

Sharp high-resolution Si 2*p* core level on the Sb-terminated Si(111) surface: Evidence for charge transfer

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An Sb/Si(111) $\sqrt{3}\times\sqrt{3}$ surface has been studied by high-resolution core-level spectroscopy. All the components of the Si 2*p* core level related to the clean surface have disappeared, and one strong Sb-induced component could be identified at a binding energy +0.13 eV with respect to the bulk peak. Such a component is mainly due to charge transfer between Si atoms at the top layer and Sb trimers. Two more small components are observed: one at +0.29 eV, due to Sb atoms residing at a different position, and one at −0.14 eV, due to local disorder. On the Si 2*p* core level taken in bulk sensitive mode, we found a very narrow bulk component with a total full width at half maximum of 140 meV at $T=100$ K.

I. INTRODUCTION

The interaction of antimony with Si surfaces is of great interest, since Sb is an important dopant material used in Si molecular beam epitaxy and is used as a surfactant for Ge/Si heterostructures.^{1,2} Core-level spectroscopy was extensively used to study Sb-terminated Si(100),^{3,4} Si(111),^{5,6} and Si(110) (Ref. 7) surfaces with some controversial results due to the limited energy resolution. In the case of Sb/Si(100) (Ref. 4) and Sb/Si(110) (Ref. 7) surfaces, the improved energy resolution of the third-generation synchrotron radiation facilities has shown the presence of a strong interfacial component (*S*) shifted 0.2 and 0.24 eV, respectively, on the high binding-energy side with respect to the bulk peak. Such a shift has been explained as mainly due to charge transfer caused by the electronegativity difference between Sb and Si atoms.^{4,7} In both surfaces, a small component (*C*) was present on the high kinetic-energy side and suggested to be due to surface defects.^{4,7} The 1 ML Sb-terminated Si(111) surface exhibits a $\sqrt{3}\times\sqrt{3}$ reconstruction⁸ composed of Sb trimers regularly residing above the top layer of silicon atoms on *T*4 sites.^{9–11} Some minor contributions are observed as Sb trimers residing on *H*3 sites or as different reconstructions.¹¹ Such $\sqrt{3}\times\sqrt{3}$ reconstruction is still controversial, since in one core-level study no surface components were observed in the Si 2*p* core level.⁵ Another group, by making similarities with some other surfaces, has shown, in the fit procedure of the Si 2*p* spectrum, the presence of an interfacial component shifted +0.2 eV on the high-binding-energy side with respect to the bulk peak.⁶

Core-level photoemission is also a sensitive probe for studying the effects of the different coordination at the surface: in fact, each core-level spectrum can be deconvolved

into components that are representative of the surface and the bulk. By taking into account the Lorentzian broadening related to the core-hole lifetime and the Gaussian broadening introduced by the experimental resolution, it is possible to extract the phonon and inhomogeneity broadening for the surface and bulk components.

In this paper we report on a high-resolution core-level spectroscopy study of the Sb/Si(111) $\sqrt{3}\times\sqrt{3}$ surface at 100 K, utilizing a total-energy resolution better than 70 meV. Under these conditions, we could easily identify a surface-induced component (due to Sb atoms adsorbed in a trimer configuration), shifted by +0.13 eV (i.e., towards higher binding energy with respect to the bulk one). A small component is present on the high kinetic energy side at −0.14 eV, resembling the *C* component observed on the Sb/Si(100) and Sb/Sb(110) surfaces.^{4,7} Another small contribution (*S'*) is present at +0.29 eV and is due to Sb atoms residing at a different position. On the Si 2*p* core level taken in bulk sensitive mode at $T=100$ K, we found a very narrow bulk component with a total full width at half maximum (FWHM) of 140 meV, which is indicative of an ideal bulk termination.

II. EXPERIMENT

The measurements were performed on the high-energy resolution VUV beam line¹² at Elettra in Trieste, Italy, which provides high photon flux in the range 20–900 eV. For all measurements a hemispherical analyzer with an angular resolution of $\pm 1^\circ$ was used; the axis of the analyzer was at 45° from the sample normal. A total-energy resolution better than 70 meV has been derived from the Fermi level of a gold foil mounted on the sample holder. The sample temperature was measured with a Chromel–Alumel thermocouple in close

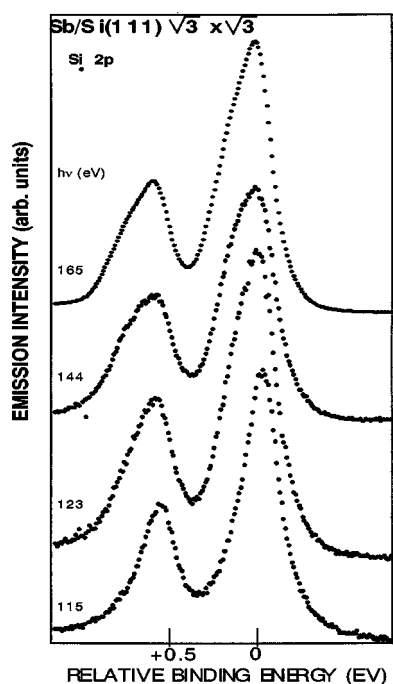


FIG. 1. A set of Si 2*p* core-level spectra acquired from the Sb/Si(111) $\sqrt{3}\times\sqrt{3}$ surface obtained with a resolution of <70 meV for various photon energies (as indicated).

contact with the sample holder. Before insertion into the vacuum chamber, the silicon sample (P doped, 3 Ω cm), was degreased and etched according to the Shiraki procedure.¹³ In ultrahigh vacuum it was thoroughly outgassed at 500 °C and then annealed at 950 °C for 10 min. Sb was evaporated from a thoroughly outgassed Knudsen cell at a rate of 0.5 ML/min, as monitored with a quartz microbalance. 1 ML of Sb is defined as the site density for the unreconstructed surface, which is 7.85×10^{14} atoms/cm². The pressure during Sb deposition and sample heating did not exceed 1.0×10^{-9} Torr. Core-level spectra for the Sb/Si(111) $\sqrt{3}\times\sqrt{3}$ surface were recorded from a surface obtained by evaporating 2 ML of Sb onto a clean 7×7 surface (prepared according to the procedure described above) held at about 600 °C, a temperature at which only 1 ML of Sb sticks to the surface.

Core-level spectra were recorded at several photon energies between 107 and 165 eV that result in kinetic energies between 3 and 61 eV, respectively, for the Si 2*p* electrons. A kinetic energy around 30 eV corresponds to a minimum escape depth of about 5 Å, thus maximizing the surface layer contribution to the Si 2*p* emission. In the case of electrons with a kinetic energy of 3 eV the escape depth is markedly larger and we consider the 107 eV spectrum to be representative of the bulk.

In the analysis, the experimentally obtained spectrum is normally decomposed into one (the bulk line) plus eventually several other components (new components in addition to the bulk one), which may represent different contributions from atoms with different binding energies in the surface region. The experimental spectrum lies on a background of secondary electrons: this background must be adjusted during the fitting procedure. In general, low-energy electrons (few eV) are around the maximum of the secondary ones, so that a polynomial background needs to be subtracted; elec-

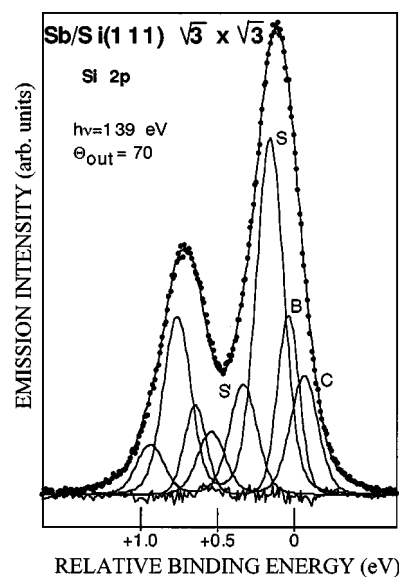


FIG. 2. Surface-sensitive Si 2*p* core-level spectrum from the Sb/Si(111) $\sqrt{3}\times\sqrt{3}$ surface taken at 70° emission angle with $h\nu = 139$ eV. The different contributions introduced in the fit are discussed in the text. All components refer to the bulk Si 2*p*_{3/2}, and an integrated background has been subtracted.

trons with higher kinetic energy are on the tail of the secondary ones, and an integrated or a linear background needs to be subtracted; no differences in peak positions are observed in our fits within the experimental uncertainty. The theoretical line shape of each component is a Voigt function, that is a convolution of a Lorentzian that represents the natural line shape and a Gaussian that represents broadening contributions, both instrumental (limited experimental resolution from the monochromator and analyzer) and material related (phonon excitation and surface inhomogeneities giving rise to structures with slightly different binding energies). In all the Si 2*p* spectra the splitting between the two spin-orbit components is fixed at 0.6 eV; the origin of energies is taken as the Si 2*p*_{3/2} peak of the bulk component B, and increasing binding energies are counted positive. Which Lorentzian should be used to fit the Si 2*p* core level? Results from gas-phase Si 2*p* core-level spectroscopy of SiH₄ give a Lorentzian width of 45 meV,¹⁴ while a value of 35 meV was used in the study of the chemically prepared 1 \times 1:H surface.¹⁵ Silicon surfaces, clean^{16,17} and after Sb absorption,^{4,7,17} could be fitted with either 20 or 80 meV. We have, however, used a Lorentzian width of 14 ± 5 meV, because it is the expected theoretical value¹⁸ and it gave a better fit for the most bulk-sensitive spectra. However, the spectra in this study can be fitted with a different Lorentzian width without altering any conclusion in this paper.¹⁹

All fitting parameters have been held constant for all spectra. With the above described procedure and values it was possible to achieve high-quality fits of all spectra with a variation of the surface core-level shifts within ± 5 meV.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows a set of high-resolution Si 2*p* core-level spectra taken at normal emission with various photon energies, corresponding to different surface sensitivities, from a

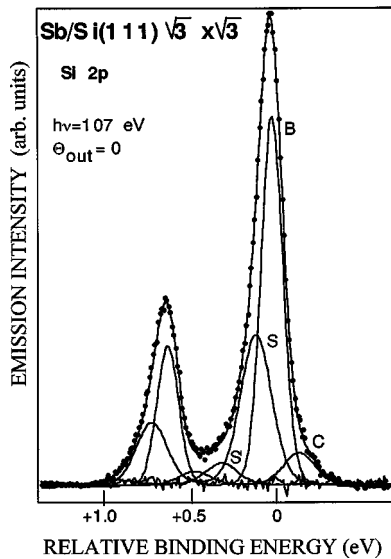


FIG. 3. Bulk-sensitive Si $2p$ core-level spectrum from the Sb/Si(111) $\sqrt{3} \times \sqrt{3}$ surface taken at normal emission with $h\nu = 107$ eV. The different contributions introduced in the fit are discussed in the text. All components refer to the bulk Si $2p_{3/2}$, and a polynomial background has been subtracted.

Sb/Si(111) $\sqrt{3} \times \sqrt{3}$ reconstruction. The spectra taken with the lowest photon energies have a dominant bulk contribution, while the surface contribution becomes, obviously, more important by increasing the photon energy, broadening the Si $2p$ core-level spectra.

Figure 2 shows the measured spectrum for a Sb/Si(111) $\sqrt{3} \times \sqrt{3}$ surface together with Si $2p$ components produced by the fitting procedure for $h\nu = 139$ eV and 70° emission angle. In this case the surface sensitivity is further increased due to the reduction in escape depth following the increased electron emission angle. The black dots are the measured data while the bulk (B) and surface contribution (S , S' , and C), both offset in the vertical direction for clarity, are the result of the deconvolution. The solid line running through the data points is the overall fit, and an integrated background has been subtracted. The presence of one strong surface component (S) around $+0.13$ eV and two other small components (S' and C) around $+0.29$ and -0.14 eV, respectively, is evident from the fitting procedure. The small S' and C components are needed to obtain decompositions into four components with the same energy shifts and widths for all spectra.

Figure 3 shows a core-level spectrum acquired from a Sb/Si(111) $\sqrt{3} \times \sqrt{3}$ surface at normal emission for 107 eV photon energy together with its fitted components: due to the chosen photon energy, the spectrum has a dominant bulk contribution (B) over the three small Sb-induced components (S , S' , and C). The spectrum of Fig. 3 closely resembles in shape the Si $2p$ of an ideally H-terminated Si(111)-H(1×1) surface:¹⁵ in this context we support the view of an ideal bulk position for the Si atoms after Sb passivation. However, the measured width of the Voigt function, 140 meV against 160 meV, is narrower in the case of a Sb/Si(111) $\sqrt{3} \times \sqrt{3}$ surface; such value is the narrowest ever found experimentally for Si $2p$ core level.

The Sb $4d$ core level (Fig. 4), taken at normal emission, is

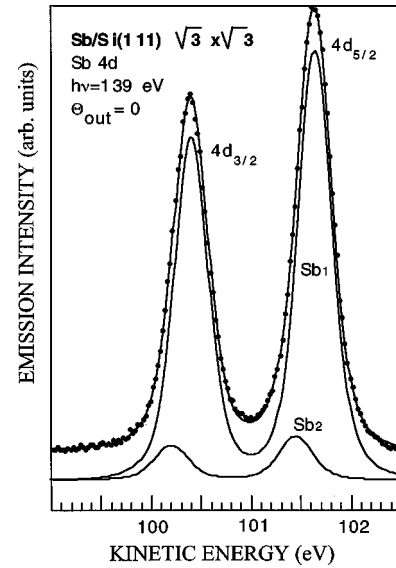


FIG. 4. A typical photoemission spectrum of the Sb $4d$ core level. In the fit a spin-orbit splitting of 1240 meV has been used, and a linear background has been subtracted.

fitted with two components, Sb_1 and Sb_2 . The Gaussian width is 0.3 eV, while the Lorentzian width is 0.18 eV for both components. The 0.84 branching ratio is in good agreement with a previous result from Luh *et al.*²⁰ that found such a value in the case of an Sb/Si(111) surface, for an electron kinetic energy around 100 eV. These fitting parameters are the same as in the case of the Sb/Si(110) 2×3 surface, where a single doublet is needed to fit the Sb $4d$ core level. In the case of Sb/Si(111) $\sqrt{3} \times \sqrt{3}$, a second small component (Sb_2) is needed in order to obtain the best quality of the fit, and we take the two resulting doublets to accurately represent the Sb $4d$ core-level line shape. This result is indicative of Sb atoms as adsorbed, mainly, in a single bonding configuration with the formation of trimers.⁹⁻¹¹ The second component indicates the presence of another absorption site, so that some Sb atoms are residing at a different position.¹¹

Figure 5 shows the fraction of total intensity for the decomposed components of the Si $2p$ core level obtained from

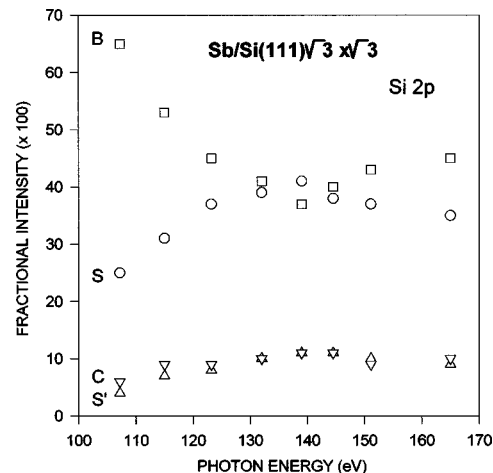


FIG. 5. Fraction of total intensity for the decomposed components obtained from fits of the Sb/Si(111) $\sqrt{3} \times \sqrt{3}$ surface recorded at normal emission.

the fits of the Sb/Si(111) $\sqrt{3}\times\sqrt{3}$ spectra recorded at normal emission with different photon energies. It clearly shows that the surface component S has maximum weight around 140 eV, as expected, while the bulk component reaches its minimum. The S' and C components have a very small intensity in all the spectra and show a slight increase in intensity when the photon energy is changed to get higher surface sensitivity. The C component is observed also on the Sb/Si(100) 2×1 (Ref. 4) and Sb/Si(110) 2×3 (Ref. 7) surfaces at similar binding energy; this, together with the fact that the compressive strain induced by the mismatch in lattice size between Sb and Si should cause numerous vacancy and antiphase defects in the Sb overlayer, suggests that it might be due to defects at the Sb-Si interface.⁹⁻¹¹ The S' component was not observed on the other Sb-induced surfaces, as well as the second Sb component (Sb₂) observed in the Sb 4*d* spectrum; the fact that S' is positioned at an energy that is very close to that of the S component on the Sb/Si(110) 2×3 surface,⁷ opens the possibility of its being related to single adatoms saturating three Si atoms, as is the case for the Sb/Si(110) surface. In fact, the scanning tunnel microscope images¹¹ show the presence of some minor trimer structures with a bonding distance between Sb atoms larger than the majority of Sb trimers. This configuration is very close to single adatoms, as in the case of a Sb/Si(110) 2×3 surface. This means that most of the surface is covered by Sb atoms as trimers, plus a small part is covered with the same reconstruction but with single Sb adatoms and a small percentage of single trimer vacancies.

The observed shifted component S can be due to charge transfer between silicon atoms at the topmost layer and the adsorbed Sb atoms with the silicon ones remaining positively charged, and/or to a local rearrangement of the topmost silicon atoms following Sb adsorption. Even though electronegativity arguments are a very crude approximation in the interpretation of such a chemical shift, we would like to discuss the core-level results by comparing our data with previous core-level studies of Sb/Si(110) 2×3 (Ref. 7) and Sb/Si(100) 2×1 (Ref. 4) surfaces. The shifts for these three surfaces (0.13, 0.24, and 0.21 eV, respectively) are very similar, suggesting the dominant role of charge transfer. The small difference between the shift of the S components might be related to the different geometry of the adsorbed Sb

atoms; in fact, the largest shift (0.24 eV) is observed for the Sb/Si(110) 2×3 (Ref. 7) surface where Sb is adsorbed as a single adatom; in the case of a Sb/Si(100) 2×1 (Ref. 4) surface, Sb forms symmetric dimers at the surface with a shift of 0.21 eV, while in the case of a Sb/Si(111) $\sqrt{3}\times\sqrt{3}$ surface we have the formation of trimers with a resulting shift for the S component of 0.13 eV. These differences could claim the interplay of final states screening effects and charge transfer with the possibility of additional bond rotation and distortion contributions to the core-level shifts, which are generally different for different crystallographic orientations. In this respect, *ab initio* density-functional theory calculations of the surface core-level shifts,^{21,22} taking into account final state effects, are needed to associate the observed position of the Si 2*p* component with charge transfer or with building blocks of the different surface reconstruction.

IV. CONCLUSIONS

We have performed high-resolution core-level spectroscopy of an Sb/Si(111) $\sqrt{3}\times\sqrt{3}$ surface. The sharp spectra revealed one strong Sb-induced component at approximately +0.13 eV with respect to the bulk one. Due to the strong similarity with core-level results of Sb/Si(110) 2×3 and Sb/Si(100) 2×1 surfaces, such components are ascribed to be mainly due to contributions from charge transfer between Si and Sb atoms adsorbed in a trimer configuration. Two more small components are observed: one at +0.29, due to Sb atoms residing at a different position, and one at -0.14, due to local disorder. A very narrow bulk component with a total (FWHM) of 140 meV at $T=100$ K has been observed on the Si 2*p* core level taken in bulk-sensitive mode.

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