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Intrinsic (111) surface states of Ge, GaAs, and ZnSe†

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The intrinsic (111) surface states of Ge, GaAs, and ZnSe are studied using the tight-binding method. The local density of states of atoms on different layers are calculated and the various types of surface states are discussed. The effects of relaxation on the surface states are examined for Ge.

I. INTRODUCTION

The tight-binding (TB) method is very useful in providing a practical and relatively simple way of studying the electronic surface states of semiconductors. By using a small number of interaction parameters it is possible to obtain good results for both bulk[1] and surface states of diamond[2] and zinc-blende-type[3] compounds. We have previously[1] obtained the (TB) parameters appropriate for Ge, GaAs, and ZnSe and have discussed[3] briefly the results of our calculations on the (111) surface states of Ge and GaAs. Similar calculations on the (110) surface of diamond and zinc-blende semiconductors have also been done[4] recently. In this paper we wish to describe in more detail the (111) surface states of Ge, GaAs, and ZnSe. Surface reconstruction is not considered in our calculation; however, the effects of surface relaxation are studied for Ge. The local density of states (LDS) for surface atoms and atoms close to the surface layer is calculated. The character and degree of localization of the charge density associated with the various surface states are also calculated.

This paper is organized in the following way. In Sec. II we briefly discuss some aspects of the calculation and give the interaction parameters we have used. The surface states of Ge with and without relaxation effects are studied in Sec. III. The (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces of GaAs and ZnSe are discussed in Sec. IV.

II. CALCULATION

The calculation of surface states by the TB method for group-IV materials has been discussed by Hirabayashi[5] and we have extended the method to zinc-blende compounds. In the calculation of surface states we have taken a system consisting of a finite number N of atomic layers. To distinguish surface states from bulk states without ambiguity we have taken $N=16$. For GaAs or ZnSe the atomic layers are composed of only one type of atom, which alternates between Ga-type and As-type atoms.

The interaction parameters for Ge, GaAs, and ZnSe were determined[1] by fitting the bulk valence bands. Figure 1 shows the directed orbitals on two two adjacent tetrahedra in a diamond or zinc-blende crystal with the orbital 1 being along the (111) direction. Denoting the Hamiltonian matrix elements between orbitals i and j by $(i|j)$ we have taken the following interactions (in eV) into account for Ge:

$$\gamma_1=(1|1)=0, \qquad \gamma_2=(1|2)=-2.10,$$
$$\gamma_3=(1|8)=-5.46, \qquad \gamma_4=(2|8)=-0.07,$$
$$\gamma_5=(2|5)=-0.45, \qquad \gamma_6=(2|7)=0.60.$$

For GaAs, (ZnSe), assuming the orbitals 1–4 and 5–8 refer to As (Se) and Ga (Zn), respectively, we have used the following parameters (in eV):

$$\alpha_1=(1|1)=-1.36(-2.14),$$
$$\beta_1=(8|8)=2.25(5.57),$$
$$\alpha_2=(1|2)=-1.55(-2.26),$$
$$\beta_2=(7|8)=-2.35(-1.93),$$
$$\alpha_3=\beta_3=(1|8)=-4.4(-4.12),$$
$$\alpha_4=(2|8)=-0.92(-0.51),$$
$$\beta_4=(1|5)=-0.03(-0.32),$$
$$\alpha_5=(2|5)=-0.28(-0.23),$$
$$\alpha_6=(2|7)=0.66(0.62).$$

To simulate the effects of surface relaxation for Ge we have assumed that the surface layer moves inward[6] by 0.3 Å and we have changed the interatomic interaction parameters at the surface according to[7]

$$H_{ij}=H_{ij}^0 e^{-\beta\Delta R}, \tag{1}$$

where H_{ij}^0 is the matrix elements given above and ΔR is the change in the nearest-neighbor distance. This is a reasonable approximation that has been shown to work well in the case of Si. Its main effect is to increase appreciably the strength of $(1|8)$-type interactions (Fig. 1) between the back-

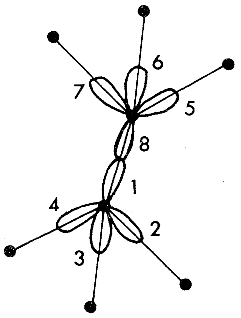

FIG. 1. Directed orbitals on two adjacent tetrahedra in a diamond or zinc-blende semiconductor. The (111) plane is normal to the bonds 1, 8. The possible interactions between these orbitals are discussed in Sec. II.

bonding orbitals on the first two layers at the surface. The smaller increase in the magnitude of the other interactions given by Eq. (1) is also reasonable because of the larger overlap between the orbitals resulting from relaxation. We have used $\beta = 10.4/a$, where a is the cubic lattice constant, in our calculation. The intra-atomic interaction parameter γ_2 was also changed (as in Ref. 8) to account for the change in the s-p character of the orbitals resulting from relaxation.

We have calculated the local density of states $N_l(E)$ of atoms on different layers for Ge, GaAs, and ZnSe. To do this the expression

$$N_l(E) = \sum_{i} \sum_{\vec{k},n} \delta[E - E_n(\vec{k})] \, |\langle \psi_{\vec{k},n} | \phi_i \rangle|^2$$

was used, where $\psi_{\vec{k},n}$ is the total wave function corresponding to the nth eigenvalue and the sum i is over the orbitals of the atoms on a particular layer. All the density-of-states curves discussed in Sec. III have been normalized to the bulk (or crystalline) density of states to facilitate comparison between them.

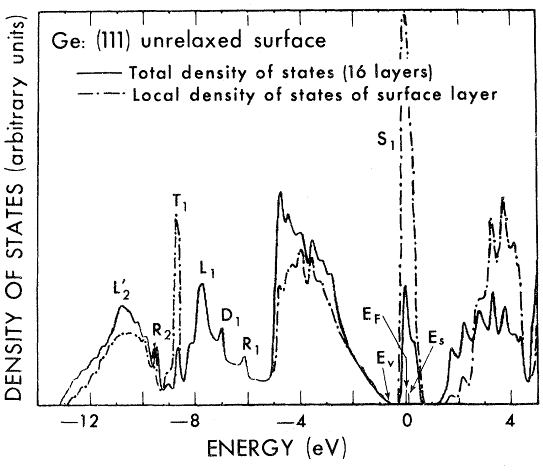

FIG. 2. Total density of states (solid line) of Ge for a system consisting of 16 layers. The local density of states (dashed line) of surface atoms has been normalized to the total density of states for a better comparison between the two.

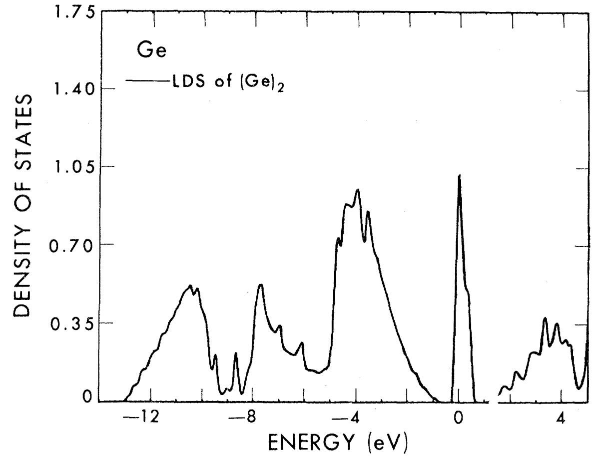

FIG. 3. Local density of states (LDS) of Ge atoms on the layer below the surface. Surface states are labeled in Fig. 2.

III. RESULTS

A. Ge: unrelaxed surface

In Fig. 2 we show the total density of states of 16 layers together with the LDS of the surface layer. Figures 3 and 4 show the LDS of a layer just below the surface [denoted by $(\mathrm{Ge})_2$] and the LDS of atoms four layers below the surface $(\mathrm{Ge})_5$. The total density of states of 16 layers (Fig. 2) is very similar to the bulk (or crystalline) density of states shown in Fig. 4, except for structure arising from the two surfaces. In particular the structures S_1 and T_1 are associated with localized surface states and can be seen to become weaker as we go away from the surface. The peak denoted S_1 is seen in energy-loss spectroscopy[9]; it has an integrated weight equal to one electron per surface atom. The total width of the S_1 peak is about 1 eV and it lies 0.4 eV above the top of the bulk valence bands denoted by E_v. Over 70% of the charge density associated with this peak is localized in the first two layers at the surface, 52% at the surface layer and 20% on the layer below. The Fermi energy E_F lies about 0.6 eV above E_v inside the S_1 peak. The energy E_s in Fig. 1 gives the energy at which the integrated LDS of surface atoms equals the number of surface atoms (so that the surface is neutral); it is less than 0.1 eV away from E_F in the unrelaxed surface configuration.

The contribution to the S_1 peak comes mainly from the dangling bond states and also from the back-bonding states of the atoms on the layer below the surface. As seen in Figs. 2–4 these states become progressively weaker as we go away from the surface and virtually disappear within

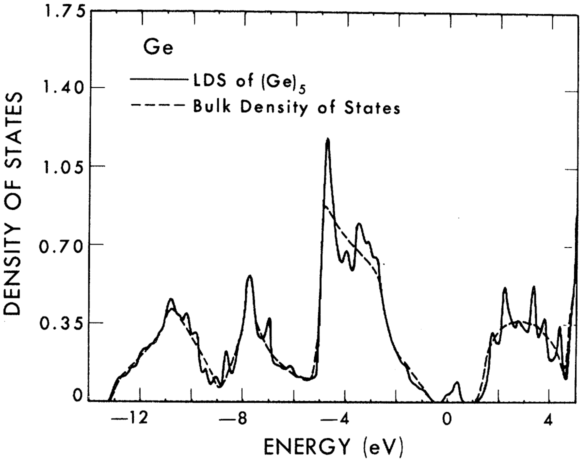

FIG. 4. Local density of states of Ge atoms four layers below the surface (solid line) and the bulk (or crystalline) density of states (dashed line).

four to five layers below the surface.

The T_1 peak in Fig. 2 corresponds to back-bonding surface states. Only certain wave vectors in the region near the point K (corner of the hexagonal Brillouin zone) contribute to this peak. At K the charge density associated with T_1 has a concentration of 80% on the surface layer. The average contribution over the Brillouin zone is however much smaller, and the integrated weight of the structure is equivalent to 0.25 electrons per surface atom.

The structures R_1 and R_2 (Fig. 2) are resonant states also associated with back-bonding states. The wave functions associated with these states have a charge density of about 0.15 electrons per atom at the surface layer. The D_1 structure (Fig. 2) is not associated with any surface states, but apparently results from the use of a finite number of layers; the states involved have a small dispersion throughout the Brillouin zone.

Figures 2–4 show that the LDS of atoms on the surface layer and on layers near the surface is remarkably similar to the total density of states (of 16 layers) or to the bulk density of states (except, of course, for the presence of surface structure). Most of the small steplike structures evident in these figures result from the use of a finite number of planes in the calculations and they gradually disappear as more planes are used. We have smoothed out the steplike structures and the noise in the densities of states by using Gaussian functions 0.15 eV wide at half-maximum.

The structures we have obtained for the (111) surface of Ge are very similar to those for a (110) surface[4] except for the T_1 peak, which is absent for the (110) surface. The existence of the T_1 structure is, however, very sensitive to the value of the structure factor describing the relative positions of the atoms on the surface.

B. Ge: relaxed surface

The effect of surface relaxation on the LDS of the atoms on the surface layer is shown in Fig. 5. As can be seen, relaxation results in the appearance of new surface states denoted by S_2 and S_3 and a weakening of the S_1 and T_1 states. There is a broadening of about 0.4 eV in the top valence bands for states near the surface.

The energy E_s which corresponds to the neutrality level for the surface layer is 2.0 eV below E_F. This shift in E_s (relative to the unrelaxed case) would result in an excess charge density of 0.07 electrons per surface atom, but this is unlikely since band bending near the surface would cause a redistribution of the surface charge.

The integrated weight of the S_1 peak in the total density of states (Fig. 5) is still equivalent to one electron per surface atom. However, the charge density associated with this peak is not strongly concentrated on the surface layer, but extends over the first four layers at the surface.

The S_2 and S_3 surface states result from surface relaxation and correspond to back-bonding orbitals of the first two atomic layers. At the K point of the zone the charge associated with the S_2 structure is completely localized on the first two layers. The localization is, however, much smaller (about 10%) for most of the other points in the zone. The S_3 structure has a weight of 0.35 electrons per surface atom over an energy range of about 3 eV. The T_1 structure is strongly damped by relaxation and this may explain why it has not been observed experimentally. A comparison of Figs. 2–5 shows

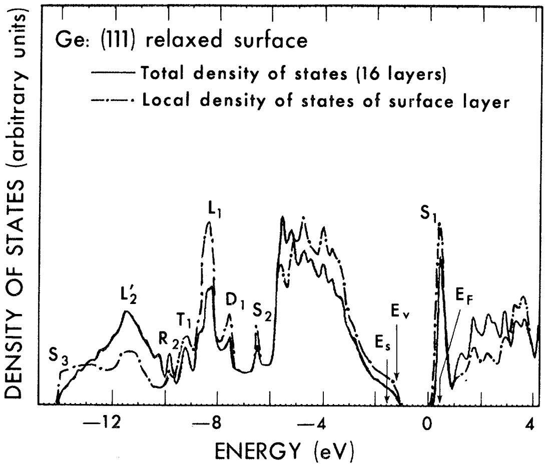

FIG. 5. Total density of states (solid line) of Ge for a system consisting of 16 layers and for a relaxed surface. The local density of states of surface atoms is also shown.

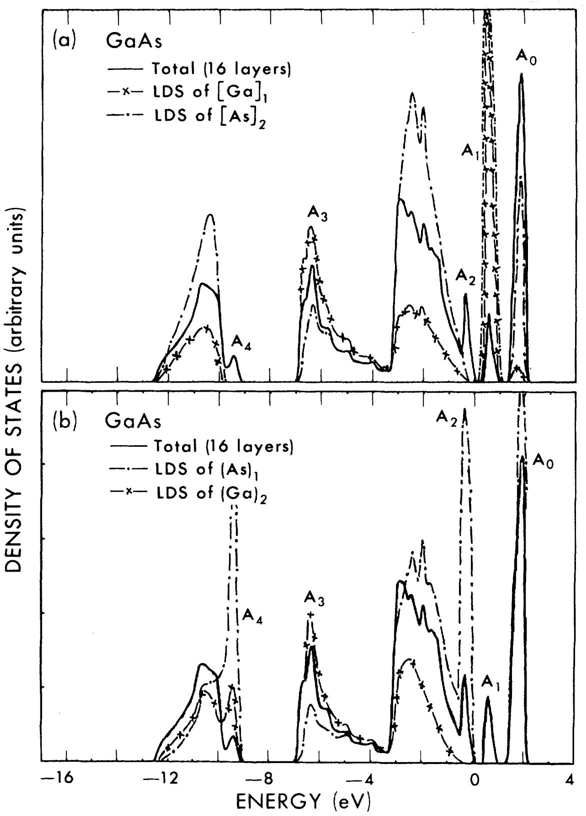

FIG. 6. Total density of states (solid line) of GaAs for a system of sixteen layers (a) and (b). The local densities of states (LDS) of Ga surface atoms denoted by $[\mathrm{Ga}]_1$ and the LDS of the As layer $[\mathrm{As}]_2$ next to $[\mathrm{Ga}]_1$ are also shown in (a). The corresponding LDS for the As surface is shown in (b).

that relaxation effects are very important in the description of surface states. Although we have treated surface relaxation only approximately here, the results give an indication of the type of changes that occur as a result of relaxation.

C. GaAs and ZnSe

The (111) surface is not a cleavage plane for zinc-blende crystals; however, it has recently become possible to prepare such surface by Ar^+ bombardment and annealing under ultrahigh-vacuum conditions,[10–12] and photoemission[10,11] and energy-loss[12] experiments have been done on GaAs and GaP samples. The (111) surfaces are polar, i.e., the layers alternate between Ga-type and As-type atoms.

In Figs. 6–10 we show the results of our calculations on a system consisting of 16 layers. The notation used in these figures is as follows. The various layers are numbered consecutively so that $[\mathrm{Ga}]_1$ refers to the gallium and $(\mathrm{As})_1$ to the arsenic surface layers, respectively. Layers near the Ga surface are denoted by brackets and those near the As surface by parentheses. Thus $[\mathrm{As}]_2$ refers to the arsenic layer just below the Ga surface layer and $(\mathrm{Ga})_2$ to the gallium layer next to the As surface layer. A similar procedure is used for identifying the Zn and Se layers in ZnSe.

Let us now examine the detailed structure in the densities of states. A comparison of Figs. 6 and 9 shows the structures in GaAs and ZnSe to be very similar. The only differences between the two are in the width of the surface peaks and the degree of charge localization in each peak. We will discuss these in detail below. For the moment we will give a general description of the surface states and concentrate on GaAs.

Figure 6(a) shows the LDS of the gallium surface layer ($[\mathrm{Ga}]_1$) and the LDS of the arsenic layer below it ($[\mathrm{As}]_2$), together with the total density of states for 16 layers. The LDS of the As surface layer, $(\mathrm{As})_1$, and the gallium layer next to it, $(\mathrm{Ga})_2$, are shown in Fig. 6(b). The structure A_0

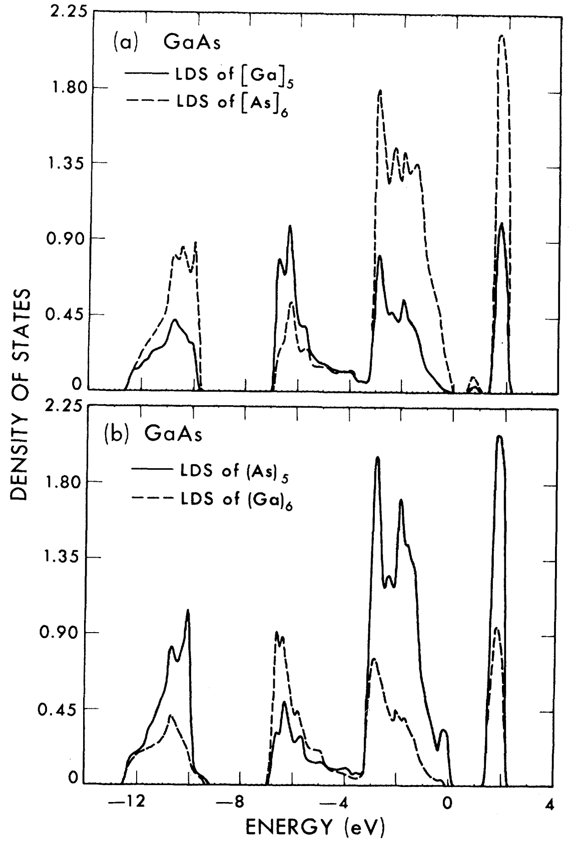

FIG. 7. LDS of Ga atoms $[\mathrm{Ga}]_5$ on a plane four layers below the $[\mathrm{Ga}]_1$ surface (solid line) and the LDS of $[\mathrm{As}]_6$ atoms five layers below the $[\mathrm{Ga}]_1$ surface (dashed line) are shown in (a). The corresponding features for atoms below the As surface are shown in (b).

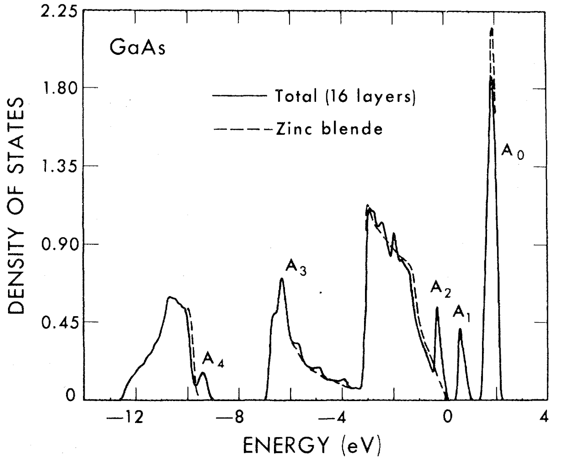

FIG. 8. Total density of states of GaAs for a system consisting of 16 layers (solid line) as compared to the bulk crystalline density of states calculated using the same interaction parameters. The dotted zinc-blende curve refers to the bulk.

corresponds to the first conduction band in the zinc-blende phase (see also Fig. 8). The peaks $A_1, \ldots, A_4$ are, however, associated with the various surface states. The peak A_1 corresponds to a mixture of dangling-bond Ga states together with back-bonding As states. The peak A_2, however, is almost totally an As dangling-bond state. It is interesting to note that nearly all the contribution to the A_1 (A_2) peak comes from atoms near the Ga (As) surface layer. There is, for example, practically no contribution to the A_2 (As dangling-bond state) from As atoms near the Ga surface layer; only As atoms near the As surface contribute to this peak.

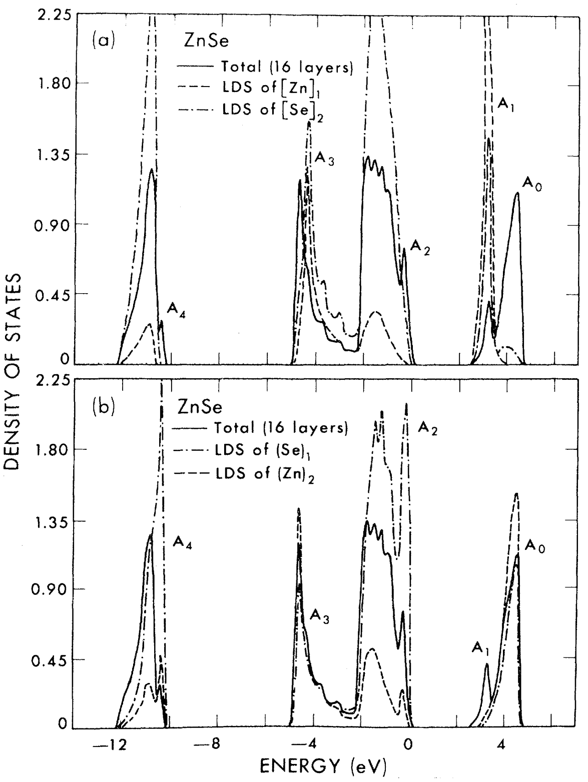

FIG. 9. LDS of $[\mathrm{Zn}]_1$, $(\mathrm{Se})_1$ surface atoms and the LDS of $[\mathrm{Se}]_2$ and $(\mathrm{Zn})_2$ atoms next to the surface layers. See also caption for Fig. 6.

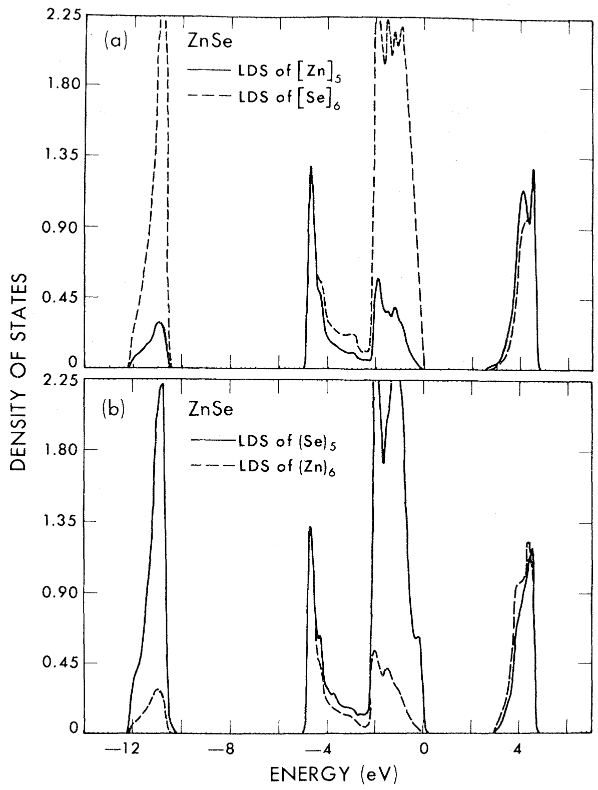

FIG. 10. See caption for Fig. 7.

The A_3 structure corresponds to Ga surface states which overlap with the bulk valence bands. These surface states are associated with Ga back-bonding orbitals. Gallium atoms on both the Ga-rich and As-rich sides contribute to the A_3 peak. The localization of the charge density at the surface layer is less for this state than for the A_1 and A_2 peaks. Our calculation also shows As surface states overlapping with bulk bands at -3 eV, near the region that corresponds to the $\Sigma_1^{\min}$ edge for the zinc-blende case. [The zero of energy in Figs. 6–10 has been chosen at the top of the bulk valence bands. This also happens to be (see Fig. 8) the energy for the top As (Se) surface states.] The A_4 structure corresponds to As back-bonding states and the major contribution to it comes from the As surface layer. There is no contribution to

A_4 arising from As or Ga atoms near the Ga-rich surface.

We will now examine the character and degree of localization of the various peaks in GaAs and ZnSe. The A_1 structure in GaAs (ZnSe) has an integrated weight of one electron per Ga (Zn) surface atom and the Fermi energy lies in the middle of this peak. The Ga (Zn) dangling-bond orbitals contribute 0.32 (0.55) electrons to the whole peak, while the As (Se) back-bonding states next to the surface layer contribute 0.47 (0.33) electrons. About 80% of charge density associated with A_1 is therefore seen to be localized within the first two surface layers, with a stronger localization in the case of the more ionic ZnSe.

The integrated weight of the A_2 structure is one electron per As (Se) surface atom. The As (Se) dangling-bond orbitals contribute 0.71 (0.82) electrons to this structure. The Ga (Zn) atoms next to the surface layer make no contribution to this peak, but other As (Se) layers near the surface make smaller contributions to A_2, as can be seen from Figs. 6–10.

In the A_3 structure surface states begin near the edge of the band and extend over an energy range of about 1 eV. The localization at the surface of the states associated with A_3 is on the average smaller than those for A_1 and A_2. The A_3 peak is very interesting in that Ga (Zn) and As (Se) atoms near both the Ga- (Zn) rich and As-(Se) rich surfaces contribute to it, as can be seen from Figs. 6 and 9. The major contribution in GaAs is from Ga back-bonding orbitals located at the Ga surface layer or on Ga atoms on the layer below the As surface. The contribution of As back-bonding orbitals on both the Ga and As sides of the surface is about half as large as that coming from the Ga orbitals. In ZnSe the Zn and Se atoms contribute almost equally to the A_3 structure.

The As (Se) back-bonding orbitals on both the As (Se) surface and on atoms next to the Ga (Zn) surface layer also give rise to surface states which are very similar to A_3. These states occur at -3 (-2) eV in GaAs (ZnSe) for wave vectors near K.

The A_4 states are very strongly localized on the As (Se) surface atoms. Figure 5 shows the A_4 structure to have a very small overlap with the bulk states. The integrated weight of A_4 is equivalent to 1 electron per As (Se) surface atom. The As (Se) back-bonding surface orbitals contribute about 0.36 (0.78) electrons and the Ga back-bonding orbitals next to the As surface atoms contribute 0.11 (0.10) electrons.

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