayers (1 ML = 6.8×10^{14} atoms/cm^2) contributing to the *S* emission is given by the product of the following three quantities: the ratio of the average weights between *S* and *S*2, the established 12/49 site density of the Si(111) *S*2 adatoms, and a geometric factor accounting for the size difference between the Si(100) and Si(111) unreconstructed unit cells. The re-

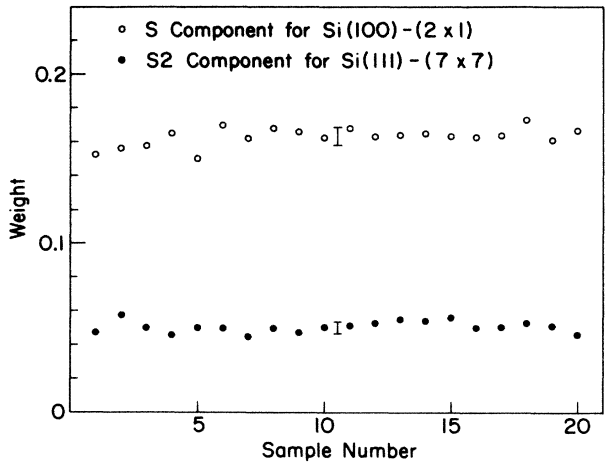

FIG. 2. Weights (fraction of total intensity) of the $S2$ and S components for 20 Si(111)-(7×7) and 20 Si(100)-(2×1) samples, respectively. Error bars indicating a length of two standard deviations for the average weight of each component are shown next to each group of data points. The assigned sample numbers for each point are arbitrary; there is no special relationship between Si(111) and Si(100) points possessing the same sample number.

sult is an S emission corresponding to 0.92 ± 0.07 ML. Since the Si(100)-(2×1) surface consists of roughly equal numbers of buckled and nonbuckled dimers, the fact that nearly a full monolayer contributes to the S emission implies immediately that the S emission results form all three types of dimer atoms. The 0.08 ± 0.07-ML deviation in the S emission from the ideal, fully dimerized surface is consistent with the defect density measured in the STM study.[1]

The question of a total negative charge transfer from the "down" atom to the "up" atom in a buckled dimer has been investigated by several authors as noted above. Evidence for such a charge transfer would necessitate the existence of additional surface-shifted core-level components to account for the different types of dimer atoms. From previous studies of chemisorption-induced shifts on Si and Ge surfaces, the energy shift is found to be approximately 1 and 0.5 eV for highly ionic and covalent adsorbate-to-substrate bonding, respectively, suggesting roughly a 1-eV shift per one effective electron transfer.[3,4,12,18,19] Chadi's calculation for the buckled dimer configuration on Si(100) yields a $0.36e$ charge transfer between the up and down atoms.[5] Such a charge transfer would then manifest itself in a 0.7-eV energy separation between the up and down atom core-level binding energies. Final-state screening effects could cause an additional overall shift for both the up- and down-atoms in the same direction, possibly rendering one component indistinguishable from the bulk component.[4,20] But this would cause the S emission intensity to correspond to less than $\frac{1}{2}$ ML, which is not the experimental finding here. The inability to distinguish between the different dimer atoms contributing to the S emission may be limited by our 0.2 eV resolution for this core-level deconvolution procedure, which scales into an approximate upper limit of $0.1e$ charge transfer between dimer atoms.

A more recent STM study suggests the possibility that the nonbuckled dimers appearing in the topographs may actually be the time-averaged position of buckled dimers which are rapidly switching between the two buckling directions; the buckled dimers which appear predominantly near missing dimer defects may be stabilized by such defects.[21] The photoemission technique, being a much faster probe than STM, would sample a continuous distribution of dimer orientations which might be expected in a typical dynamic buckling scenario (the buckling frequency would be on the order of a surface phonon frequency). In any case, the present photoemission result simple indicates that all dimer atoms contribute to the core-level shift, regardless of the instantaneous dimer bond orientation, and the charge transfer is at most $0.1e$. This conclusion is also not affected by the (remote) possibility that our samples and the STM samples might have significantly different ratios between the buckled and nonbuckled dimers.[22]

In summary, we have demonstrated that the surface core-level shift contribution for a given surface can be quantified by an *in situ* comparison with a well-characterized reference sample. The known structure of the Si(111)-(7×7) surface enables a convenient means for determining the number of Si surface atoms exhibiting the 0.52-eV core shift on Si(100)-(2×1). The result is that 0.92 ± 0.07 ML of Si dimer atoms contribute to the surface core-level shift for Si(100)-(2×1). The statistical analysis in the comparison has been carried out with a sufficiently larger number of samples. From the result, we conclude that all Si dimer atoms, whether buckled, nonbuckled, or dynamically buckled, contribute to the emission for the surface-shifted core-level component, ruling out large asymmetrical charge distributions about the buckled dimer atoms. This result also establishes a firm foundation for future quantitative core-level analysis works on the chemistry and interface formation of the Si(100) surface.

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[22]It is expected that our Si(100)-(2×1) samples and the STM samples have very similar overall surface atomic structure, because the same thermal annealing technique was used to generate the surfaces. Furthermore, in the present work as well as the STM work, the results (core-level spectra and diffraction patterns or STM images) are consistently reproduced, implying that the results correspond to a typical Si(100)-(2×1) surface.