# Surface-Induced Perturbation of *LVV* Auger Spectra

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Measurements of *LVV* Auger-electron spectra from a Si(111) surface before and after Ge deposition reveal that atoms at the surface have a qualitatively different Auger line shape than atoms in the bulk. In particular, the redistribution of electron density at the Si(111) surface enhances the ratio of *pp* to *sp* contributions to the *LVV* line shape. This surface effect is expected to be a general property of *LVV* spectra from all surfaces, which must be considered when comparing theory to experimental data.

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The Auger effect is a three-electron process in which a missing electron from a deep atomic core level $A$ is replaced by an electron from a higher level $B$, which moves the hole to $B$. The difference in energy $\Delta E_{AB}$ between having a hole in level $A$ and a hole in level $B$ can be taken up by an electron in a level $C$, causing it to leave the atom with a kinetic energy of $\Delta E_{AB}$ minus the binding energy of $C$. This electron is called the $ABC$ Auger electron, and its kinetic energy serves a signature of the type of atom from which it came. These characteristic Auger energies are largely insensitive to the chemical environment of the atom, except when valence levels are involved. A qualitative understanding of Auger line shapes for transitions of the type $CVV$ ($C$ denotes core level, $V$ denotes valence) was developed by Jennison (1978),[1] when he pointed out that the interatomic bonding components of covalent wave functions do not significantly contribute to Auger processes; i.e., Auger spectroscopy is a probe of local charge. In this Letter, we demonstrate that perturbations of the local charge induced by a free surface can have important effects on $CVV$ Auger processes.

We consider the $L_{2,3}VV$ Auger transitions from a Si surface, which has a prominent peak near 90 eV in the Auger spectrum. Electrons at this kinetic energy have an elastic mean free path[2] of only 5–7 Å, and so the top layer of Si atoms makes a relatively large contribution to the Auger yield. As described by Jennison, the Si $3s^2 3p^2$ valence configuration can lead to *ss*, *sp*, and *pp* final states, but because the *s* orbitals contribute to interatomic bonding to a much greater extent than the *p* orbitals, the Auger line shape is dominated by the *pp* terms. The *sp* terms cause a weak shoulder in the *pp* peak, while the *ss* terms are completely negligible. For atoms at the surface, however, some of the bonding orbitals are left unoccupied because of the reduced number of near neighbors. Although Si surface atoms are driven into reconstructions to partially satisfy the bonding requirements, there remains excess charge localized about the surface atoms. This should alter the relative contributions of the *ss*, *sp*, and *pp* final states to the Auger line shape, which ought to be observable in the surface-sensitive Si $L_{2,3}VV$ transition.

The central experimental challenge is to distinguish the *LVV* line shape of surface atoms from that of the bulk. We approach this problem by comparing Auger spectra obtained from a clean Si surface before and after deposition of a half monolayer of germanium. We note that Ge is isoelectronic with Si, has a lattice constant only 4% larger, and can be grown epitaxially onto Si surfaces for small coverages.[3] We assume that a Si atom at the interface with a Ge layer is in an environment much more like bulk Si than would be a Si atom at a free surface, for the same reason that an isoelectronic impurity is a much less perturbing point defect than is a vacancy. We make the assumption that the *LVV* spectrum from a Ge-covered Si surface is nearly the same as the spectrum from Si atoms in the bulk. Differences between this and the spectrum from the clean Si surface are therefore attributed to the Si surface atoms, due to the altered valence-bonding configuration of the Si atoms at a free surface.

A (111) Si wafer was cleaned by ion bombardment and annealing in an ultrahigh-vacuum chamber until the reflection high-energy electron diffraction (RHEED) pattern showed the characteristic 7×7 reconstruction, and the Auger spectrum showed no contamination other than carbon, whose coverage was less than 5% of a silicon monolayer ($7.8\times10^{14}$ atoms/cm$^2$). Auger spectra were obtained with a single-pass cylindrical mirror analyzer (CMA) operated in the standard-derivative mode, with a nominal energy resolution of 0.6%. Germanium was evaporated from an alumina crucible in a resistively heated oven, with the system pressure remaining below $8\times10^{-10}$ Torr during depositions.

Because the CMA energy resolution increases linearly with energy, the derivative spectra is proportional to $[dN(E)/dE]E$, where $N(E)$ is the number of electrons at kinetic energy $E$. The raw data are numerically integrated to produce results more like the true spectral line shapes. Integrated data are shown in Fig. 1 for three surfaces: the original clean Si surface, after deposition of 43% of a monolayer of Ge, and after a total deposition of 77% of a monolayer.[4] The substrate was held at room temperature during the depositions. Auger data presented here were obtained after annealing each Ge-

 

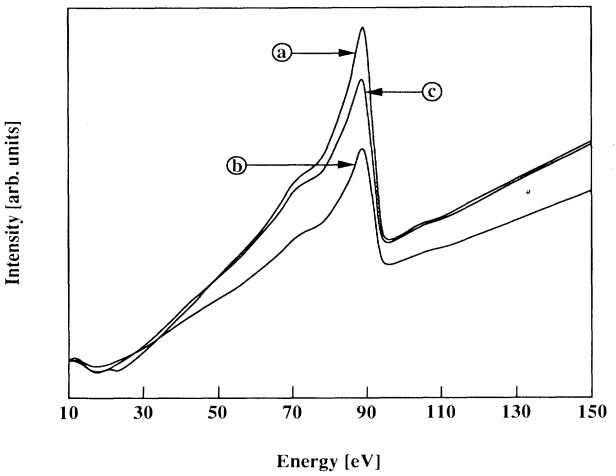


FIG. 1. Auger-electron yields for (curve *a*) a clean 7×7 Si(111) surface, (curve *b*) this surface after deposition of 43% of a monolayer of Ge, and (curve *c*) after total deposition of 77% of a monolayer of Ge. Data were recorded by a cylindrical mirror analyzer operated in the standard-derivative mode, and were numerically integrated to produce these curves. The peak at 90 eV is the *pp* contribution to the Si *LVV* transition, which is bracketed by plasmon-loss structure near 70 eV and a weak satellite near 105 eV.

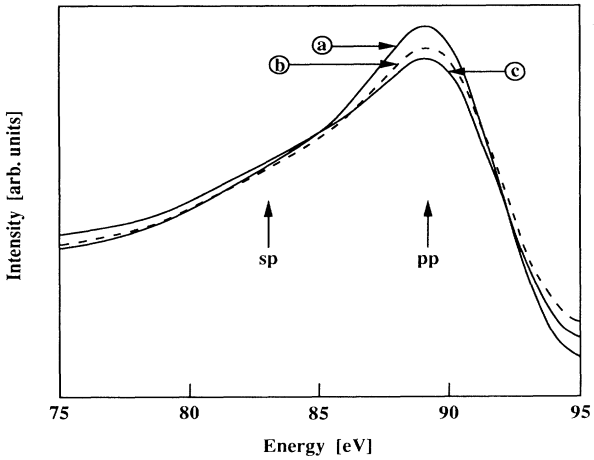


FIG. 2. Normalized Auger spectra for (curve *a*) a clean 7×7 Si(111) surface, (curve *b*) this surface with 43% of a monolayer of Ge, and (curve *c*) with 77% of a monolayer of Ge. The data from Fig. 1 between 75 and 100 eV have been shifted by small amounts to line up the steepest part of the curves, and have been rescaled to have equal areas to compensate for the overall loss of signal caused by the Ge overlayers. Arrows denote the positions of the *sp* shoulder and *pp* peak. Note that the ratio of intensity at the *pp* peak to the *sp* shoulder changes with Ge coverage.

covered surface for 1 h at 450°C. The initial 7×7 RHEED pattern was still present after the first deposition and anneal, but the second deposition and anneal almost completely removed this reconstruction, leaving a sharp 1×1 RHEED pattern.

The $L_{2,3}VV$ profile is bracketed by a weak multiple ionization satellite[5] at 107 eV and plasmon-loss structure[6] near 70 eV. Auger peaks from Ge are not yet visible in this energy range for these coverages. Differences amongst the $L_{2,3}VV$ profiles are apparent in Fig. 2, where the data from 75 to 100 eV are shown, after shifting the curves slightly[7] to line up the steepest part of the curves, and scaling the curves to have equal areas between 75 and 100 eV. All three curves clearly show the *pp* peak at 90 eV and the *sp* shoulder around 84 eV, but the ratio of *pp* to *sp* intensity is smaller as the amount of Ge increases. A more accurate picture of these differences can be obtained by deconvoluting the instrument response function from the data to produce the "true" spectra. Following the approach in Ref. 8, the response function is approximated by measuring the spectrum generated by an electron beam with an incident energy equal to the elastic Si *LVV* Auger electrons (90 eV). The results of this iterative deconvolution procedure (Ref. 8) are shown in Fig. 3. The presence of surface effects both in the raw integrated data (Fig. 2) and in the deconvoluted data (Fig. 3) strongly indicate a real change in the Si *LVV* Auger process with increasing Ge coverage.

We conclude from the change in the line shapes that atoms at the Si surface have a different *LVV* Auger profile than Si atoms at a Si-Ge interface. Assuming that the data from the Ge-covered surface approximates that from bulk Si, the trend in *pp*-*sp* ratios reveals that the intrinsic surface line shape has an enhanced *pp* peak.

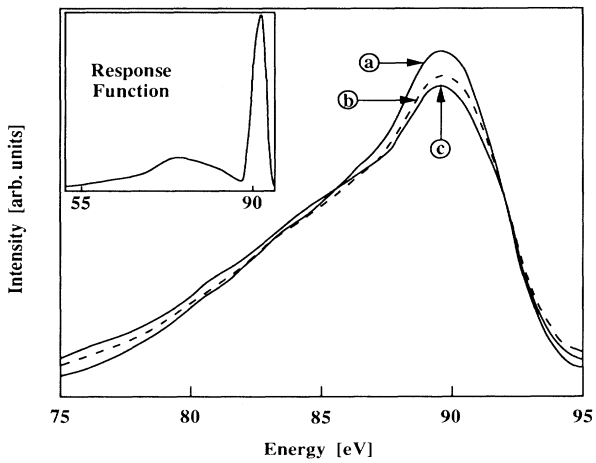


FIG. 3. The results of deconvoluting the instrument response function from the data in Fig. 1. Again, curve *a* is the clean surface, and curves *b* and *c* have 43% and 77% of a Ge monolayer, respectively. The changes in *pp* to *sp* ratios are very similar to those in Fig. 2. Inset: Electron spectrum obtained from an incident beam with an energy of 90 eV. This was used to approximate the instrument response function.

This could be the result of dangling $p$ orbitals, which increase the intra-atomic valence electron density because they cannot bond with a neighboring atom.

This discovery of surface-induced perturbations of *CVV* Auger line shapes has several important implications. Theoretical models for bulk atoms which are otherwise correct may not produce line shapes in good agreement with data, since Auger measurements generally include a contribution from a free surface. In addition, quantitative Auger experiments which include *CVV* transitions must be more carefully considered. The present study was partly motivated to explain the contradictory conclusions among x-ray standing-wave (XSW) measurements of a possible surface contraction in the Si(111) surface. Results from Ge-covered surfaces[9,10] showed little or no contraction, whereas an XSW study of a clean Si(111) surface[11] which monitored *LVV* and *KLL* Auger electrons found a relatively large contraction. The assumption made in the latter experiment that surface and bulk atoms have identical Auger yields is shown to be invalid by the above results. The magnitude of any surface contraction would in fact be exaggerated if Si surface atoms are a brighter source of Auger electrons at the 90-eV *pp* peak.

Finally, we note that although the surface-induced perturbation of *CVV* Auger line shapes can make the interpretation of some experiments more complicated, it also provides a new opportunity for measuring certain electronic properties of surface atoms. Careful measurements combined with first-principles treatment of the various background processes should permit the deconvolution of the intrinsic surface-atom Auger line shapes.

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