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Determination of the Sb/Si(111) interfacial structure by back-reflection x-ray standing waves and surface extended x-ray-absorption fine structure

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Based on the surface extended x-ray-absorption fine-structure (SEXAFS) *absolute* surface coordination numbers, Woicik *et al.* [Phys. Rev. B **43**, 4331 (1991)] argued that Sb trimers adsorb on the Si(111) surface in a modified "bridge" configuration rotated by 60° relative to the atop "milk stool" geometry proposed by Abukawa, Park, and Kono [Surf. Sci. Lett. **201**, 513 (1988)]. Using the accurate near-neighbor bond lengths as determined from SEXAFS, these models predict perpendicular distances of 1.76 and 2.60 Å between the top Si atoms and the Sb layer, respectively. New back-reflection x-ray standing-wave data find the Sb atoms to reside 2.53 ± 0.1 Å above the Si surface, in clear support of the milk stool geometry. Polarization-dependent SEXAFS *relative* coordination numbers support the milk stool model as well.

Recently, there has been a large research effort devoted towards understanding the electronic and geometric structure of Sb adsorption on Si surfaces. This interest has been driven, in part, by the desire to improve the quality of III–V epitaxy on Si substrates. Additionally, other workers have shown that Sb layers can be used as δ-function dopants in Si homoepitaxy[1] and as surfactants in Ge-Si heteroepitaxy.[2] In an early contribution, Abukawa, Park, and Kono[3] used x-ray photoelectron diffraction (XPD) to study the geometric structure of Sb on Si(111). They reported that the Si(111)$\sqrt{3}\times\sqrt{3}$-Sb structure, which occurs at 1-monolayer (ML) Sb coverage,[4] consists of Sb trimers adsorbed in Si(111)$\sqrt{3}\times\sqrt{3}R30°$ sites. However, as these authors pointed out, neither the Sb-Si bond length nor the registry of the Sb trimers with the Si substrate could be determined from the XPD patterns. These authors also could not determine in which threefold site of the Si(111) surface the Sb trimers reside.

To determine uniquely this adsorption site geometry, Woicik *et al.*[5] performed surface extended x-ray absorption fine-structure (SEXAFS) and high-resolution core and valence-photoelectron spectroscopy (PES) measurements of Sb overlayers on Si(111). Because the most readily available structural parameters from a SEXAFS study are the adsorbate-surface atom bond length and the adsorbate-surface atom coordination number, SEXAFS data should provide the needed information to determine unambiguously the structure put forth in the XPD work. From the determination of the SEXAFS *absolute* surface coordination numbers, it was concluded that Sb trimers occupied threefold sites of the Si(111) surface, where each Sb atom is bonded to two Si atoms in a modified "bridge" configuration. Analysis of the Si $2p$ core-level line shape suggested that the occupied threefold site of the Si(111) surface was the threefold atop (T_4) rather than the threefold hollow (H_3).

Immediately prior to the publication of the SEXAFS work, Martensson *et al.*[6] reported scanning-tunneling-microscopy (STM) pictures of the Si(111)$\sqrt{3}\times\sqrt{3}$-Sb surface. These pictures give conclusive evidence for the trimer reconstruction, and were supplemented by first-principles theory. However, as emphasized in a study of Sb adsorption on Si(001),[7] STM typically does not determine bond lengths, coordination, registry, or the chemical species of the atoms which form the trimers. What the STM pictures do yield is the orientation of the trimer axis with respect to the basis vectors of the Si(111) 1×1 surface. In the interpretation of their data, Martensson *et al.* calculated the surface charge density for Sb adsorption in the "milk stool" structure of the threefold atop site, as had been proposed by Abukawa, Park, and Kono based on valence arguments. This structure, however, conflicts with the structure derived from SEXAFS since each Sb atom of the trimer is bonded to only one Si atom. We note that if the Sb trimers adsorbed in the adjacent threefold site (i.e., the threefold hollow rather than the threefold atop), then the SEXAFS determination of the surface coordination numbers would be consistent with the STM pictures because the trimers would be rotated by 60° about their vertical axis with respect to the Si substrate. Unfortunately, the STM pictures do not determine in which site the Sb trimers reside, and this alternative model was not considered theoretically by Martensson *et al.* In view of the recent STM pictures, it is clear that additional data is needed to determine which of the two models most accurately describes Sb adsorption on Si(111).

In this work, we present x-ray standing wave data recorded in the back-reflection (BRXSW) diffraction geometry. This technique is an ideal complement to both SEXAFS and STM because it can easily establish perpendicular distances at surfaces and interfaces.[8] Based on the SEXAFS determination of the Sb-Sb and Sb-Si bond lengths, it will be shown that the BRXSW data is consistent with only an atop model for the Sb adsorption. Although the SEXAFS absolute surface coordination numbers are indicative of an Sb bridge model, the *relative* surface coordination numbers are consistent with an Sb atop model as well.[9]

The BRXSW experiment was performed on beam line X24A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, New York in a standard ultrahigh vacuum chamber equipped with a double pass cylindrical-mirror analyzer (CMA). Data from the 1 ML Sb/Si(111) interface were collected in a fixed angle normal-incidence diffraction geometry by scanning a pair of InSb and KDP (potassium dihydrogen phosphate) monochromator crystals through the Si(111) Bragg condition which occurs near 1977 eV. The sample was prepared by evaporating approximately 2 ML of Sb onto a thoroughly outgassed and cleaved Si(111) surface. After evaporation, the interface was annealed at ~550 °C to desorb Sb in excess of 1 ML.[10]

In a single BRXSW scan, the back-reflected photon intensity and the Sb *MNN* Auger yield (~450 eV) are measured as a function of photon energy around the Bragg condition. Similar data are also recorded with the CMA kinetic energy set above the Sb *MNN* Auger line. This is necessary because the Sb Auger peak rides on top of a background of inelastically scattered electrons which reflect the standing wave characteristic of the bulk substrate. Subtracting the background from the signal at the Auger peak leaves the absorption profile of the overlayer in the field of the standing wave. The reflectivity spectra were measured by the incident flux monitor upstream of the sample; it consisted of an 80% transmitting Ni grid and a channeltron. As the energy is swept through the Bragg condition, the back-reflected beam intensity from the crystal at normal incidence is observed on top of the signal from the incident flux. The detection of the reflectivity peak is critical for the analysis because it provides fiducial information on the energy resolution and energy calibration as well as control of the sample alignment.

Figure 1(a) shows the Si(111) reflection curve along with the best fit to the data points.[11] The fit is the result of convolving the theoretical reflectivity with a Gaussian of width 0.70 eV and adjusting it for a small energy offset. Figure 2(a) shows the fit to the Sb standing wave pattern using the energy offset and Gaussian width obtained from the fit to the reflectivity. The two pertinent fitting parameters here are *D*, the adsorbate-substrate distance in units of the reflecting plane spacing, and *F*, the coherent fraction of atoms at *D*. These values are determined to be 0.933 ± 0.03 and 0.70 ± 0.1, respectively, which locates the Sb atoms 2.53 ± 0.1 Å above the Si(111) surface with a fractional occupancy of 70%.

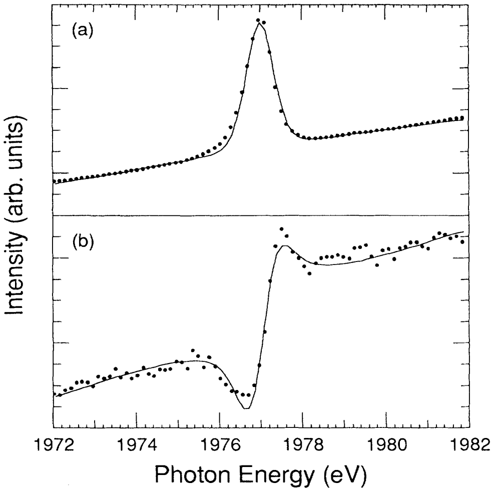

FIG. 1. (a) Photon energy dependence of the reflectivity around the Bragg condition of Si(111). (b) Photon energy dependence of the Sb Auger emission in the field of the standing wave. The solid lines are the best fits to the data points.

Figure 2 shows the structural models under consideration. The bridge model was proposed in the earlier SEXAFS work;[5] it was based on the SEXAFS determination of the absolute surface coordination numbers. Each Sb atom has two Sb and two Si near neighbors. The milk

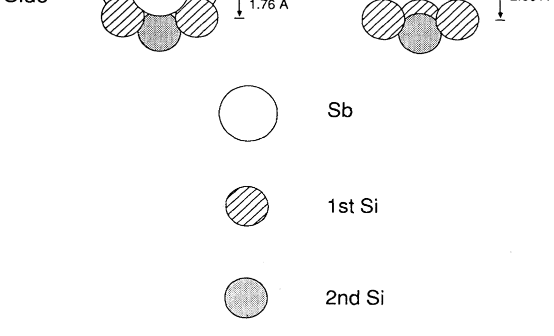

FIG. 2. Top and side views of the models considered in this work. (a) The Sb bridge model. (b) The Sb milk stool model. In both cases, Sb trimers occupy the threefold atop sites of the Si(111) surface.

stool model was proposed by Abukaw, Park, and Kono; it was based on valence arguments. Each Sb atom has only one Si near neighbor. In each case, we have scaled the sizes of the Sb and Si atoms to their covalent radii, and have placed the Sb trimers in the threefold atop sites of the Si(111) surface. The near-neighbor bond lengths are as determined by SEXAFS. Note that in the latter model the Sb atoms reside atop the Si atoms, whereas in the former they bridge them. This observation leads to the large difference in perpendicular distance (1.76 versus 2.60 Å) between the Sb plane and the Si surface for the two models. This distance may therefore be used to distinguish between the two models independently *without* reference to the surface coordination. Clearly, the Sb bridge model may be ruled out from the BRXSW data. Because SEXAFS can determine near-neighbor distances very accurately but often produces misleading coordination numbers,[12] this is the power of the BRXSW method when used in concert with SEXAFS.

To reconcile this site determination with the SEXAFS measurement, Fig. 3 shows SEXAFS data recorded at normal ($\epsilon \perp \mathbf{n}$), glancing ($\epsilon \parallel \mathbf{n}$), and magic, 54.7° from glancing, ($\epsilon \angle \mathbf{n}$) incidence. As described previously,[5] these data were collected on beamline X15B at the NSLS using a fixed exit double-crystal monochromator operating with a pair of Ge(111) crystals. The sample photocurrent was measured as a function of incident photon energy and flux as the photon energy was scanned across the Sb L_3 absorption edge ($h\nu = 4132$ eV). Sample preparation was similar to that used in the BRXSW experiment, but the initial Sb coverage was somewhat less, ~1.2 ML, and annealing was performed at ~375 °C.

The Fourier filtered first-shell contributions to the k^2-weighted Sb L_3 SEXAFS from the Sb monolayer are plotted with the best fits to the data points. These fits assume both Sb and Si backscattering, which was justified in previous work.[5] The presence of two interfering components is evident from the Fourier filtered data which show strong beating near $k = 6.3$ Å^{-1}. The Sb-Sb and Sb-Si components are closely represented by the experimentally determined EXAFS from Sb metal and crystalline AlSb, which have known structures. The parameters determined from the magic angle data are 2.0 ± 0.3 Sb atoms at 2.87 ± 0.02 Å and 2.0 ± 0.4 Si atoms at 2.65 ± 0.03 Å. These absolute surface coordination numbers indicate that each Sb atom has two Sb and two Si near neighbors. The bond lengths obtained from the fits to the data recorded at normal and glancing incidence do not deviate by more than the experimental error, ~0.02 Å, from these values.

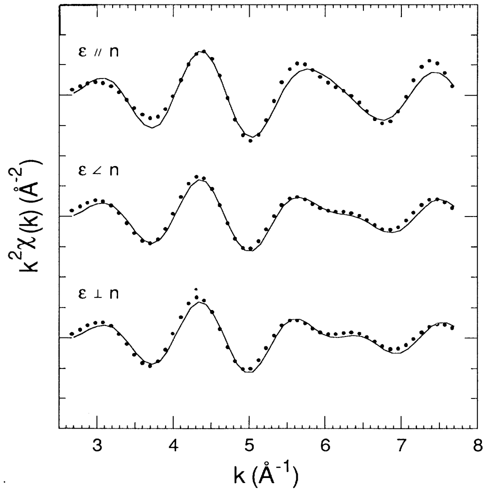

FIG. 3. The Fourier filtered first-shell contributions to the k^2-weighted Sb L_3 SEXAFS from the Sb monolayer. The solid lines are the best fits to the data points. These data were recorded at normal ($\epsilon \perp \mathbf{n}$), glancing ($\epsilon \parallel \mathbf{n}$), and magic, 54.7° from glancing, ($\epsilon \angle \mathbf{n}$) incidence.

Table I shows the SEXAFS relative coordination numbers[9] along with the theoretical values for the two geometries under question: the milk stool model proposed by Abukawa, Park, and Kono and the bridge model deduced from the absolute coordination numbers. The merit of the relative coordination numbers lies with the ln-ratio method[13] since they may be determined without reference to a model compound. In the case at hand, however, the first Sb shell contains unresolvable backscattering from both Sb and Si neighbors;[14] it must be deconvoluted by a two component fit using the phase and amplitude functions derived from the standards. Stohr and Jaeger[15] have shown that the interference term between the two dipole-allowed $p \rightarrow s$ and $p \rightarrow d$ absorption processes can lead to significant errors in the derived bond lengths and erroneous chemisorption geometries if standard analysis methods are applied. It has been argued that symmetry considerations allow determination of the absolute coordination numbers directly from the magic angle data and the model compounds.[5] These arguments do not apply to the data recorded at normal and glancing incidence. Nevertheless, the relative values are in better agreement with the milk stool geometry for the Sb-Si coordination although agreement of the Sb-Sb coordination is somewhat unsatisfactory for either model. This result itself is surprising since Sb metal is assumed a better phase and amplitude standard for analysis of the Sb-Sb bond than crystalline AlSb is for the Sb-Si bond.

We may speculate that the SEXAFS absolute coordination numbers failed to determine the adsorption site geometry since SEXAFS is an area averaging technique compared to STM which is area specific. The large-scale STM picture of Martensson *et al.* shows substantial (at least 25%) disorder which is in accord with the fractional occupancy of 70% as determined from the BRXSW data. This large amount of disorder could seriously affect the SEXAFS (which sees all the Sb atoms) determination of the coordination numbers. Additionally, it has been documented that while SEXAFS determines first-neighbor dis-

TABLE I. The experimental relative SEXAFS coordination numbers (glancing divided by normal incidence) and the calculated values for the Sb bridge and Sb milk stool models of Fig. 2.

	Bridge	Milk stool	Expt.
Sb-Sb	0.6	0.6	0.9 ± 0.2
Sb-Si	1.1	2.1	1.9 ± 0.3

tances very accurately, coordination numbers are often in error due to the nontransferability of the inelastic terms of the EXAFS equation.[16] Both types of errors tend to cancel in the relative measurement.

In conclusion, a unique combination of SEXAFS and BRXSW techniques has determined the Sb/Si(111) interfacial structure. Using the accurate near-neighbor bond lengths as determined from SEXAFS together with the accurate perpendicular distance as determined from BRXSW, it is found that Sb trimers occupy threefold sites of the Si(111) surface where each Sb atom is bonded to one Si atom. Combined with this information, STM images[6] determine the occupied site on the Si(111) surface to be the threefold atop rather than the threefold hollow.

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