# Sb-Induced Surface States on (100) Surfaces of III-V Semiconductors

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The existence of both empty and filled surface states derived from the rehybridization of dangling Sb bonds is demonstrated for the first time in GaSb. The empty states are nearly degenerate with those derived from dangling cation bonds and are located near the bottom of the conduction band. The filled states lie ~ 0.8 eV below the valence-band edge. Similar sets of states were observed for Sb adsorbed on GaAs and InAs.

The generally conceived notion of dangling-bond states on surfaces of binary semiconductors attributes empty, localized states to the metallic surface atoms (cations) and filled surface states to the nonmetallic atoms (anions).[1-6] We report in this Letter the first observation of localized, Sb-derived, empty surface states, which are located close to the cation-derived surface states near the bottom of the conduction-band edge. These states seem to be characteristic of (100) surfaces, as they have not been observed on the GaSb(110) surface.[2] Their existence has been deduced by electron-energy-loss spectroscopy (ELS) from electron excitation out of the $4d$ core levels of Sb surface atoms, in complete analogy to similar excitations associated with the metallic surface atoms.[2-4] In addition to their intrinsic contribution on GaSb(100), Sb atoms induced similar, extrinsic surface states on (100) surfaces of InAs and GaAs, which reconstructed into new surface structures.

The surfaces of GaSb, GaAs, and InAs were prepared by homoepitaxial, molecular-beam overgrowth on (100)-oriented substrates. The advantages of this method of preparation of clean and nearly atomically smooth surfaces have been discussed elsewhere.[3] Whereas InAs and GaAs could be grown in the As-stabilized $c(2\times8)$ (As coverage ~ 0.5) or the metal-stabilized $c(8\times2)$ structures (As coverage ~ 0),[3] only a $c(2\times6)$ surface reconstruction was observed for GaSb(100) during growth.[7] Upon annealing the $c(2\times6)$ surface, which resulted in the removal of some Sb surface atoms, the closely related $(2\times3)$ reconstruction was observed. When the $c(2\times6)$ surface was exposed only to the Sb molecular beam a new Sb-rich $(2\times5)$ surface reconstruction appeared below ~ 350°C. A similar treatment of the metal-stabilized (100) surfaces of GaAs and InAs resulted in new Sb-induced surface structures: GaAs-$(8\times2)$-Sb and InAs-$c(2\times6)$-Sb. Exposing the As-stabilized GaAs-$c(2\times8)$ surface to Sb near 350°C resulted in a $(1\times3)$ surface reconstruction.

ELS and Auger spectra were taken soon after the samples had cooled to room temperature. Energy-loss spectra of various surfaces are shown in Fig. 1. I have only labeled the energy positions of surface-related loss structure. The remaining structures are of bulk origin and their assignments have been discussed elsewhere.[3,7] Prominent features in the loss spectra for GaSb (Fig. 1, part I) are the doublet structures near 33 eV, which are due to electron excitations from the spin-orbit–split Sb $4d$ core levels into empty surface states. That these excitations are sur-

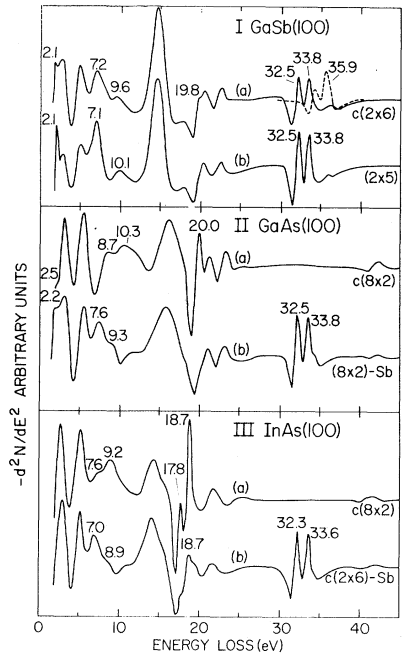


FIG. 1. Second-derivative loss spectra of as-grown (100) surfaces (*a* curves), and after Sb adsorption (*b* curves). Dashed curve in part I, curve *a*: ~ $10^7$ langmuirs of $O_2$ exposure (1 langmuir = $10^{-6}$ Torr sec). Primary electron energies: 80 eV.

face related may be ascertained from various experimental observations: (1) The sharpness of the structure, which is limited here by experimental resolution of ~0.5 eV, suggests a localized final state which is not bulklike. (2) Exposure to oxygen suppresses the loss structure with a gradual emergence of a new, oxygen-related structure shifted to higher energies by 2.1 eV. The specific case for an exposure of $\sim 10^7$ langmuirs is indicated by a dashed curve in Fig. 1, part I, curve *a*. (3) The addition of Sb to the $c(2\times6)$ surface, which results in the generation of the $(2\times5)$ reconstruction, increases the intensity of the doublet structure. (4) Identical loss peaks appear when Sb is adsorbed on GaAs and InAs (Fig. 1, curves *b* in parts II and III). The sharpness of this doublet is comparable to the Ga $3d$ and In $4d$ core- to surface-state excitations at 20.0 and 18.7 eV, respectively (Fig. 1, curves *a* of parts II and III), whose sharp spectral features are attributed to electron-hole interactions (excitons).[4,5]

The existence of empty, anion-derived surface states may be understood by the following arguments[6]: The two $sp^3$ dangling orbitals inherent to a (100) surface atom rehybridize to form a $p_z$ orbital normal to the surface (dangling-bond–like) and a $p_y$-like orbital in the plane of the surface and directed along the broken-bond direction. For a surface terminated in group-V anions, each atom contributes $\frac{5}{2}$ electrons to be distributed among these orbitals: Two will fill the lower-energy $p_z$ orbital; the remainder will go in the $p_y$ orbital, which will be one-fourth filled. Similar arguments for a group-III–cation–terminated surface result in a $p_z$ orbital, which is three-fourths occupied, and an empty $p_y$ orbital. Since overlap between orbitals is likely to occur (banding), it may be energetically more favorable for the formation of a surface superlattice which produces an even number of electrons per unit cell. Such a metal-insulator transtion has been suggested to occur on the Ga-stabilized GaAs(100)-$c(8\times2)$ and -$c(4\times2)$ surfaces.[6] For the GaSb(100) surfaces, on the other hand, surface reconstructions with these symmetries have not been observed, but rather ones with a threefold or fivefold periodicity. If a metal-insulator transition is the principal driving mechanism for GaSb(100) as well, the surface reconstructions can only be explained by invoking the presence of surface vacancies. The number of possible Sb vacancy concentrations necessary to achieve an even number of "dangling" electrons per unit surface cell is quite limited: 0.1 for the $(2\times5)$; 0.17, 0.33, 0.67, and 0.83 for the $c(2\times6)$; and 0.17, 0.5, and 0.83 for the $(2\times3)$ structures.[8] An estimate of the approximate surface concentrations of Sb atoms can be made from the variation of the ratio of the Sb and Ga Auger lines for the various surfaces, as well as that of the Sb-stabilized GaAs(100)-$(2\times8)$-Sb. For the latter structure we have assumed a monolayer coverage of Sb, which is consistent with the extinction of the Ga $3d$ surface excitons at 20 eV in Fig. 1, part II (no dangling Ga bonds), as well as with the criterion for a metal-insulator transition. In conjunction with the Auger data, the relative intensities of both the Ga $3d$ and Sb $4d$ surface excitons, and the reconstruction criterion, the best estimates of Sb vacancy concentrations are 0.1, 0.17, and 0.5 for the $(2\times5)$, $c(2\times6)$, and $(2\times3)$ surface reconstructions, respectively.

The filled and empty surface bands derived from the unperturbed dangling Sb bonds are expected to split and move apart in energy as a result of the reconstruction. Whereas the empty surface states are readily probed by core-electron excitations, details of the filled dangling-bond–derived states can only be obtained by energy-loss events arising from excitations from these states into the empty surface states. The strong loss peak at 2.1 eV in Fig. 1, part I is attributed to such excitations. Whereas in GaAs the filled and empty dangling-bond states are spatially separated and the loss peak due to inter-surface-state excitations reaches a maximum for equal surface density of Ga and As atoms,[9] in GaSb both empty and filled dangling-bond–derived surface states can arise from the Sb. Consequently, the intensity of interstate excitation is proportional to the density of Sb surface atoms. The narrow linewidth of the 2.1-eV loss peak furthermore suggests that both filled and empty surface bands have low dispersion in energy, and are consequently quite localized. The 2.2-eV loss peak in the spectrum of the GaAs(100)-$(8\times2)$-Sb surface (Fig. 1, part II, curve *b*) is due to the presence of Sb and is likewise attributed to excitations between the Sb-derived dangling-bond states. A similar loss peak could not be resolved for the InAs(100)-$c(2\times6)$-Sb surface (Fig. 1, part III, curve *b*). The loss peaks in the 7–10-eV range are due to excitations from the filled back-bond surface states into the empty, dangling-bond–derived states. The strong peaks in the 7–7.6-eV range are characteristic of the Sb back bond, as they are only observed when Sb is on the surface.

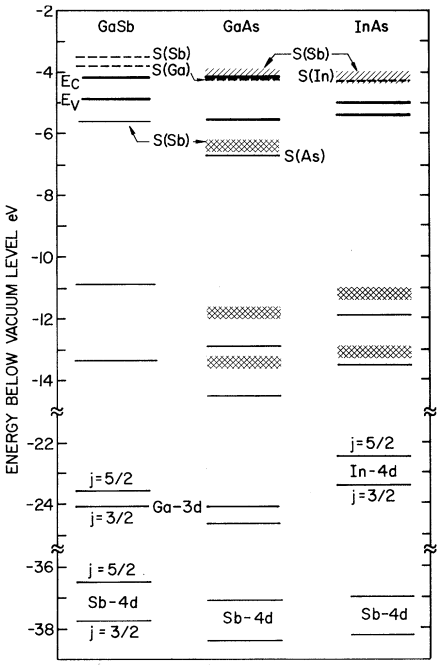


FIG. 2. Energy-level diagrams of intrinsic and Sb-induced surface states. Empty and filled levels are indicated, respectively, by broken and solid lines for intrinsic states, and by hatched and cross-hatched areas for Sb-induced states. *S* indicated dangling-bond–derived states. Heavy lines mark the positions of bulk valence- ($E_v$) and conduction-band ($E_c$) edges. Positions of *d* core levels are also indicated.

In contrast to Sb, As on the GaSb(2×3) surface exhibited only a weak and broad loss peak arising from the As 3*d* core level, in appearance similar to the loss peak near 43 eV in Fig. 1, part II. Neither did the As induce a surface reconstruction, but only weakened the GaSb diffraction patterns. The differences in the electronic and structural properties of these two group-V elements on (100) surfaces suggest the interesting posibility that the As atoms have only a single dangling bond. This arrangement, the result of the more ionic character of GaAs, may be generated by the selective removal of Ga atoms, in a manner similar to that proposed for the ZnSe(100) surface.[10]

From the energies of the core- to surface-state excitations (surface excitons) and the known binding energies of the Ga 3*d*, In 4*d*, and Sb 4*d* core levels,[2,11] relative to the bulk valence-band edge, it is possible to deduce the location in energy of the empty, dangling-bond–derived surface states. The results for the *intrinsic* empty surface states are shown as dashed lines in Fig. 2. We have assumed here exciton binding energies of 0.5 eV. This values has been deduced for the Ga 3*d* and In 4*d* surface excitons on (110) surfaces.[4] The binding energy of the Sb 4*d* exciton is not known, but should be comparable or even less because of the large screening in GaSb. The binding energies of the Sb 4*d* core levels for Sb on GaAs and InAs were assumed to be the same as those in GaSb. This assumption is supported by the experimental observation that the binding energies of a given core level vary by only a few tenths of an eV among related III-V compounds.[2,11] The empty, Sb-induced *extrinsic* surface states are indicated in Fig. 2 by hatched areas, whereas the filled states have been indicated by cross-hatched areas. Their locations, as well as those of the intrinsic filled surface states (thin solid lines), have been determined from the loss spectra by assuming that the empty surface states are the sole final states. All surface states labeled with an *S* are derived from the dangling bonds, with their origin in parentheses.

The unique feature of Sb on (100) surfaces is its ability to induce empty, localized surface states which are nearly degenerate with the cation-derived surface states and lie near or slightly above the conduction-band edge. This location limits the overlap with bulk conduction-band states, and, consequently, contributes to the enhancement of the electron excitation spectra. These effects are not observed for As: Evidence for any empty, As-derived surface states suggests their location to be ~1 eV higher in energy, which increases considerably the overlap with the bulk conduction-band states.

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[8]Further details of the GaSb(100)-(2×3) will be published in Ref. 7. Its loss spectrum, compared to that of the $c(2\times 6)$, exhibits a stronger Ga 3*d* surface excitation at 19.8 eV, and a weaker one for Sb 4*d* at ~ 33 eV, which is consistent with Auger results of a decreasing Sb surface concentration.

[9]The 2.5-eV loss peak in Fig. 1, part II, curve *a* is a remnant of this excitation. For details see Ref. 2.

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