

Site-Dependent Fine Structure in Photoemission Branching Ratios

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The photoemission intensity ratio between the $4d_{3/2}$ and $4d_{5/2}$ spin-orbit-split states of the Sb $4d$ core level, known as the branching ratio, shows fine-structure oscillations as a function of photon energy, which are different for the Sb/Si(111)-($\sqrt{3} \times \sqrt{3}$) and ($5\sqrt{3} \times 5\sqrt{3}$) adsorbate structures. We demonstrate that this branching ratio fine structure is related to the diffraction χ function, and can be used to deduce the adsorbate atomic structure. The dependence of the branching ratio on atomic bonding geometry has important implications for high-resolution core-level line shape analyses.

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Experimental surface science techniques based upon the detection of photoexcited core electrons have made countless contributions to our knowledge of the atomic structure of surfaces. Several of these techniques, such as photoelectron diffraction (PED) [1], photoemission extended fine structure (PEFS) [2], and photoelectron holography (PEH) [3], rely upon the measurement of the interference due to the photoelectron wave scattering from nearby atoms as a function of incident photon energy and/or emission direction. This interference is typically manifested in the experimental data as small-amplitude, short-period oscillations in the photoemission intensity on top of a smooth background. The oscillatory part of the data, expressed as a χ function, is then related to the emitter bonding geometry by comparison of the data to theoretical models (PED), direct inversion to yield bond lengths (PEFS), or direct inversion to obtain a three-dimensional image (PEH). All of these measurements involve small changes in the absolute photoemission intensity, and are therefore made difficult by a stringent requirement on the system stability and response. This study shows that the same information can instead be derived from the intensity ratio (branching ratio) of the two spin-orbit-split peaks of a given core level. Such intensity ratio measurements involving two peaks with nearly the same energy can be much more accurate than absolute intensity measurements. Variations in the characteristics of the apparatus, including the system resolution, the natural decay of the synchrotron light source intensity, and the system throughput as a function of photon energy, tend to divide out. Branching ratios thus offer an attractive alternative for χ -function measurement.

We have chosen Sb adsorbed on Si(111) as a model system for this study. The structure of Sb/Si(111) has received much attention in recent years due partly to Sb's role as a surfactant in Si epitaxial growth. Sb is known to form a ($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ and a ($5\sqrt{3} \times 5\sqrt{3}$) $R30^\circ$ reconstruction on Si(111), which have good long-range

order as evidenced by low-energy electron diffraction [4]. To avoid the cumbersome notation, we will hereafter refer to these reconstructions as the $\sqrt{3}$ and $5\sqrt{3}$ surfaces, respectively. The Sb $4d$ core-level photoemission from these surfaces shows two well-resolved peaks due to the $4d_{3/2}$ and $4d_{5/2}$ spin-orbit-split states, as shown in Fig. 1. The intensity ratio between these two peaks has a statistical value of 2/3. It is well known that photoemission measurements of the branching ratio show long-period deviations from this statistical value due to the nonzero slope of the atomic photoionization cross section [5]. In this study we have observed additional short-period, fine-structure oscillations in the branching ratio, which are different for the $\sqrt{3}$ and $5\sqrt{3}$ surfaces. The thrust of this work is twofold. First, we show how this branching ratio fine structure is related to the intensity χ function, and how this fine structure reveals

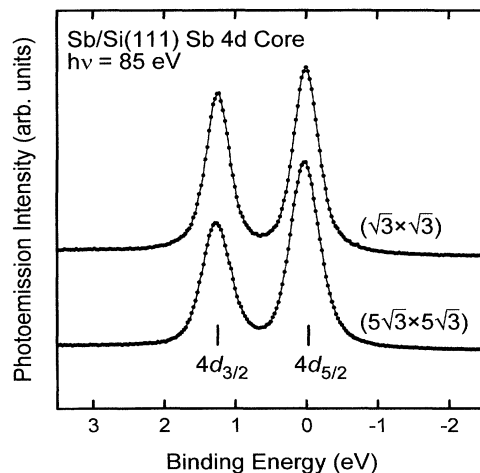


FIG. 1. Sb $4d$ core-level spectra for the $\sqrt{3}$ and $5\sqrt{3}$ phases of Sb on Si(111) obtained at a photon energy of 85 eV. The binding energy scale is referenced to the $4d_{5/2}$ peak. Peak height has been normalized to the $4d_{5/2}$ maximum.

structural information about these surfaces. Second, we will discuss the implications of branching ratio fine structure for the fitting and analysis of photoemission core-level spectra in general, especially for systems that exhibit multiple unresolved components [6,7]. With the advent of new synchrotron light sources and ultrahigh-resolution instruments, this is an area of increasing importance and activity, and the issue of a varying branching ratio will have major impact on the way that such data are analyzed.

The photoemission experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin-Madison at Stoughton, Wisconsin, on the 1-GeV storage ring Aladdin. An angle-integrating hemispherical analyzer centered near the normal-emission direction and with a collection angle of 7×13 degrees was used to detect the photoelectrons. The incident photon flux was polarized near normal to the surface. The *n*-type Si(111) substrates were cleaned *in situ* by heating to $\sim 1300^\circ\text{C}$ for several seconds to adsorb the oxide layer. This procedure routinely yields high-quality (7×7) surfaces. 99.999% pure Sb was evaporated from an electron-beam heated crucible, with the evaporation rate monitored by a quartz-crystal thickness monitor. The $\sqrt{3}$ phase was prepared by exposing the clean (7×7) surface to an incident Sb flux at 600°C . At this deposition temperature, the Sb coverage is known to saturate at about one monolayer [8]. The $5\sqrt{3}$ surface was obtained by annealing the $\sqrt{3}$ phase for 5 min at 700°C . Both surfaces showed sharp and well-ordered electron diffraction patterns.

Figure 1 shows selected Sb $4d$ core-level spectra for the two surfaces. It is clear from inspection that the branching ratio of the $\sqrt{3}$ spectrum is significantly larger than that of the $5\sqrt{3}$ at the same photon energy. Since the Sb atomic photoexcitation cross section is the same, this difference must be due to the change in bonding structure between the two cases. Figure 2 plots the observed branching ratio as a function of incident photon energy. It is evident that there are short-period oscillations, and that the overall branching ratio is different for the two surfaces, by as much as 20% near 85 eV. This energy dependence of the branching ratio has two parts: first, the long-period variation due to the atomic photoemission cross section [5]; and, second, short-period oscillations which are dependent on the atomic structure. These differences in branching ratios are well reproduced on samples prepared over several runs.

As mentioned earlier, the fine-structure function for photoemission intensity is the basic quantity required for a standard structural analysis using either PED, PEFS, or PEH. It is defined by

$$\chi(E) = \frac{\sigma_j(E) - \sigma_j^0(E)}{\sigma_j^0(E)}, \quad (1)$$

where $\sigma_j(E)$ is the measured intensity and $\sigma_j^0(E)$ is a smooth background function [1-3]. Here the subscript *j*

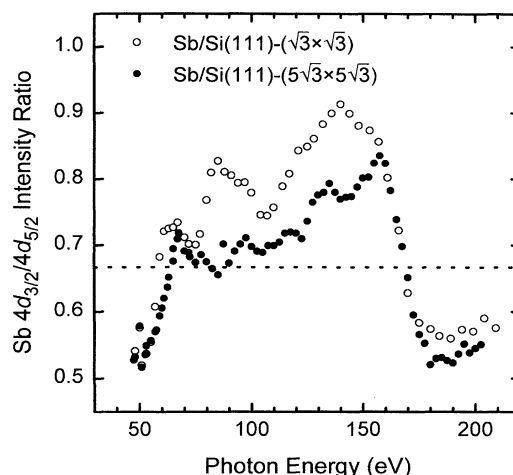


FIG. 2. The variation of the measured branching ratio with incident photon energy for the two reconstructions. Dashed horizontal line represents the statistical value of $2/3$.

denotes the total angular momentum and equals either $5/2$ or $3/2$ for the two spin-orbit-split Sb $4d$ core components. The χ function characterizes the short-period oscillations caused by photoelectron interference, and depends on the local bonding structure and the photoelectron kinetic energy E . It is the same for the two spin-orbit-split components [9]. A similar fine-structure function $\xi(E) = [B(E) - B^0(E)]/B^0(E)$ can be defined for the branching ratio $B(E)$. It is straightforward to show that these two fine-structure functions χ and ξ are related by

$$\xi(E) = -\Delta \frac{\chi'(E)}{1 + \chi(E)}, \quad (2)$$

where Δ is the spin-orbit splitting, and terms of order $(\Delta/E)^2$ and higher are neglected. Since χ is small compared to unity, it is easy to see that $\xi \cong -\Delta\chi'$, and the branching ratio measurement yields basically a derivative of the intensity χ function. In a sense, branching ratio measurement is a difference method, which tends to emphasize the short-period oscillations in the χ function. Solving the above first-order differential equation for χ , we obtain

$$\chi(E) = \exp\left(-\frac{1}{\Delta} \int \xi(E) dE\right) - 1. \quad (3)$$

Therefore, to determine the χ function, one simply needs to measure the branching ratio and apply Eq. (3).

Figures 3(a) and 3(b) show $\chi(k)$ for the $\sqrt{3}$ and $5\sqrt{3}$ phases of Sb/Si(111), respectively (here, k is the photoelectron momentum). Empty circles represent the χ function derived from the photoemission intensity of the $4d_{3/2}$ peak, and empty squares are derived from the $4d_{5/2}$ intensity. Filled circles represent the χ function derived from the branching ratios using Eq. (3). Overall, the

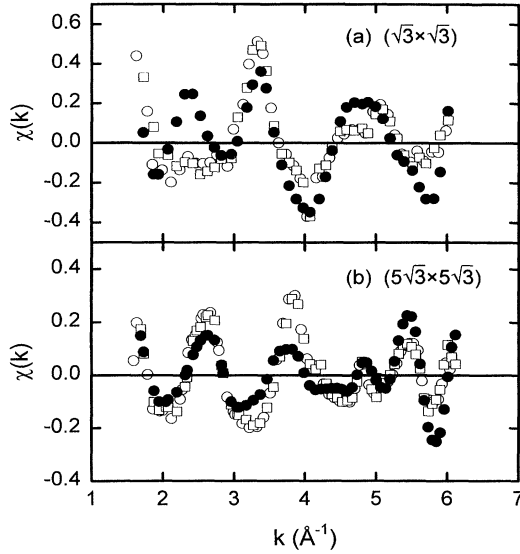


FIG. 3. χ functions derived from the absolute intensity of the $4d_{3/2}$ (empty circles) and $4d_{5/2}$ (empty squares) photoemission peaks and from the measured branching ratio (filled circles) for (a) the $\sqrt{3}$ and (b) $5\sqrt{3}$ surfaces.

agreement is very good. We tend to trust the branching ratio data more, because the intensity measurement is noisier and can be affected by the photon flux calibration, which itself may not be represented by a completely smooth function.

Since we employed an angle-integrating collection geometry, it is appropriate to perform a structural analysis of the χ function using PEFS [2,9], which is similar to the standard extended x-ray absorption fine-structure (EXAFS) analysis. Figure 4 shows the result of such an analysis based on the measured branching ratio ξ function. The function $F(R)$ is given by

$$F(R) = \int \chi(k)W(k)e^{-2ikR}dk, \quad (4)$$

where $W(k)$ is a modified Hanning window used to avoid truncation errors, and χ is given by Eq. (3). The positions of the peaks of the function $|F(R)|^2$, after phase shift correction, should correspond to the near-neighbor bond lengths. With our experimental geometry, the contributions will be mainly from atoms located directly beneath the emitter [9].

Our discussion will focus on the first-shell distance. The first-shell peak of the $5\sqrt{3}$ surface is at a distance ~ 0.35 Å longer than that of the $\sqrt{3}$. It is known that the $\sqrt{3}$ surface consists of Sb trimers, with a first-shell Sb-Si bond length of 2.59 Å [10]. The structure of the $5\sqrt{3}$ surface is somewhat unclear, but, based on a scanning tunneling microscopy measurement in the appropriate coverage range, it appears that the structure mainly involves Sb adatoms bonded in T_4 sites [10]. We can expect a bond length of ~ 2.98 Å between the Sb emitter and a Si atom located directly beneath it in a

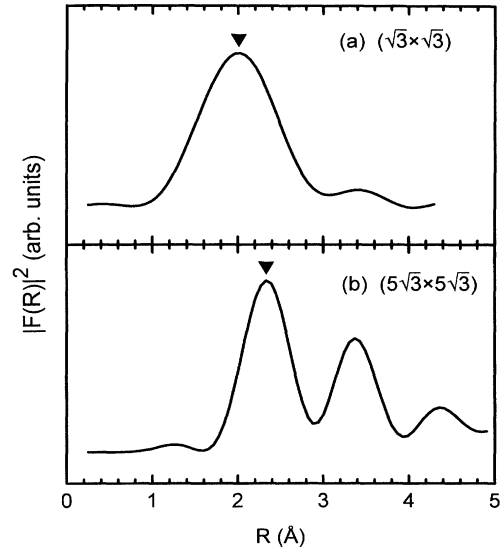


FIG. 4. $|F(R)|^2$ for the (a) $\sqrt{3}$ and (b) $5\sqrt{3}$ surface, where $F(R)$ is the Fourier transform of the χ function derived from the branching ratio measurement. Triangles mark the first-shell peaks.

T_4 geometry, based upon an x-ray scattering study of the related In/Si(111) T_4 structure [11]. The expected difference in bond length between the two reconstructions, ~ 0.39 Å, matches our observed value well, and this comparison is independent of the phase shift. Extracting the absolute bond length from our data requires rigorous EXAFS central-atom phase shift information for d -edge excitations. If we assume that the relevant final state is mainly of p character within the energy range of interest [12], the first peak positions as observed in Fig. 4 should be corrected by about $+0.6$ Å [13]. This phase-shift correction then brings our experimental observations into excellent agreement with the bond lengths for the trimer structure for the $\sqrt{3}$ surface, and the T_4 structure for the $5\sqrt{3}$ surface.

Having established the structural origin of the branching ratio fine structure, the consequences on core-level decomposition and fitting should be discussed. This topic reaches far beyond the present system. High-resolution, core-level spectroscopy has been increasingly used for structural analysis of clean surfaces and adsorbates. In many cases, the core level of interest consists of multiple components that are either unresolved or partially resolved. Si(100) [6] and Si(111) [7] are perhaps the best known examples. With recent advances in synchrotron-radiation instrumentation and the resulting improvement in resolution and intensity, the trend has been to fit the data with more and more components (up to seven, sometimes), and the residue of the fit has been reduced to remarkably low levels [6,7]. However, it has been almost universally assumed in such fits that the branching ratio is the same for all components. This assumption can

be inaccurate in view of the fact that the branching ratio can differ significantly between surface atoms bonded in different sites. While this assumption might be all right for earlier semiquantitative, lower-resolution studies, it is unjustified for recent ultrahigh-resolution studies where components with very small intensities are employed, and extremely detailed atomistic interpretations are extracted from such fits. A reassessment is needed for a proper analysis and interpretation of these data.

In summary, a study of the branching ratio of the Sb core level for the Sb/Si(111) system has revealed interesting new results: (1) The branching ratio exhibits fine-structure oscillations; (2) these oscillations are dependent on the atomic structure; (3) these oscillations can be used to deduce the usual intensity χ function, allowing a standard structural analysis based on photoelectron diffraction or interference; and (4) the difference in branching ratio for different bonding sites is sufficiently large that the usual assumption of a fixed branching ratio is unjustified and may lead to incorrect interpretations. *Branching ratio fine-structure spectroscopy* provides an alternative and much simpler route to structural analyses than traditional cross section measurements, and the results are likely to be more accurate.

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