Extended Photoemission Fine Structure Analysis of the Si(111)-(7×7) Surface Core Levels

J. A. Carlisle,* M. T. Sieger, T. Miller, and T.-C. Chiang
Department of Physics, University of Illinois, 1110 West Green Street, Urbana, Illinois 61801
and Materials Research Laboratory, University of Illinois, 104 South Goodwin Avenue, Urbana, Illinois 61801

(Received 9 August 1993)

The surface- and bulk-derived components of the Si $2p$ core levels, acquired by photoemission from Si(111)-(7×7), show strong and different oscillations caused by extended fine structure above the $2p$ edge. An analysis of these oscillations yields the bulk and surface bond lengths which agree well with the known structure. The heretofore controversial issues of the photoemission escape depth and the atomic origin of the surface core levels are resolved.

PACS numbers: 68.35.Bs, 61.10.Lx, 79.60.Bm

One of the main thrusts of surface physics is to explore the causal relationships between the geometric and electronic structures of clean, well-ordered crystalline surfaces. To this end, synchrotron-radiation photoemission, particularly surface core-level photoemission, has played a major role. The atoms which comprise the surface reconstruction often display core-level binding energies which differ significantly from the bulk, and in many cases an analysis of these surface core-level components has elucidated surface atomic structure as well as the atomic scale interactions of submonolayer adsorbate films with surfaces [1–4]. It is surprising then that the surface core levels derived from the prototypical Si(111)-(7×7) surface have yet to find a consensus as to their atomic origins [1,5–9]. A similar problem exists for other Si and Ge surfaces [1,10,11]. Both the *coverages* [i.e., the number of monolayers (ML)] associated with the surface core-level intensities as well as the physics behind their binding energy difference from the bulk binding energy (i.e., *the surface core-level shifts*) have been subjects of debate.

For the Si(111)-(7×7) surface, which is the focus of this investigation, we show in Fig. 1 a set of photoemission spectra taken with various photon energies, corresponding to different surface sensitivities. These line shapes have been investigated extensively in the past, and can be decomposed into three major components: B (bulk), $S1$ (surface component one), and $S2$ (surface component two) [1,5–9]. At the center of the controversy is the atomic assignment of $S2$, i.e., whether it corresponds to the adatoms or rest atoms of the (7×7) reconstruction. These are the only atoms on this surface with a dangling bond, and there are twelve adatoms and seven rest atoms in each (7×7) unit cell. The adatoms are bonded above the first Si(111) double layer. The rest atoms are threefold coordinated surface atoms, six of which lie in the first double layer, plus one lying in each of the corner holes. The coverages for these two kinds of atoms differ by about a factor of 2.

Several previous studies have adopted the rest-atom assignment based on (a) the predicted partial charge transfer from the adatom dangling bond to the rest-atom dangling bond, which may give rise to a more electronegative environment for the rest atoms, and (b) the $S2$ intensity, as compared to other "model" intensities for various adsorbate-covered Si(111) surfaces [1,5–7]. This latter argument is in turn based on the well-known *layer attenuation model* [1,2], which is used to describe the observed intensities of the bulk and surface components in terms of varying contributions from different layers at and beneath the surface. Other work has suggested that the $S2$ component is derived from adatom emission [8,9]. This assignment has also been supported by layer attenuation model arguments (with a longer escape path as compared to the above studies), as well as adsorption experiments. To explain the apparent discrepancy between this assignment and charge-transfer arguments, final-state effects have been evoked [9].

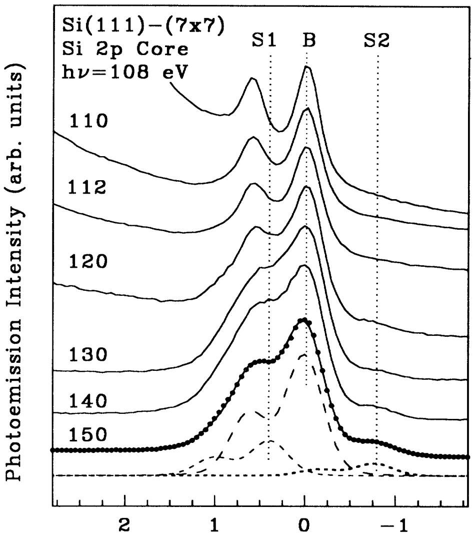

FIG. 1. A set of Si $2p$ core-level spectra acquired from the Si(111)-(7×7) surface for various photon energies as indicated. The bottom spectrum is fitted to three spin-orbit split doublet components, labeled B, $S1$, and $S2$.

0031-9007/93/71(18)/2955(4)$06.00

Although the layer attenuation model has served for years as the standard tool for surface core-level intensity analysis, its accuracy has not been scrutinized. In this model, the emission intensity from each atom is assumed to be proportional to $\exp(-d/\lambda)$, where d is the distance of the atom from the surface, and λ is the escape depth. The escape depth is a smooth function of energy, and thus the predicted surface to bulk emission intensity ratio is also a smooth function. This model ignores quantum mechanical effects, but by and large it has worked quite well—except for a few cases including the Si and Ge surfaces mentioned above. The work to be presented in this paper uncovers the source of this problem. It turns out that quantum mechanical effects are not negligible for Si(111) as assumed in previous studies. In particular, the surface and bulk core-level intensities exhibit strong oscillations similar to extended x-ray absorption fine structure (EXAFS) [12,13]. Thus, any conclusion based on measurements of the surface to bulk intensity ratio using a few photon energies can suffer large errors. The oscillations in our data permit a standard EXAFS analysis, and the derived bond lengths are in excellent agreement with the known structure. Our results show, beyond doubt, that $S2$ corresponds to the adatoms. This study also demonstrates that surface EXAFS analyses can be carried out for *clean* surfaces based on surface-shifted core levels, even for complex reconstructions [14]. Different variations of photoemission EXAFS techniques (not based on surface-shifted core levels) have been demonstrated to yield results for simple reconstructions [13].

Our photoemission measurements were carried out at the Synchrotron Radiation Center of the University of Wisconsin-Madison. An angle-integrating hemispherical analyzer was used to collect the data. The energy resolution was in the range 0.16–0.22 eV, depending on the photon energy used. The sample preparation and characterization followed standard procedures as described previously [8,9]. The measured core-level emission intensity was normalized to the beam current. The variation of the output of the monochromator as a function of photon energy gave rise to a smooth varying background, which was removed by a polynomial fit in the data analysis.

Figure 2 shows the measured intensity ratio between the $S2$ and B components. Different symbols correspond to different runs. Strong oscillations are seen. Also shown are two curves depicting the behavior based on the layer attenuation model assuming the adatom and rest-atom assignments as indicated. The escape depth used in this illustration is the nominal "universal curve" taken from Ref. [15]. The adatom curve is twice as high as the rest-atom curve because of the factor of 2 difference in coverage. The large deviation of the layer attenuation model from the experiment is quite clear. Note, in particular, the strong variation of the measured ratio by more than a factor of 2 in the photon energy range 130–160 eV, which is the standard energy range used previously (for reasons of maximum surface sensitivity based on the universal curve). Clearly, using just one arbitrary photon energy within this range can easily lead to a factor of 2, or larger, discrepancy in the coverage assignment using the layer attenuation model.

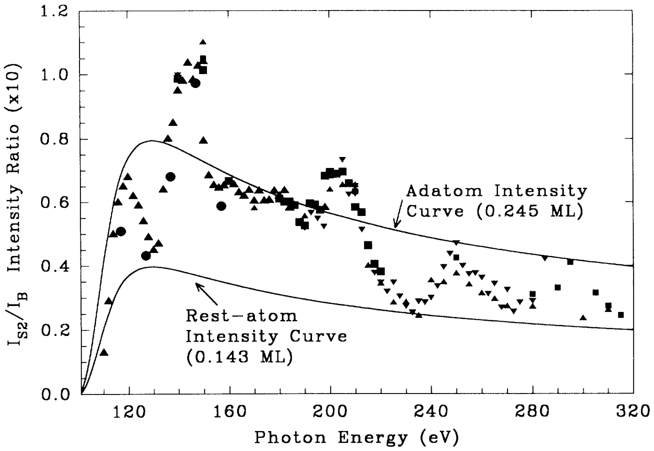

FIG. 2. The intensity ratio between the $S2$ and B components. The different symbols denote different samples. The curves show the behavior as predicted by the layer attenuation model, assuming that $S2$ corresponds to either the adatoms or the rest atoms.

The physics behind the oscillations in the intensity is the extended fine structure above the Si $2p$ edge. Our analysis of the core-level intensities follows standard EXAFS procedures [12,13]. We show in Fig. 3 the absolute value of the weighted Fourier transform of the experimental data, $|F(R)|$, where $F(R)$ is given by

$$F(R)=\int k^3\chi(k)W(k)e^{-2ikR}dk\,.$$

In the above equation, k is the photoelectron momentum, χ is the oscillatory part of the data for each core-level component, and $W(k)$ is a window function used to avoid truncation errors. Each component shows a number of shells of nearest neighbors. To filter out the contribution from each shell, the $F(R)$ function was multiplied by another window function, $W(R)$, centered on each shell, and inverse Fourier transformed. The resulting filtered data are then fitted to model functions involving the phase shifts, from which the bond lengths are deduced. In our analysis, we used the scattering phase function of Ref. [16] and the absorber phase function of Ref. [17]. The resulting experimental distances for the first two shells are shown in Table I, which are the most important for making atomic assignments. The accuracy for these distances is estimated to be better than 0.03 Å except for the $S1$ component, for which the first two shells shown in Fig. 3 are fairly close, causing a greater uncertainty (~0.1 Å). It is clear from Fig. 3 that peak A shows a significant shift between the $S2$ and B components, giving rise to a considerably larger first shell distance for $S2$.

We now compare the experimental results with the

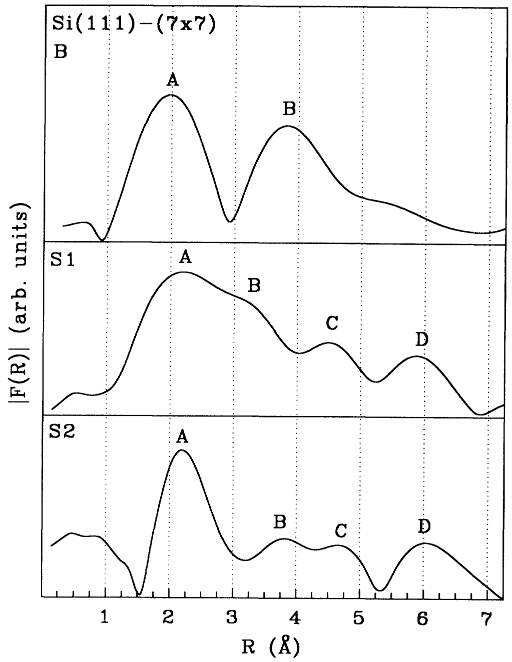

FIG. 3. The absolute value of the Fourier transform $F(R)$ of the EXAFS signals for the B, $S1$, and $S2$ components.

TABLE I. First and second shell distances (in Å) deduced from our measurements (expt.) and from the calculation of Ref. [22] (theory). The true bulk values are deduced from the lattice constant of Si, 5.431 Å.

Atomic and spectral entities	First shell distance	Second shell distance
$S2$ (expt.)	2.53	4.30
$S1$ (expt.)	2.45	3.50
B (expt.)	2.31	3.91
Adatom (theory)	2.49 ± 0.02	4.22 ± 0.12
Rest atom (theory)	2.38 ± 0.01	3.97 ± 0.12
True bulk	2.35	3.84

known structure of the Si(111) surface. The detailed atomic positions have been investigated by x-ray diffraction [18], which is sensitive to in-plane atomic locations, by low energy electron diffraction [19], which is sensitive to vertical atomic layer spacings, and by *ab initio* energy minimization super-large-scale calculations [20–22]. These results show that there is considerable surface strain, and some of the bond lengths near the surface are significantly modified. Although there are some slight numerical differences, the major features derived from these studies are consistent. For simplicity, we will use the results from Ref. [22] for numerical comparison; these are summarized in Table I. The first and second nearest neighbor distances in bulk Si are 2.35 and 3.84 Å, respectively. Each rest atom on the surface has three first nearest neighbors corresponding to three back bonds with a bond length of 2.38 ± 0.01 Å. This is very close to the bulk value. The ± 0.01 Å here indicates the spread among symmetry inequivalent bonds. For the adatoms, each has four nearest neighbors, three in the triangular pedestal, and one directly beneath the adatom for the T_4 geometry. Because of the large distortion in the tetrahedral bond angles, the adatom complex relaxes to give a significantly larger bond length, 2.49 ± 0.02 Å. Our measured $S2$ bond length of 2.53 Å is also significantly larger than the bulk value. Thus, we conclude that the $S2$ component corresponds to the adatoms, not the rest atoms. This conclusion is further corroborated by the second shell distance. Each adatom has 6 neighbors in the second shell, consisting of dimers and atoms bonded to rest atoms. The average over all 12 adatoms within the unit cell gives 4.22 ± 0.12 Å from the theory. This is much larger than the bulk value, and again compares very well with the measured value of 4.3 Å for $S2$. In contrast, the theoretical second shell distance for the rest atoms is 3.97 ± 0.12 Å, much too small compared to the experiment.

In the adatom assignment, the $S1$ component mainly corresponds to atoms in the first layer below the adatoms, but we do not know exactly which atoms are contributing. Within this layer, there are 36 atoms from the pedestals of the adatoms and 6 rest atoms in each unit cell. It is possible that the 18 dimer atoms are also contributing. Many of the first neighbor distances for these atoms are significantly larger than the bulk value by up to about 0.2 Å, and thus, the measured first shell distance of $S1$, 2.45 Å, is consistent with this trend. The measured second shell distance for $S1$ is 3.5 Å. This is significantly shorter than the bulk value of 3.84 Å, but corresponds very well to the sides of the pedestal triangles, 3.6 ± 0.1 Å. Since $S1$ represents an unresolved component in the core-level data, we do not wish to push the interpretation any further.

The measured first and second shell distances for the B component, 2.31 and 3.91 Å, respectively, are fairly close to the true bulk values of 2.35 and 3.84 Å. It is important to note that the B component in our experiment represents a weighted average of subsurface atoms, where some slight departures of bond lengths from the true bulk values are not unexpected [20–22].

In summary, we have performed a detailed analysis of the $2p$ core-level photoemission spectra of Si(111)-(7×7). The surface to bulk intensity ratio, traditionally assumed to be a smooth function of photon energy and describable by the layer attenuation model, shows instead strong EXAFS oscillations. This necessitates reevaluation of previous conclusions about the surface structure based on a core-level intensity analysis at just one photon energy. The measured EXAFS oscillations permit bond length determination, and the results agree well with the known structure of Si(111)-(7×7). The $S2$ component is shown to be derived from the adatoms. This study demonstrates that extended photoemission fine structure measurements, utilizing intrinsic surface-shifted core levels, are a practical method for surface structural analysis, even for complex reconstructions. Our measurement here also indirectly confirms the accuracy of state-of-the-art calculations for Si(111)-(7×7), which show significant strain near this surface.

This material is based upon work supported by the U.S. Department of Energy (Division of Materials Sciences, Office of Basic Energy Sciences), under Grant No. DEFG02-91ER45439. Acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the U.S. National Science Foundation (Grant No. DMR-92-23546) for equipment and personnel support of our beam line operation. The Synchrotron Radiation Center of the University of Wisconsin-Madison is supported by the U.S. National Science Foundation.

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*Present address: Chemistry and Materials Science Division, Lawrence Livermore National Laboratory, Livermore, CA 94550.

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