R. Ludeke

Electronic Properties of (100) Surfaces of GaSb and InAs and Their Alloys with GaAs

Abstract: Smooth, monocrystalline (100) surfaces of the alloys $In_{1-x}Ga_xAs$ and $GaSb_{1-y}As_y$ were prepared by molecular beam epitaxy. Both As-stabilized c(2 × 8) and metal-stabilized c(8 × 2) surface reconstructions were observed for $In_{1-x}Ga_xAs$ over the entire alloy range. $GaSb_{1-y}As_y$ exhibited a c(2 × 6) or (2 × 3) structure for $y \lesssim 0.2$, and, after a transition region, the anion-stabilized c(2 × 8) or the Ga-stabilized c(8 × 2) structures for $y \gtrsim 0.5$. Electron energy loss spectroscopy revealed the simultaneous presence of two empty, dangling-bond-derived surface states in both alloy systems. For $In_{1-x}Ga_xAs$ the In-derived empty surface state lies $\approx 0.4 - 0.5$ eV below that of Ga and moves from above the conduction band edge into the band gap for $x \gtrsim 0.6$. The overlap between the Ga- and In-derived empty surface states causes the quenching of the Ga(3d) surface exciton. For $GaSb_{1-y}As_y$ the Sb dangling bonds generate an empty, localized surface state which lies $0.2 - 0.3$ eV above the empty, Ga-derived surface state. Both levels lie above the conduction band edge throughout the alloy range.

Introduction

Whereas spectroscopic studies of the electronic surface states of semiconductors have been well documented over the last few years, similar studies of alloys of semiconductors have not yet been reported. Such studies are of potential interest because they afford an assessment of the effect of atomic surface concentrations on the distribution of surface states in a similar but more generalized way to that reported for varying Ga and As surface concentrations on GaAs [1]. By the use of the appropriate binary semiconductor alloys, it is thus possible to evaluate the contribution of competing cations to the dangling-bond surface states, and similar properties for competing anions, albeit for different alloy systems. Toward this end, we have chosen to investigate the two alloy systems $In_{1-x}Ga_xAs$ and $GaSb_{1-y}As_y$, for which, respectively, the cations (In, Ga) and anions (Sb, As) may be varied arbitrarily.

The principal conclusions of this study are 1) the observation of both In- and Ga-derived surface states (dangling bonds), with the Ga surface state lying 0.2 eV above that of In and the latter moving from the conduction band *into* the energy gap region for $x \gtrsim 0.6$; and 2) a Sb-derived empty surface state located approximately 0.2 eV above the empty Ga-derived surface state. This represents the first observation of an empty, dangling anion bond state of predominantly p-like symmetry [2].

The alloys were prepared in ultra high vacuum (UHV) by molecular beam evaporation on (100) oriented substrates and subsequently analyzed *in situ* by electron-energy loss spectroscopy (ELS). Details of the preparation of the alloy films are presented in the next section. The structural rearrangements of surface atoms were studied by reflection-high energy electron diffraction (RHEED). A variety of new and unusual surface reconstructions were observed that are presented in detail in the third section. The energy loss data are presented in the fourth section, and the results are analyzed and discussed in terms of a one-electron approximation in the final section.

Experiment

Because of the general difficulty of obtaining samples of alloys, as well as the problems associated with conventional cleaning methods of the binary semiconductors, we have resorted to a molecular beam method of sample preparation with *in situ* facilities for their analysis. Molecular beam epitaxy (MBE) has shown itself to be an effective UHV deposition method for the preparation of electronic-grade, monocrystalline semiconductors, which exhibit nearly atomically smooth surfaces [3]. The growth apparatus and the accompanying analytical tools have been described previously [1], with the exception that for the present application four separate effusion ovens containing elemental Ga, In, As, and Sb were used. Polished (100) oriented wafers of GaAs, InAs, and GaSb were used for substrates. These were either chemically polished or ultrasonically cleaned prior to their placement in the UHV system. A final cleaning step of Ar^+ ion bombardment and annealing removed the surface contaminants (mostly oxygen and carbon) below the detectability of Auger analysis (< 0.01 of a monolayer). A relatively thin (0.1–0.2 μm) homoepitaxial overgrowth, or buffer layer, preceded the alloy growth. Substrate temperatures ranged from about 450 to 550°C, the lower values being used for the deposition of $In_{1-x}Ga_xAs$ and the higher ones for $GaSb_{1-y}As_y$. Deposition rates varied from 0.18–0.3 nm/s (1.8–3 Å/s), and overgrowth thickness from 1–2 μm. The films were grown under anion-rich (i.e., As or Sb) conditions to assure stoichiometric growth [3]. The alloy composition was independently checked by x-ray lattice constant determination, electron microprobe analysis, and *in situ* Auger electron spectroscopy (AES). Further details of the control of alloy compositions, the effects of matching lattice parameters of substrate and overgrowth (there is a 7.9 percent mismatch between GaAs and GaSb), and the electronic and optical properties of the alloys, are presented elsewhere [4, 5].

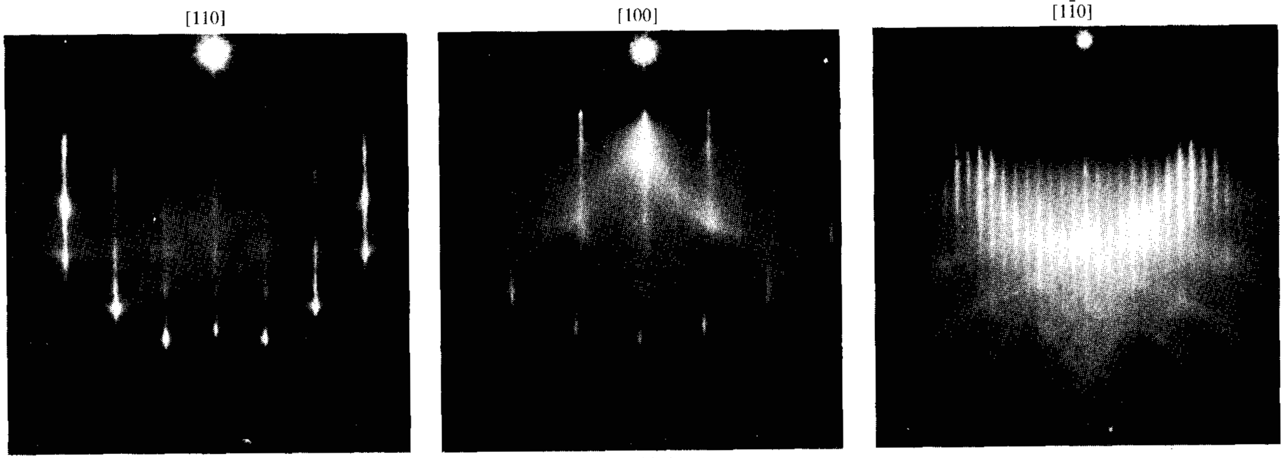
The morphological condition of the growing surface was monitored frequently by RHEED. Both the symmetry of atomic surface rearrangements and a qualitative assessment of surface smoothness are readily obtained. A surface is considered suitably smooth for surface studies if there is an absence of bulk diffraction spots. Visibly, such a surface has a mirror-like appearance even under an optical microscope.

After the deposition, the substrate temperature was lowered by about 100°C with the anion beams still impinging. All sources were then turned off while the substrate was maintained at the lowered temperature until the background As vapor pressure was reduced to below the 0.133 μPa (10^{-9} torr) range. This treatment ensured that the surface was maintained in the as-grown, anion-stabilized condition observed during growth. We found no evidence that As or Sb replaced each other by this process. However, cooling the substrate to room temperature in the presence of an appreciable As background pressure ($\gtrsim$ 1.33 μPa) would result in an As-rich surface which could exhibit a characteristic surface reconstruction of its own [1].

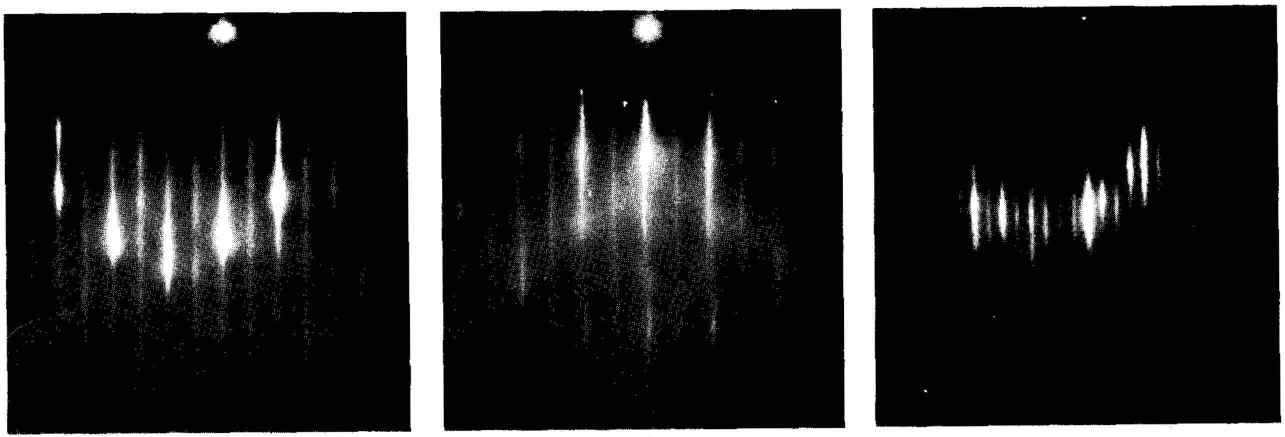
RHEED studies

It should be recalled that the zinc blende crystal structure (for example, GaAs) is made up of alternating (100) fcc planes of As and Ga atoms. Thus the ideal (100) surface is polar and may consist entirely of one type of atom. Due to its large surface energy—a consequence of the two dangling bonds per surface atom—the ideal (100) surface is expected to lower its energy. This may be accomplished by a variety of mechanisms, such as surface bond rehybridization or pairing of surface atoms, formation of surface vacancies, and surface atom relaxation. There is evidence for pairing and, in particular, for the formation of vacanices on the GaAs(100) surface, which is a direct consequence of the weaker surface binding energy of As relative to that of Ga [1].

A variety of surface reconstructions have been reported for the GaAs(100) surface [1, 6, 7] that have been found to depend critically on the relative abundance of As and Ga surface atoms, as well as on the surface temperature and the As background pressure at the time of observation [7]. Of these, the most relevant to the study of intrinsic electronic surface states are the (1 × 1), c(2 × 8), and c(8 × 2) structures, which correspond to surfaces with approximate As monolayer coverage ratios of 1, 0.5 and 0, and are termed As-rich, As-stabilized, and Ga-stabilized, respectively [1, 7]. The As-stabilized c(2 × 8) structure is commonly observed during growth, which generally occurs under As/Ga arrival rate ratios in excess of 2 [3]. The c(8 × 2) structure may be generated by annealing the c(2 × 8) structure or by film growth under nearly comparable As and Ga arrival rates. The diffraction patterns for the As-stabilized c(2 × 8) structure are shown in Fig. 1(a). Unlike LEED, several diffraction patterns of differing azimuthal directions must be taken with RHEED in order to identify the surface reconstruction. The most informative azimuthal patterns are along the two orthogonal [110] and [$1\bar{1}0$] directions and along the [100] direction. These directions are indicated in Fig. 2, which also depicts the reciprocal lattice and real-space representation of the c(2 × 8) structure, as well as of others discussed shortly. The electron diffraction pattern is, of course, represented by a nearly planar cut (actually a portion of the Ewald sphere) through reciprocal space, that is, normal to the plane of the figure in the present case. The diffraction patterns for both the [110] and the [100] azimuths in Fig. 1(a) show diffraction streaks separated by a distance proportional to the inverse of the bulk atomic spacing normal to the respective azimuths, whereas that for the [$1\bar{1}0$] azimuth exhibits 1/4 order streaks as well. That these patterns correspond to the c(2 × 8) structure can be readily ascertained from Fig. 2. The [100] azimuthal pattern in Fig. 1(a) also indicates a curving set of diffraction spots which have been displaced laterally by one-eighth of the distance separating the principal diffraction streaks. These spots are derived from the second Laue zone of the 1/4 order reciprocal lattice space. Faint 1/2 order streaks are also observable and represent a small degree of surface disorder. The disorder is shown schematically in reciprocal space (Fig. 2) by a line drawn through the reciprocal lattice points. Diffraction streaks due to disorder have also been observed



c(2 × 8)
(a)



(2 × 4)
(b)

Figure 1 RHEED patterns of (a) c(2 × 8) and (b) (2 × 4) surface reconstructions for [110], [100] and [1$\bar{1}$0] azimuths. Electron energy: 20 keV.

by LEED [8] and are, most likely, a manifestation of pairing of surface atoms along the [1$\bar{1}$0] direction [9], which may occur somewhat randomly between any two pairs of like surface atoms. It should be noted that the real-space representation in Fig. 2 is only schematic and does not imply any particular reconstruction model. In fact, because of the extreme complexity of the (100) surface, any detailed reconstruction model at this time would be highly speculative.

The Ga-stabilized c(8 × 2) structure (not shown) exhibits the same diffraction patterns as the c(2 × 8) structure, but with the two ⟨110⟩ azimuths interchanged. This means that in real space the two structures are also separated by a 90° rotation. We have observed both of these structures on InAs(100), and they seem to be in every respect analogous to those for the GaAs(100) surface. A (4 × 4) surface reconstruction was also observed when the In-stabilized c(8 × 2) structure was annealed above 450°C (723 K). For this structure both ⟨110⟩ azimuths exhibited 1/4 order diffraction spots.

A (2 × 4) structure has been observed on occasion and is closely related to the c(2 × 8). Its diffraction patterns are shown in Fig. 1(b), and its reciprocal and real-space representations in Fig. 2(b). It should be noted that this structure is readily generated from the c(2 × 8) structure by an atomic displacement along the [1$\bar{1}$0] direction of every eighth atomic column. It is thus difficult to distinguish this structure from that of a disordered c(2 × 8) structure. Streaking in the diffraction pattern is indicative of a poor coherence length in the azimuthal direction and is generally the result of surface disorder rather than of a limited coherence length of the incident electron beam [10]. A diffraction pattern from an ideal surface consists of a series of spots lying on a circle that passes through the image of the incident electron beam [10]. Based on these criteria, the coherence length and hence surface order are superior along the [1$\bar{1}$0] azimuth for both the c(2 ×8) and (2 × 4) structures. We have observed that in general the As-stabilized surfaces exhibit more disorder, particularly in the [110] azimuth for which 1/2 order streaks are frequently observable, than the metal- (In- or Ga-) stabilized surfaces. This represents another manifestation of the weaker surface binding energy of As.

Since the (100) surfaces of Both GaAs and InAs exhibit identical surface sturctures, one would expect similar sturctures to be observed thoughout the alloy range. This was indeed noted, although the resulting diffraction patterns indicated increased surface disorder. Both As-stabilized c(2 × 8) and metal-stabilized c(8 × 2) structures were observed. Diffraction patterns during growth of the alloys often indicated disordered (3 × 1), (3 × 2), or (1 × 1) structures. However, the As-stabilized structures were generally regained after the growth and at lower substrate temperatures. The (3 × 1) and (3 × 2) structures seem to be analogous to the transition structures observed during growth of GaAs(100) [3, 11].

As with the InAs(100) surface, the GaSb(100) surface has not been previously investigated. Unlike the two arsenides, however, the GaSb surface exhibits only a c(2 ×6) reconstruction during growth. Under Ga-stabilized conditions, or subsequent to an anneal at about 500°C (773 K), a (2 × 3) structure was observed. The diffraction patterns for these structures are shown in Fig. 3 and their reciprocal and real-space representations in Figs. 2(c) and (d) respectively. The (2 × 3) structure is closely related to the c(2 × 6) in a manner analogous to the relationship between the (2 × 4) and c(2 × 8) structures, and may also be interpreted as a c(2 × 6) structure with considerable real-space disorder in the [110] direction. Half-order streaks due to disorder are readily observed in Fig. 3(b) and are also indicated in the reciprocal lattice space pattern of Fig. 2(d). The disorder arises from a partial depletion of Sb surface atoms as a result of the heat treatment. This point is discussed further in the next section. Diffraction spots from higher order Laue zones are again clearly visible in the diffraction patterns.

An additional GaSb(100) surface reconstruction could be generated by exposing the c(2 × 6) structure only to the Sb molecular beam near or below 350°C (623 K). The diffraction patterns of the resulting GaSb(100) (2 × 5) structure are shown in Fig. 4(a), and its reciprocal and real-space representation in Fig. 2(e). A similar Sb exposure of the Ga-stabilized GaAs c(8 × 2) structure resulted in an Sb-stabilized GaAs(100) (2 × 8) structure, whose diffraction pattern and representations are shown in Figs. 4(b) and 2(f), respectively.

Because of the differences in the surface reconstructions between GaAs and GaSb, those for the $GaSb_{1-y}As_y$ alloys are expected to change over the compositional range. The anion-stabilized surfaces, during growth as well as afterwards, exhibited the c(2 × 8) structures for $y \gtrsim 0.5$ and the c(2 × 6) or (2 × 3) structures for $y \lesssim 0.2$. For values of y between these limits a transitional, pseudo-(3 × 2) structure was observed. This structure is characterized by unevenly spaced fractional diffraction streaks and suggests a complex, competitive surface arrangement of the anions. The Ga-stabilized alloy surfaces that we have analyzed exhibited either a (4 × 2) or c(8 ×2) reconstruction for $y \gtrsim 0.5$ and a (2 × 3) structure

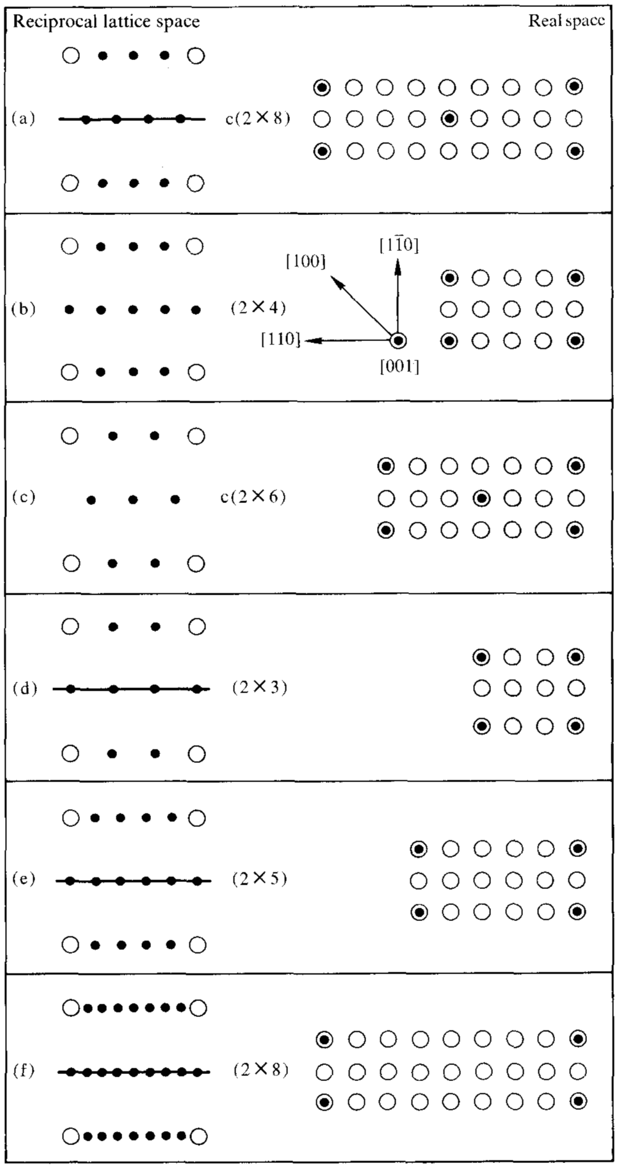
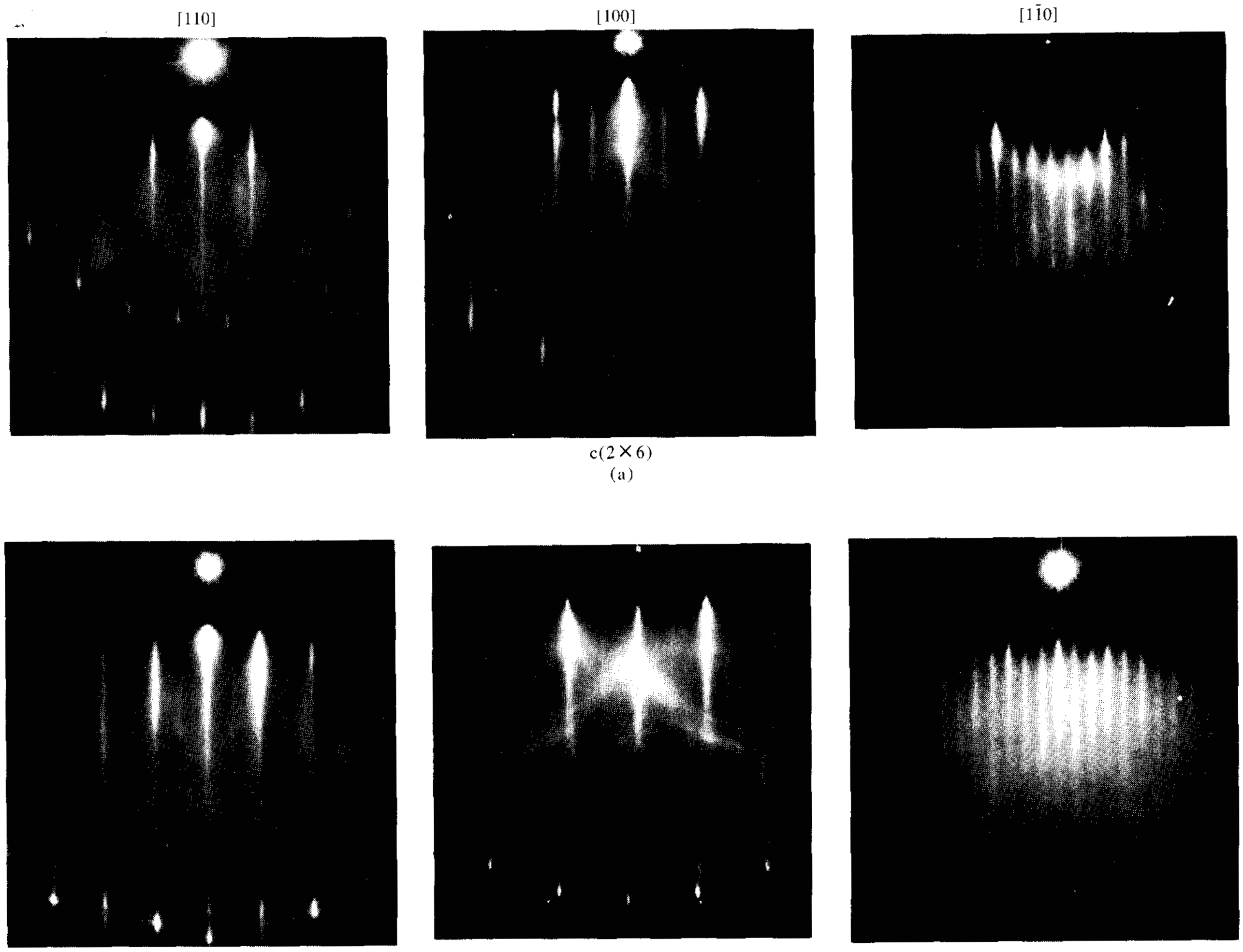


Figure 2 Reciprocal space and real-space representation for several surface reconstructions on the (001) surface. Open circles represent bulk periodicities; solid circles represent superlattice periodicities.



c(2×6)
(a)

(2×3)
(b)

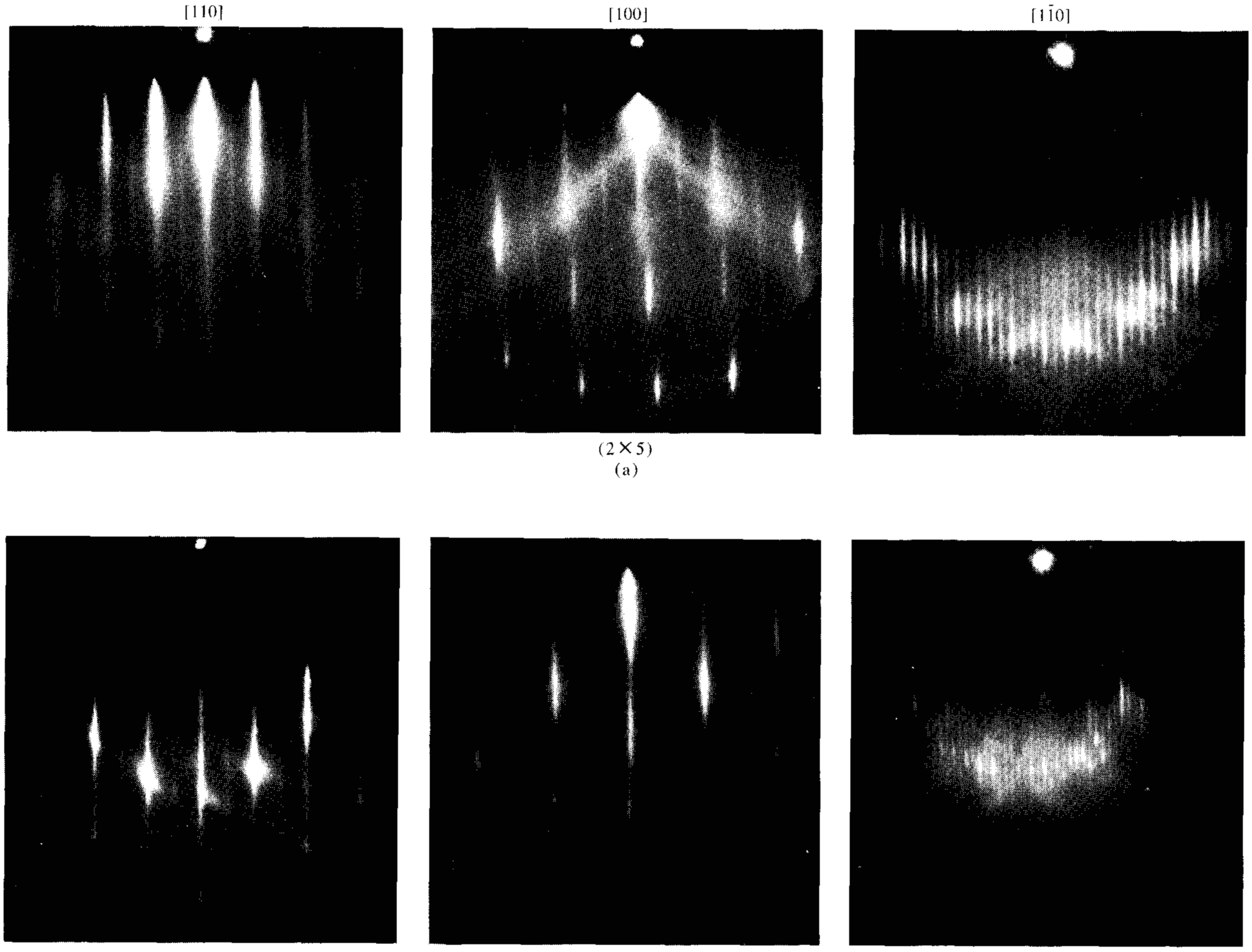
Figure 3 RHEED patterns of (a) c(2 × 6) and (b) (2 × 3) surface reconstructions for [110], [100] and [1$\bar{1}$0] azimuths. Electron energy: 20 keV.

for $y \lesssim 0.3$. Surfaces with compositions between these limits were not investigated. However, because of the more stable and homogeneous nature of the Ga-stabilized surface, the transition region from one surface structure to the other is not expected to be very wide.

Energy loss measurements

Energy loss spectra were taken as soon as the deposited film had cooled to room temperature. Spectra were taken with a single pass, cylindrical mirror analyzer (CMA) with a concentric electron gun. The primary electron beam, typically in the energy range of 70–100 eV, impinged normal to the surface. The backscattered, secondary electrons were collected by the CMA about a conical surface with an 85° apex angle. The second derivative of the loss spectrum was recorded to enhance detail. The estimated energy resolution for the present experiments is about 0.6 eV.

The loss spectra for the As-stabilized $In_{1-x}Ga_xAs(100)$ surfaces are shown in Fig. 5. With the exception of curve b, which corresponds to a surface with a (3 × 1) transition structure, the spectra are from c(2 × 8) reconstructed surfaces. From the bulk-derived, dielectric loss function for GaAs and InAs one can readily ascertain that certain features in their loss spectra are related to bulk excitations [1, 12] and, by extension, determine those in the alloys. Thus the loss peaks near 3 and 5.5 eV are due to electron excitations from valence to conduction bands. The broad prominent loss structures near 14.5 eV (curve a) to 16.3 eV (curve e) are due to bulk plasmon excitations. The broad doublets at the higher end of the loss spectra (e.g., 19.2 and 21.9 eV in curve a, and similar structures in the others) are due to excitations from In(4d) and Ga(3d) core levels into the conduction bands. The remaining loss peaks, with the possible exception of the shoulder near 12 eV, are attributed to surface-related ex-



(2×5)
(a)

(2×8)
(b)

Figure 4 RHEED patterns of (a) (2 × 5), and (b) (2 × 8) surface reconstructions for [110], [100] and [1$\bar{1}$0] azimuths. Electron energy: 20 keV.

citations: the doublet near 18 eV in curves a–d to exciton-enhanced excitations from the spin-orbit split In(4d) core level to an empty surface state localized on the In atom (dangling bond); the peak at 20 eV to a similar excitation involving the Ga(3d) core level, and discussed previously [1]; and the broad doublets near 8–10 eV to excitations from filled surface states (backbonds) to the empty, cation-derived dangling bond states. The strong loss peak at 2.5 eV for GaAs (curve e), has been assigned to a charge transfer excitation from filled dangling As-bond states to empty dangling Ga-bond states [1]. These excitations should also be present in the other spectra, but are probably disguised by the bulk excitations near 3 eV. In fact, the somewhat broader structure at 2.9 eV for InAs (curve a) compared to that for the annealed surface [Fig. 6(a)], for which this charge transfer excitation is absent (due to a lack of dangling As bonds), suggests the presence of surface-related excitations. It is of interest to note that for the cleaved InAs(110) surface, higher resolution loss measurements revealed a doublet structure at 3.2 and 2.9 eV, the latter having been attributed to the charge transfer excitation [13]. Identification of the loss peaks has been summarized in Table 1.

Annealing the As-stabilized $In_{1-x}Ga_xAs$ surfaces in the range of 450–530°C converted them to metal-stabilized c(8 × 2) structures. This heat treatment resulted in the removal of As surface atoms, which was confirmed by AES. The As/Ga Auger ratio decreased generally by about 17 percent. This value is comparable to that observed for GaAs(100) and corresponds to the removal of the ≈1/2 monolayer of As which characterizes the c(2 ×8) surface [1]. The removal of As surface atoms and the resulting increase of metal surface atoms are readily confirmed by the loss spectra for the annealed surfaces (Fig. 6), which indicate a drastic increase in the surface exciton peaks—the result of an increased density of dangling Ga

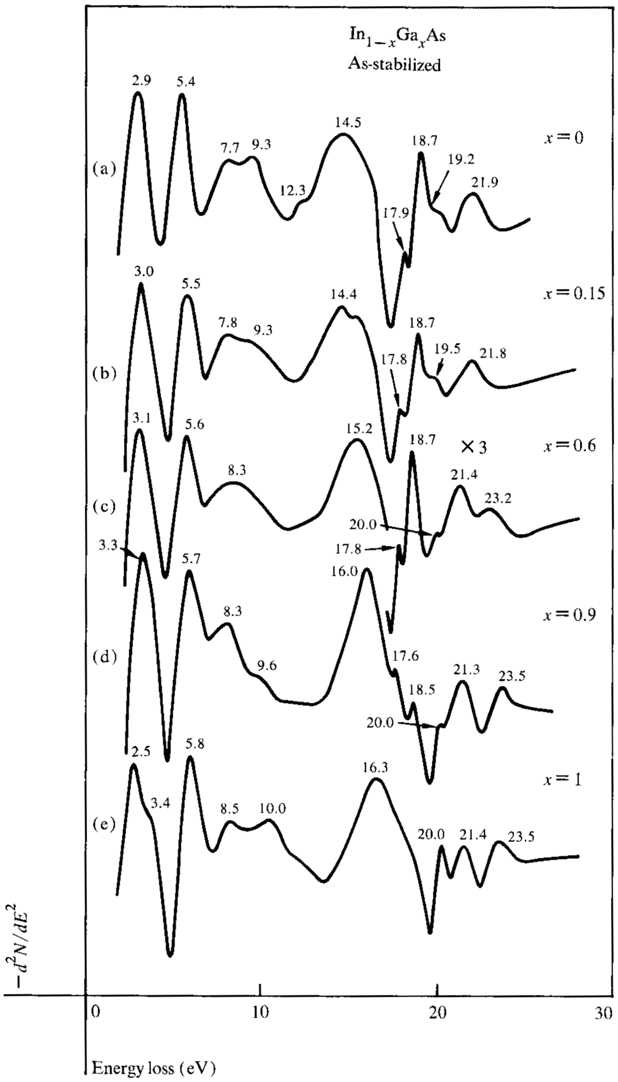


Figure 5 ELS spectra for As-stabilized In$_{1-x}$Ga$_x$As(100) surfaces. Primary energy: 90 eV.

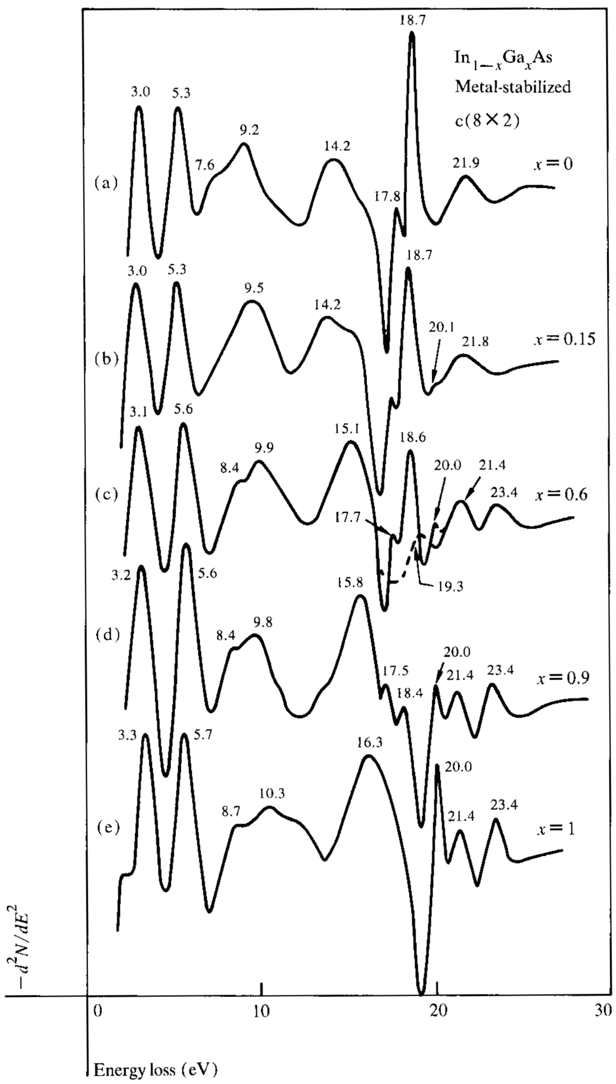


Figure 6 ELS spectra for metal-stabilized In$_{1-x}$Ga$_x$As (100) surfaces. Primary energy: 90 eV.

and In bonds. Because the density of empty surface states has been increased, the backbond-to-empty-surface-state excitation is expected to increase as well. This enhancement is clearly observed in the loss structure near 8-10 eV. That the loss structure in the 18-20-eV region is indeed due to dangling cation bonds is supported by the disappearance of the surface excitons when approximately a monolayer of As was adsorbed below 150°C on an In$_{0.4}$Ga$_{0.6}$As c(8 × 2) surface. The resulting loss spectrum in the region near 20 eV has been indicated by a broken line in Fig. 6(c).

The loss spectra for the anion- and Ga-stabilized (100) surfaces of various GaSb$_{1-y}$As$_y$ alloys are shown in Figs. 7 and 8, respectively. Identification of surface state excitations is analogous to that of the In$_{1-x}$Ga$_x$As alloy surfaces, with the peak near 20 eV again corresponding to the Ga(3d) core-to-surface-state excitation (surface exciton) and those in the 7–8 and 9–20-eV energy range to excitations from the filled backbond states into the empty dangling bond states. Assignments of the loss structures have been summarized in Table 1. A novel feature in these spectra is the sharp doublet structure near 33 eV, the width of which is limited here by instrumental resolution. The energy range corresponds to that of the binding energy of the spin-orbit split Sb(4d) core levels [14]. We attribute this structure to exciton-enhanced excitations from the Sb(4d) core level to the empty surface state arising from the dangling Sb bonds [15]. These excitations are analogous to those from the cation d-core levels, with the very important distinction that for this case an empty, dangling bond surface state arises from an anion. This is in marked contrast to the arsenides for which As-derived,

Table 1 Summary of origin of structure observed by ELS for $In_{1-x}Ga_xAs$ and $GaSb_{1-y}As_y$ surfaces.

	$In_{1-x}Ga_xAs$	
Energy (eV)	*Bulk excitations*	*Surface excitations*
2.5		DB^c(As)-DB(Ga)
2.9–3.4	VB^a-CB^b	
5.4–5.8	VB-CB	
7.6–8.7		BB^d-DB(In, Ga)
9.2–10.3		BB-DB(In, Ga)
14.2–16.3	plasmon	
17.5–17.9		In(4d)(j = 5/2)-DB(In)
18.4–18.7		In(4d)(j = 3/2)-DB(In)
19.2–19.5	In(4d)-CB	
21.9	In(4d)-CB	
20.0		Ga(3d)(j = 3/2)-DB(Ga)
21.3–21.4	Ga(3d)-CB	
23.2–23.5	Ga(3d)-CB	

	$GaSb_{1-y}As_y$	
Energy (eV)	*Bulk excitations*	*Surface excitations*
2.5		DB(As)-DB(Ga)
2.6–3.4	VB-CB	
5.1–5.8	VB-CB	
7.3–8.7		BB-DB(Ga, Sb)
9.1–10.3		BB-DB(Ga, Sb)
14.7–16.3	plasmon	
19.8–20.0		Ga(3d)(j = 3/2)-DB(Ga)
20.4–21.4	Ga(3d)-CB	
22.6–23.5	Ga(3d)-CB	
32.6		Sb(4d)(j = 5/2)-DB(Sb)
33.8		Sb(4d)(j = 3/2)-DB(Sb)
36.4–36.8	Sb(4d)-CB	
42.5	As(3d)-CB	
46.0	As(3d)-CB	

[a] VB: valence band.
[b] CB: conduction band.
[c] DB: dangling bond surface state.
[d] BB: backbond surface state.

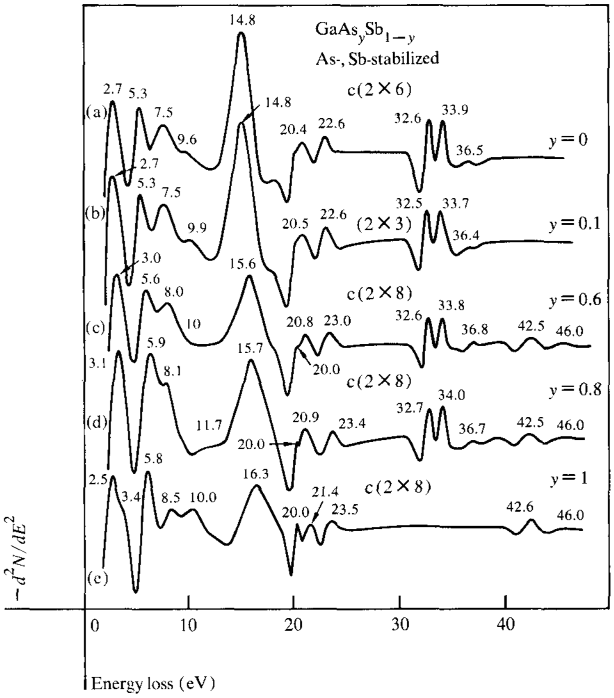
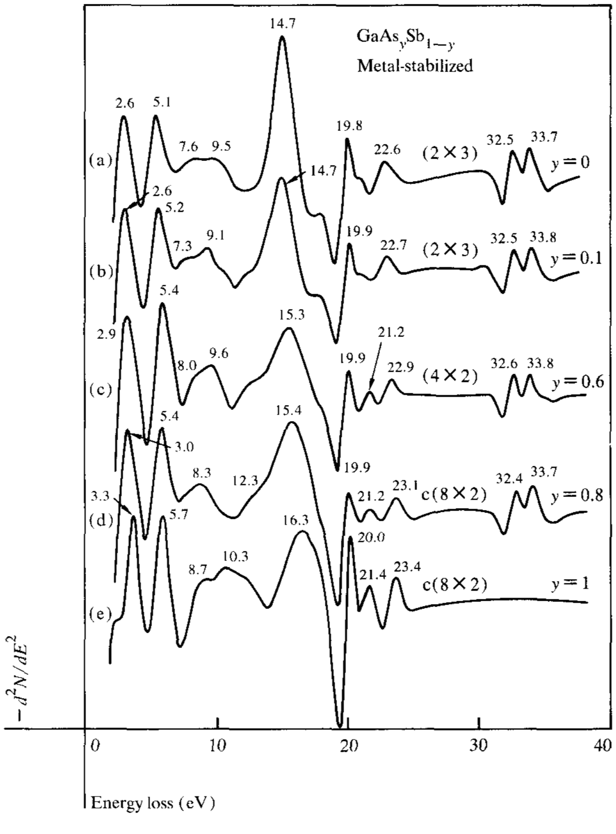


Figure 7 ELS spectra for anion-stabilized $GaSb_{1-y}As_y$ (100) surfaces. Primary energy: 90 eV.

Figure 8 ELS spectra for Ga-stabilized $GaSb_{1-y}As_y$ (100) surfaces. Primary energy: 90 eV.



empty dangling bond states have not been observed, as is evident from the loss curves of Fig. 7, in which excitations near 42.5 eV emanating from the As(3d) core level are very broad and substantially weaker than those from the Sb(4d) level. The difference in intensities is particularly noticeable in the spectra for the larger values of y (curve d) for which Sb makes up only about 20 percent of the anion surface population, yet its core excitation spectrum remains dominant.

The principal effect of annealing the anion-stabilized $GaSb_{1-y}As_y$ surfaces is to remove As surface atoms. For instance, for the $GaSb_{0.4}As_{0.6}$ surface, a 530°C anneal resulted in a decrease of the As/Ga Auger ratio of 14 percent, whereas the Sb-Ga ratio changed by only five percent. Such an anneal depletes the GaAs(100) c(2 × 8) surface of As (approximately 1/2 monolayer) and converts it to the c(8 × 2). A similar treatment of the GaSb(100) c(2 × 6) surface does not basically alter the reconstruction, but rather changes it, as discussed earlier, to the related (2 × 3) structure. The resulting loss of Sb surface atoms was estimated to be roughly 1/3 of a monolayer to about a 50 percent coverage for the (2 × 3) structure [15]. That the heat treatment removes only part of the Sb surface atom is evident from the loss spectrum in Fig. 8(a), which still indicates a strong presence of the Sb surface exciton. The removal of the Sb results in an increase in the dangling Ga bonds, with the resulting enhancement of the 19.8-eV surface loss peak. For the alloys rich in Sb, the heat treatment should not affect the total number of empty surface states, since these are common to both cation and anion. As a result, the intensities of the excitations from filled backbond states to empty surface states, near 7.5 and 9.5 eV in the loss spectra, should remain fairly constant, which is in contrast to the enhancement observed for the $In_{1-x}Ga_xAs$ surfaces.

An alternative interpretation of the origin of the loss peak in the 9-10-eV spectral region is that it arises from excitations of surface plasmons, as has been proposed for the cleaved surfaces of several III-V semiconductors [13]. However, it is unlikely that a surface plasmon can be excited on a smooth surface by a low-energy electron beam normal to the surface. This follows because the momentum vector of a surface plasmon excitation lies parallel to the surface, and the coupling to the incident electron beam must occur through another scattering process. Using a 400-eV primary beam, we have determined the surface plasmon energy for GaAs to be 11.3 eV, which is close to the value of 11.5 (bulk plasmon/$\sqrt{2}$) predicted by simple dielectric theory. Furthermore, the 10-eV loss peak of the GaAs(100) surface is a strong function of the As surface coverage and is entirely absent for the As-rich surface [1]. Clearly, this behavior is inconsistent with that of a surface plasmon, whose properties are still determined by the frequency-dependent, bulk dielectric function $\epsilon(\omega)$, and its energy by the condition $\epsilon(\text{real}) + 1 = 0$.

The shoulders observed on both sides of the plasmon loss peaks in most of the spectra of Figs. 5-8 may be artifacts and the result of the double differentiation technique. However, the possibility cannot be excluded that the shoulders in the 11-12-eV region originate from an excitation of a surface plasmon. We have observed some enhancement in this structure in the loss spectrum of an accidentaly grown rough surface, for which such an excitation is more favorable. Similar structures on (110) surfaces have been assigned to excitations from the filled backbond states to some high-lying empty surface state [13]. We have, however, no experimental evidence from core-level excitations that such higher-lying empty surface states exist on the (100) surfaces.

Discussion

An unusual feature in the loss spectra of Figs. 5 and 6 is the great disparity, in relation to the atomic concentration, of the intensity of the surface exciton associated with the In(4d) core level near 18 eV compared to that of the Ga(3d) level near 20 eV. This quenching of the Ga(3d) surface exciton, which is a consequence of the two competing cation-derived empty final states, may be understood with the help of a one-electron energy level diagram of surface states for the alloy films, which we develop in this section. Although there are potentially competing final states on GaSb(100) as well—one each due to the dangling Ga and Sb bonds—quenching effects are not observed.

In order to develop an energy level diagram of surface states, we assume that the empty surface states are the principal final states for excitations from the filled surface states. This notion has been applied previously to other semiconductor surfaces and the resulting scheme of energy levels has been compatible to those expected from theoretical considerations [1, 13, 16]. With the knowledge of the binding energies of the various 3d and 4d core levels relative to the bulk valence band edges [14], it is possible to locate the energy position of the empty surface states to within the binding energy of the core-surface exciton. The exciton binding energy has been estimated to be 0.5 and 0.45 eV for the Ga(3d) and In(4d) surface excitons, respectively [13]. We assume here a comparable binding energy for the Sb(4d) surface exciton. This estimate may, in fact, be too large in view of the increased screening in GaSb, which is manifested by its large dielectric constant. Since discrepancies of a few tenths of an Ev do not appreciably affect the conclusions, we will not belabor this point any further. The energy positions of the empty surface states for GaSb, GaAs and InAs have been drawn as heavy broken lines in Fig. 9. The heavy solid lines mark the bulk valence and conduction band edges [13]. Whereas the empty surface states for GaSb and InAs are degenerate in energy with the conduction bands, those for GaAs lie, for all practical purposes, at the conduction band edge. This location is in contrast to our earlier estimate of 0.5 eV below the band edge, which did not include the correction for the exciton binding energy [1].

The energy positions of the filled surface states for the compounds are determined relative to the empty levels by subtracting the energies of the surface state excitations determined by ELS. The resulting set of three separate filled surface states is indicated by cross-hatched areas in Fig. 9. The upper, filled surface state bands originate primarily from the filled dangling bonds associated with the anions, and their density is consequently a function of the anion concentration. The fact that the boundaries of these states are largely demarked by dashed lines indicates that their location could not be clearly deduced from the loss data, as explained in the previous section. The lower set of filled surface states arises from the region of the cation-anion backbonds, which are not affected, to first order, by the type of surface atoms. The data points within each region mark the position of the backbonds determined from both anion and cation stabilized surfaces. Their scatter is well within the accuracy of determining the energetic position of the loss structure.

The interesting feature of the GaSb(100) c(2 × 6) surface is the presence of two empty surface states. Although their energy separation is only about 0.3 eV, with the Sb-derived states above those of Ga, there is probably very little overlap between these states. The observation of a localized, anion-derived, empty surface state is in itself very interesting, since it represents the first observation of such a surface state. This state may be unique to the (100) surface, since it was not observed on the cleaved GaSb(110) surface [17]. The intensity of the Sb(4d) surface exciton furthermore suggests that the final state exhibits considerable p-like orbital character, which is consistent with theoretical considerations [18]. The existence of an empty Sb-derived surfaced state may be qualitatively understood by noting that each Sb surface atom on the (100) surface has two broken bonds occupied by 2½ electrons (the other 2½ electrons are involved in the backbonds). In analogy to the Si(100) and GaAs(100) surfaces, these two broken bonds are expected to form two surface bands. For an anion-terminated surface one of these bands will be fully occupied and the other ¼ occupied [18]. The dispersion of this band is a function of the spatial extent and overlap of the orbitals and is strongly affected by the details of the surface reconstruction [19]. The experimentally observed enhanced structure of the Sb(4d) surface state excitation indicates that the empty, Sb-derived surface state is localized (low dispersion) and has little overlap with bulk conduction band states. In contrast, the broad structure of the As(3d) core spectrum, which is invariant to surface orientations [3], suggests that any empty, As-derived surface states are broad and overlap the bulk conduction band states by several eV.

In order to determine the position of the empty surface states for the alloys, we must estimate the binding energies of the core levels in the alloys. This estimate is facilitated by the experimentally observed fact that, for the compounds of interest, the binding energies relative to the valence band edges are constant to within 0.2 eV [14, 20]; in other words, the core levels are essentially "tied" to the top of the valence band.

For the $In_{1-x}Ga_xAs$ system we have assumed a linear variation of the valence band edge between the positions of GaAs and InAs. Since their position relative to the vacuum level is nearly identical and since the valence band edge has considerable "As character," this seems a reasonable assumption. The position of the In(4d) and Ga(3d) core levels in the alloy is then simply determined by assuming the above-mentioned constancy in the binding energy relative to the valence band edge, as shown in Fig. 9. From the loss data and the previously discussed exciton binding energies, we are now in a position to determine the location of the In- and Ga-derived empty sur-

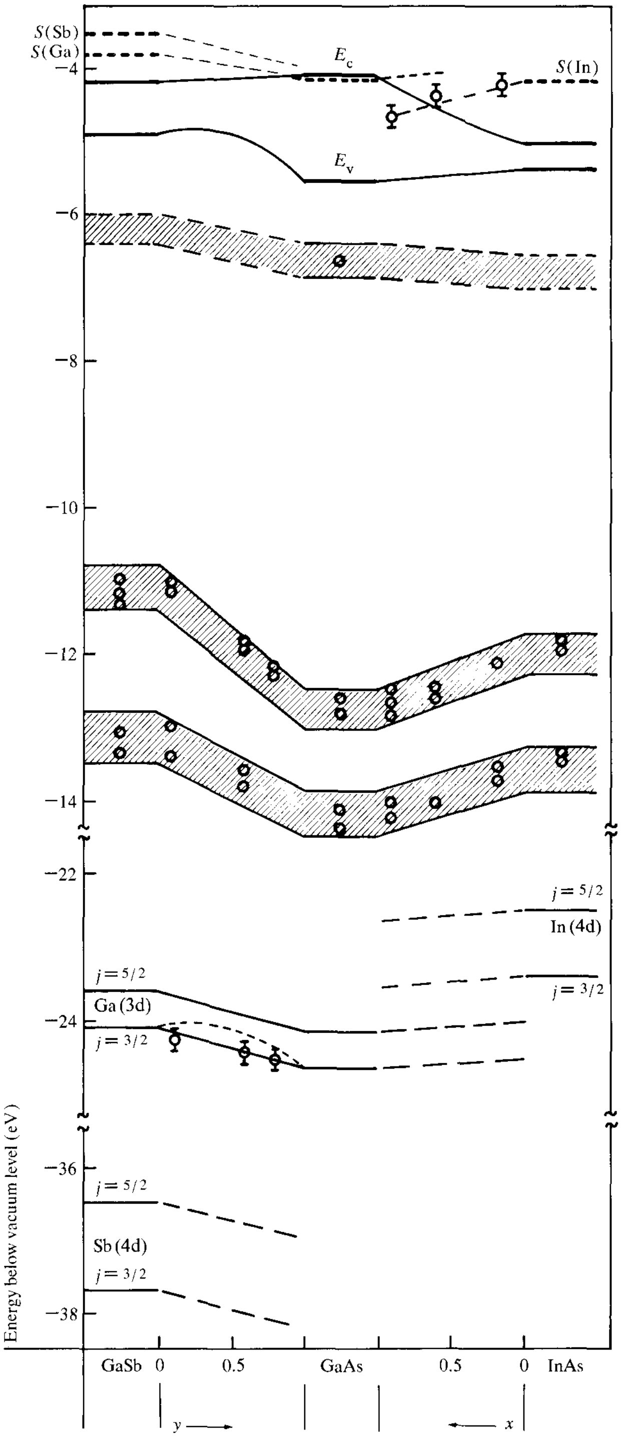


Figure 9 One-electron energy level diagram of surface states for $In_{1-x}Ga_xAs$ and $GaSb_{1-y}As_y$ (100) surfaces. The conduction and valence band edges are indicated by E_c and E_v, respectively. The location of the empty, dangling-bond-derived surface states is identified by S.

face states. The results in Fig. 9 indicate an empty, In-derived surface band located below that of Ga and lying in the band gap for $x \gtrsim 0.6$. The variation of the conduction band edge is in accordance with the experimentally observed variation of the band gap, which exhibits a slight downward bowing [5]. The Ga-derived surface state can be traced only up to $x \approx 0.4$. Because of the equivalence of the Ga and In atoms on the surface, an appreciable overlap of their wave functions is to be expected. The overlap severely limits the lifetime of an electron in the empty Ga-derived surface state and explains the observed quenching of the Ga(3d) surface exciton. In fact, this quenching may be considered as the first experimental "proof" of the excitonic nature of the core-to-empty-surface-state excitations. Because of the steric inequivalence of Ga and Sb surface atoms, which is manifested by broken bonds directed in orthogonal directions, overlap between wavefunctions and consequently quenching effects are expected to be small in $GaSb_{1-y}As_y$.

For reasons similar to those used for the valence band edge in $In_{1-x}Ga_xAs$, we have assumed a linear extrapolation for the conduction band edge in $GaSb_{1-y}As_y$. Since the energy gap in $GaSb_{1-y}As_y$ exhibits considerable downward bowing from a linear extrapolation, we have assumed that the nonlinearity arises principally from the valence band and have adjusted the band edge accordingly in Fig. 9 [5]. This behavior is believed to originate partially from the random distribution of the anion which characterizes the top of the valence band [21]. Consequently, one would not expect a similar variation for the binding energy of the Ga(3d) core level, shown as a dashed line for the Ga(3d) ($j = 3/2$) level in Fig. 9. The constancy in energy of the Ga(3d) surface exciton, as well as the expected linear variation with composition of the Ga-derived empty surface state, do indeed suggest that within experimental error the binding energy of the Ga(3d) core level varies linearly as well. We have also assumed a linear variation in the binding energy of the Sb(4d) core level, although this assumption cannot be substantiated at present without a spectroscopic determination of its binding energy.

As with the compounds themselves, the positions of the filled surface states were determined by assuming that all surface-related excitations observed in the loss spectra have empty surface states for their final states. Even though the excitations from the filled surface states (backbonds) are broad relative to the energetic separation of the final states, their positions are nevertheless fairly well defined as shown by the hatched areas in Fig. 9. Actual data points are indicated as well. In principle there should be two sets of excitations from the backbonds to the empty surface states, one for each of the two different final states. However, these have not been resolved experimentally.

Note added in proof:
Subsequent measurements of loss with improved resolution show an additional peak at 2.1 eV for GaSb(100), which is ascribed to excitations from Sb-derived, filled, dangling-bond states to the empty, dangling-bond-derived states [15].

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The author is located at the IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598.