(110) surface states of GaAs: Sensitivity of electronic structure to surface structure

D. J. Chadi
Xerox Palo Alto Research Center, Palo Alto, California 94304
(Received 21 October 1977)

The (110) surface states of GaAs for three models of surface relaxation are examined by the tight-binding method. Although these relaxations, obtained from analyses of low-energy-electron-diffraction data, involve similar atomic displacements, they give rise to noticeable differences in the relative positions of some surface states when these states are identified by their orbital symmetries. All three relaxations are found to completely remove all surface states from the band gap and to give rise to new surface states. Our calculations indicate the presence of five to six filled and four empty surface states. Results for energies, local densities of state, and the orbital characters of these states are given and compared to experimental data.

I. INTRODUCTION

There has recently been considerable interest in the surface and interface electronic properties of III-V semiconductors.[1-4] In particular, there have been a number of experimental[1-20] and theoretical[3,4,11,21-29] studies of the (110) surface states of GaAs. In this paper we present the results of our calculations on the effects of surface structure on the (110) surface states of GaAs and compare our results to experimental data.

The ability of theoretical calculations to present an accurate description of surface electronic states is limited to some extent by the accuracy with which the surface atomic structure is known. Analyses of low-energy-electron-diffraction (LEED) data[30-36] for GaAs have shown the (110) surface to be ideal (1×1) but relaxed. Different surface relaxation models, which are all basically similar in nature, have been suggested for this surface. Each involves a raising of surface As atoms and a lowering of surface Ga atoms, bringing the latter closer to bulk atoms. We consider here three different relaxation models[32-34] for the (110) surface of GaAs. One of these (a 34.8° rotational-relaxation model)[32] has been previously used in a number of theoretical studies.[23,24,26-29] The other two models[33-34] are more recent and have been obtained from more detailed analyses of LEED data. As we show below, despite the similarities between the atomic displacements involved in these relaxations, there are interesting and detectable differences in their surface electronic structures particularly in regard to the relative positions of surface states with different orbital symmetries. By comparing the theoretical results to angle-resolved photoemission measurements in which polarized radiation is used, it is possible to distinguish between some of these surface relaxation models on the basis of their electronic structures.

The surface relaxation models used in our calculations are discussed briefly in Sec. II. The tight-binding (TB) parameters used, the criteria for selecting them, and the sensitivity of the results to the choice of parameters are discussed in Sec. III. The results of the calculations are presented in Sec. IV, where surface bands, local densities of state, orbital characters of surface states, their degree of surface localization, and the anion-cation contributions to the density of states are given. The main results, which are discussed in detail in Sec. V, are as follows:

(i) Surface relaxation removes both filled and empty states from the band gap of GaAs, in agreement with the absence[5-9] of Fermi-level pinning in GaAs. This holds for all surface relaxations considered in which As surface atoms are raised and Ga atoms are lowered.

(ii) Surface relaxation leads to new surface states. In the valence-band region there are five major filled surface states. The number and position of these states are in good agreement with those determined by photoemission measurements.[7-9,11,15] The ordering (as determined by orbital character) of the filled surface states near the valence-band maximum and empty states near the conduction-band minimum is different for the three relaxations considered. It is, therefore, possible to distinguish between the different models for surface relaxation by angle-resolved photoemission measurements using polarized radiation.

(iii) The filled and empty surface states near the band gap are not purely As or Ga derived but involve an appreciable mixing of anion-cation character. This is consistent with partial-yield photoemission measurements[20] for As-$3p$ core transitions into empty-surface-state transitions which are observed to have an intensity comparable to that measured[10] for Ga-$3d$ core-state transitions into the same final state.

 © 1978 The American Physical Society

II. ROTATIONAL-RELAXATION AND BOND-RELAXATION MODELS

In the last several years a considerable effort has gone into the determination of the surface atomic structure of semiconductors.[30-36] Low-energy-electron-diffraction data show the (110) surface of GaAs to be relaxed, with the Ga surface atoms closer to bulk atoms and As atoms further away from them than is the case for an ideal, unrelaxed surface. Using a kinematical single-scattering analysis of LEED data, Lubinsky *et al.*[32] have obtained limits on the atomic displacements involved in the relaxation. Subsequent calculations of the surface structure have shown displacements which fall within these limits. An exception is the surface relaxation model that has been suggested[11] to obtain agreement between theoretical surface electronic density of states and photoemission spectra. Recently further refinements on the surface atomic structure have been made[34-35] using a constant momentum transfer averaged analysis of elastic LEED data.

The surface unit cell and the irreducible part of the Brillouin zone for the (110) surface of GaAs are shown in Fig. 1.

In this paper we consider three different surface relaxation models. These are of two basic types: "rotational relaxation" (RR) and "bond relaxation" (BR). The RR models give a structure in which the Ga-As surface bonds are rotated through an angle ω ($27° \leq \omega \leq 34.8°$) relative to the truncated bulk solid. In the 34.8° RR model suggested by Lubinsky *et al.*,[32] the bond lengths at the surface are equal to those in the bulk. The 27° RR model suggested by Tong *et al.*[33] involves small changes in the bond lengths at the surface. In addition to these two RR models, we also consider a two-layer BR model obtained recently by Kahn *et al.*[34] In this model the As (Ga) surface atoms move $0.1d_0$ ($-0.25d_0$) normal to the surface, where d_0 is the bulk interplanar distance. The displacements of subsurface atoms are opposite in direction to that of surface atoms of the same species and are about 0.05 Å in magnitude. This model gives a better description of the LEED data than the 34.8° RR model.[31,34] There are appreciable bond-angle variations in these relaxations, e.g., -22% to 14% for the 34.8° RR and -14% to 14% for the BR models. A 19° RR model has also been suggested by Pandey *et al.*[11] on the basis of photoemission data.

III. CALCULATION

A. Choice of tight-binding parameters

The TB parameters for GaAs used in our surface calculations are the same as those we have used in a previous study.[37] These parameters were designed to give the best possible four-state-per-atom description of the valence and conduction bands of GaAs. A comparison of the densities of states obtained from the TB and empirical pseudopotential methods[38] is shown in Fig. 2. The valence-band photoemission spectrum[39] used as input in both calculations is also shown. It can be seen that the TB method gives a relatively good description of the valence and conduction-band densities of state. It is possible to improve the agreement between the TB and pseudopotential results appreciably for states near the conduction-band minimum by choosing a different set of TB parameters. However, when this is done, the overall agreement (for higher conduction bands) between the TB and pseudopotential results is considerably worsened, as the TB results give a gap

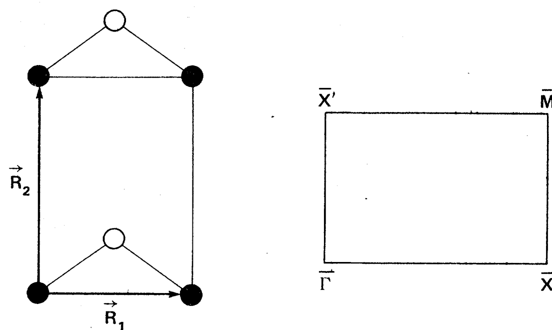

FIG. 1. Real-space unit cell and the Brillouin zone for the (110) surface of GaAs. In describing the p-derived orbital symmetries of surface states, the $\hat{x}$ direction is taken to be along $\vec{R}_1$, the $\hat{y}$ direction along $\vec{R}_2$, and the $\hat{z}$ direction along the normal to the (110) surface.

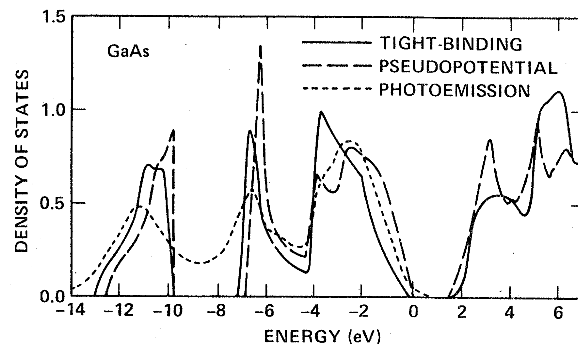

FIG. 2. TB density of states for the bulk valence and conduction bands of GaAs as compared to the pseudopotential results of Ref. 36 and x-ray photoemission spectra of Ref. 37.

of $\gtrsim 1$ eV in the density of states separating the lowest conduction band from the higher bands. Parameters nearly the same as the ones used in our present calculation were previously employed[40] in a calculation of the elastic coefficient $C_{11}-C_{12}$ of GaAs directly from the electronic spectrum. These parameters were found to give very satisfactory estimates of changes in electronic energies with atomic displacements and an accurate value for $C_{11}-C_{12}$. Since similar types of shear distortions occur for rotationally relaxed surfaces, the accuracy with which $C_{11}-C_{12}$ is calculated provides an additional criterion for the suitability of the TB parameters in studying bulk and surface electronic states. For different sets of parameters which accurately reproduce only the first conduction band (in addition to the valence bands that can be easily fitted), the results for $C_{11}-C_{12}$ were found to be much lower than the experimental values. Atomic displacements cause a mixing of the unperturbed valence and conduction states. It is, therefore, necessary to have a good overall description of both valence and conduction states and bandwidths before calculating changes in electronic energies that occur with atomic displacements.

B. Surface-state calculations

A 14-layer slab geometry, periodic in two dimensions, was found to be adequate in identifying surface states. The energies of the strongly localized surface states are insensitive to the number N of layers for $N \geq 6$. The interaction of weakly localized states on each end of the slab gives rise, however, to a splitting of the states arising from the two surface layers. This splitting can be made small by increasing N. For a 14-layer slab, the splitting is typically about 0.15 eV for states near the Brillouin-zone center and smaller for states near the extrema of the Brillouin zone.

The TB parameters at the surface were assumed to be the same as in the bulk except for a $1/d^2$ variation with nearest-neighbor distance d for a relaxation that involves bond-length changes at the surface. Our calculations indicate that the change in the energies of surface states near the band gap is caused primarily by the rehybridization of the wave functions at the surface and not by the variation of the potential at the surface. The energy changes are caused primarily by the rehybridization of wave functions resulting from surface relaxation. A $1/d^2$ variation in the potential accounts for about 20% of the change for these states; it also produces a weak split-off surface state near the bottom of the valence bands.

C. Parameter dependence of results

1. Energies

In the calculations discussed in more detail in Sec. IV, we have used the following set of parameters:

$$E_s^a=-8.21\,, \quad E_s^c=3.19\,, \tag{1}$$

$$E_p^a=1.282\,, \quad E_p^c=3.473\,, \tag{2}$$

$$V_{ss\sigma}=-1.69\,, \quad V_{s_a p_c \sigma}=2.057\,, \quad V_{s_c p_a \sigma}=2.373\,, \tag{3}$$

$$V_{pp\sigma}=3.508\,, \quad V_{pp\pi}=-0.963\,. \tag{4}$$

The zero of energy is at the top of the bulk valence bands; c and a refer to Ga and As atoms, respectively, and only interactions between orbitals on nearest-neighbor atoms have been included. For this set of parameters, we find that surface relaxation removes both filled and empty states from the band gap of GaAs. An independent[26] calculation for a semi-infinite slab of GaAs using the same parameters confirms this result. However, other TB calculations[25,26,28,29] in which different sets of parameters have been used show an overlap of the empty surface state with the band gap for a relaxed surface.

To test the parameter dependence of our results and to find the conditions under which the surface bands overlap the band gap, we have modified the TB parameters listed above. The valence bands of GaAs can be easily fitted with different sets of parameters; the effect of these changes on the conduction bands can, however, be quite substantial. By fitting various optical gaps, different sets of TB can be obtained. For the parameters of Eqs. (1)–(4), the E_0 and E_0' gaps at Γ were fitted. For small perturbations (of the order of 10%) in which the valence bands and the E_0 gap are kept unchanged, we also find that relaxation removes filled and empty states from the gap. The threshold for the first empty surface state varies by about 0.25 eV and the peak in the uppermost filled state by about 0.5 eV for such perturbations. For much larger variations in the parameters of Eqs. (1)–(4) the valence and only the first conduction bands can be well reproduced. The upper conduction bands come out too high in energy, and in the density of states they are separated by a gap of from the lowest conduction band in disagreement with pseudopotential results.[38] For these types of parameters, we find an overlap of the empty surface state with the band gap, even after surface relaxation, in disagreement with experimental results.

2. Orbital symmetries of surface states

The important question in this regard is whether the positions of surface states with different orbi-

tal symmetries are determined primarily by the surface atomic structure or by the choice of TB parameters. If the surface atomic geometry is the dominant factor in determining the relative positions of states of different symmetries, then it would be possible to gain additional information on the type of surface relaxation through a study of the surface electronic states. In particular, since angle-resolved photoemission measurements using polarized radiation give information on the energies as well as the orbital symmetries of surface states, a comparison of the experimental and theoretical results for various surface relaxation models could be very helpful in discriminating between these models. We have, therefore, studied the orbital symmetries of various surface states at the $\bar{\Gamma}, \bar{X}, \bar{X}'$, and $\bar{M}$ points of the Brillouin zone for different TB parameters. These parameters all gave equally good valence-band densities of state. For these parameters we find that the order in which surface states with different orbital symmetries occur are parameter independent but are sensitive to the surface atomic structure. For example, the surface states at $\bar{X}'$ up to 2 eV below the valence-band maximum are found to be ordered differently (independent of the TB parameters used) for the two types of surface relaxation, which we have referred to in Sec. III as "rotational relaxation" and "bond relaxation." At other points in the Brillouin zone, the differences (in electronic structure) between the different relaxations are found to be small. This indicates that by examining particular electronic states in the Brillouin zone through angle-resolved photoemission measurements, and by comparision to theoretical results it may prove possible to select among different surface relaxation models.

IV. RESULTS

A. Notation

We denote filled surface states by B_i and empty states by B_i' ($i=1,2,\ldots$), in accordance with previous notation.[21] Additional surface states arising from surface relaxation or those not previously identified are labeled in a similar manner by S_i and S_i'.

In identifying the orbital symmetry of surface states $\vec{R}_1$ is taken to be along $\hat{x}$ (Fig. 1), $\vec{R}_2$ along $\hat{y}$, and the normal to the surface to be along the $\hat{z}$ direction. The different surface states studied have different concentrations of charge at or near the surface. In the following the eigenfunction pertaining to each eigenvalue is normalized to one. The fraction of the total charge that is localized at the first two Ga and As layers at the surface and its decomposition into s, p_x, p_y, and p_z derived contributions is given for the BR model in Table I. The positions of the main surface structures with respect to the top of the bulk valence bands are given in Table II.

B. Energy bands and densities of state

The surface-state band structures for the ideal (unrelaxed), 34.8° RR and BR models are shown in Figs. 3–5. Weakly surface localized states and resonances are indicated by dashed lines. Some surface states extend only over a limited region of the Brillouin zone as indicated in Figs. 3–5. The filled surface bands for the 27° RR model are similar (except for the absence of the S_3 band) to those for the *BR model* and are not shown. The densities of states for the three models are shown in the upper portions of Figs. 6–8. The bulk den-

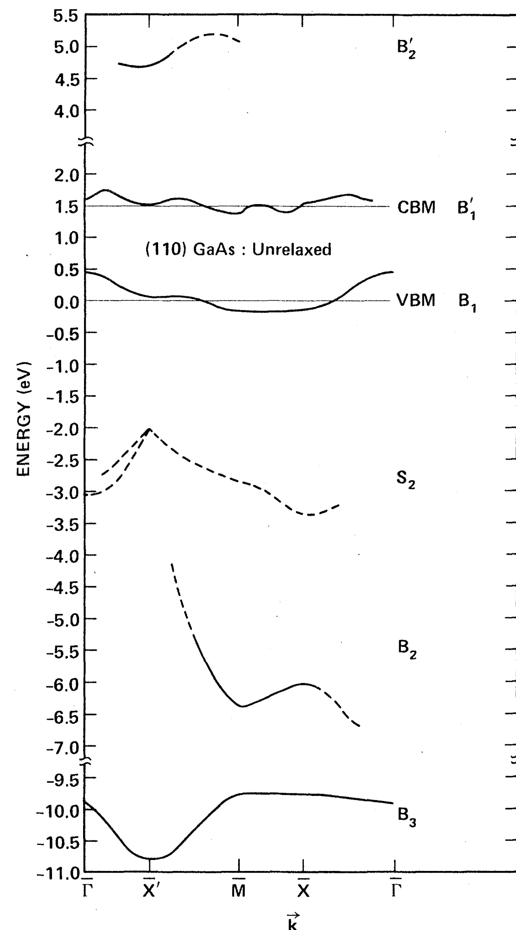

FIG. 3. Surface band structure for the ideal unrelaxed (110) surface of GaAs; VBM and CBM refer to the valence-band maximum and conduction-band minimum, respectively. Surface resonances and weakly localized surface states are indicated by dashed lines.

TABLE I. Surface states at a few points in the Brillouin zone for the bond-relaxation model of the (110) surface of GaAs. The percent f of the total charge (normalized to one) localized on the surface (top line) and subsurface (bottom line) atoms and its orbital character is given. Only strongly surface localized states are shown.

Surface band	$\vec{k}$	Energy (eV)	f	Ga s	Ga p_x	Ga p_y	Ga p_z	As s	As p_x	As p_y	As p_z
S_3	$\bar{X}'$	−11.97	8	6		1	1				
			60	7		1		52			
	$\bar{M}$	−11.14	11	8		1	2				
			67		2			64		1	
	$\bar{X}$	−11.22	10	7		1	2				
			61		2			58		1	
B_3	$\bar{X}'$	−10.67	77	14		1		61			1
			4	3			1				
	$\bar{M}$	− 9.59	79		5			73			1
			5	3			2				
	$\bar{X}$	− 9.62	73		5			67			1
			5	3			2				
B_2	$\bar{M}$	− 6.49	8		3			3		2	
			71	45		3			23		
	$\bar{M}$	− 6.14	64	49					15		
			32		8			6		13	5
	$\bar{X}$	− 5.56	35	26	1				8		
			25		4			9		11	1
S_2	$\bar{M}$	− 4.12	54	2		18	11		23		
			27		2			1		10	14
	$\bar{X}$	− 4.47	57	3		16	12		26		
			41		11					25	5
	$\bar{X}'$	− 1.77	29	4		4	3	2		15	1
			28			3	2			3	20
S_1	$\bar{M}$	− 1.62	41		3					24	14
			30			12	9		9		
	$\bar{X}$	− 2.21	38		9					28	1
			15	1			11		1		2
	$\bar{X}'$	− 1.19	93		24				64		
			5		4				1		
B_1	$\bar{X}'$	− 0.94	76	7		8		8		3	50
			20			7	5			7	1
	$\bar{M}$	− 0.92	78		18			5		20	35
			7		3		4		1		
	$\bar{X}$	− 0.90	80		12			5		8	55
			12	1		4	7				
B_1'	$\bar{X}'$	2.20	39	2		7	25	1			4
			40	24		1	2	5		8	
	$\bar{M}$	2.35	34		7			9		9	8
			9		3			4		1	
	$\bar{X}$	2.71	79	11		24	34		10		
			6	1		4	1				
B_2'	$\bar{\Gamma}$	3.57	41	2		13	21			3	2
			30	6		15	3	2		3	
	$\bar{X}'$	4.41	51	4		32	4	1		7	3
			28	4		12	3			6	
	$\bar{M}$	3.90	25			6	15	1			3
			19	5	8			3	3		
	$\bar{M}$	4.19	34		7		3	5		6	12
			23	5	10			3	3		2
	$\bar{X}$	4.77	53	15		5	8		25		
			20		2			1		1	16

TABLE II. Positions (in eV) of surface-derived peaks in the local density of states with respect to the bulk valence band maximum for the BR and RR models.

	BR	34.8° RR	27° RR
Filled states			
B_1	− 0.8	− 1.6	− 1.0
S_1	− 1.8	− 1.0	− 1.9
S_2	− 4.1	− 4.0	− 4.1
B_2	− 6.5	− 6.2	− 6.2
B_3	− 9.8	−10.0	−10.5
S_3	−11.3	...	...
Empty states			
B_1'	2.5	3.3	3.4
S_1'	3.4	2.4	2.5
B_2'	4.6	4.3	4.6

sity of states is also shown in each figure as an aid in finding the position of surface states with respect to bulk-derived structure. The decomposition of the surface density of states into p_x-, p_y-, and p_z-derived components is shown in the lower portions of Figs. 6–8. On the basis of this decomposition, it can be seen that the order of the B_1 (As dangling-bond) and S_1 (As back-bond) filled states and the B_1' (Ga dangling-bond) and S_1' (Ga back-bond) empty states are reversed in the BR and 34.8° RR models. Comparison of the BR and 27° RR models shows only a switch of the B_1' and S_1' states. It should be noted again that the surface relaxations involved in the three models considered are basically quite similar in character. It is, therefore, remarkable that the differences between these relaxations appear in the elec-

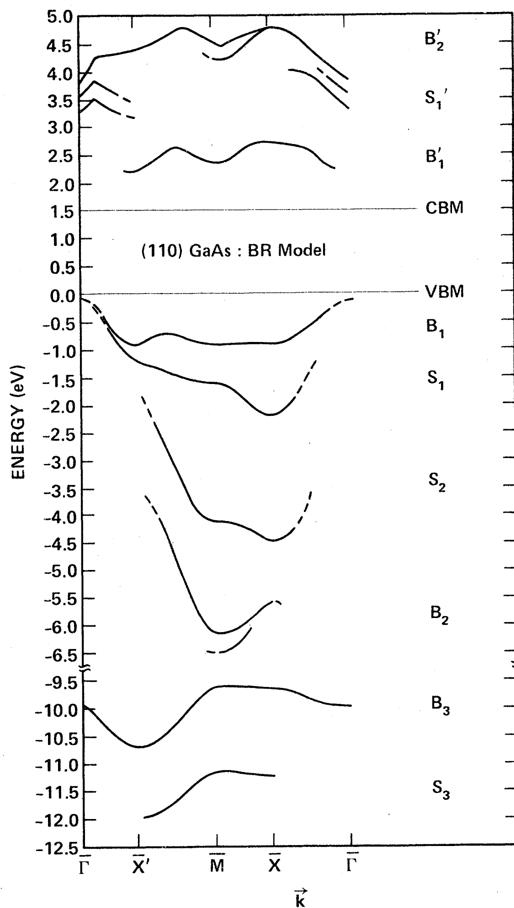

FIG. 4. (110) surface band structure of GaAs for the bond-relaxation model (Ref. 34).

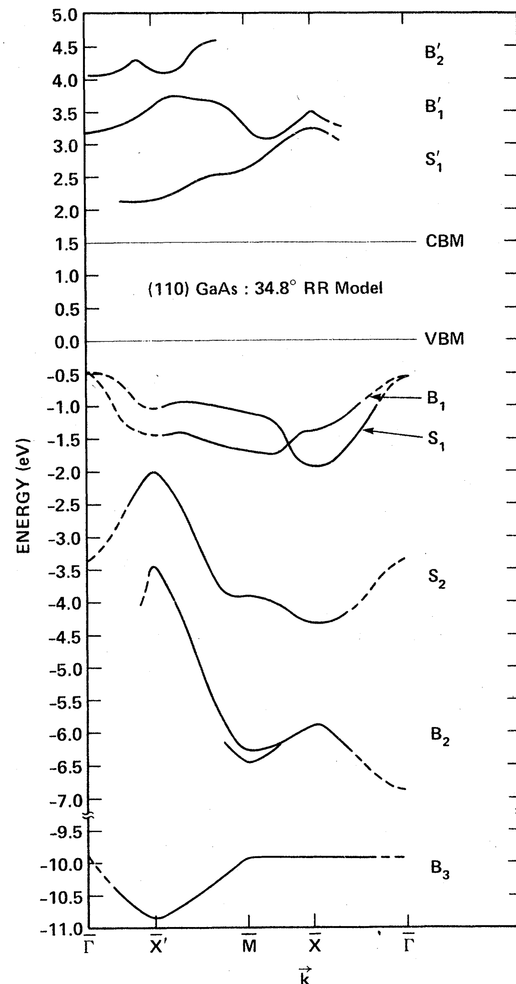

FIG. 5. (110) surface band structure of GaAs for the 34.8° rotational-relaxation model (Ref. 32).

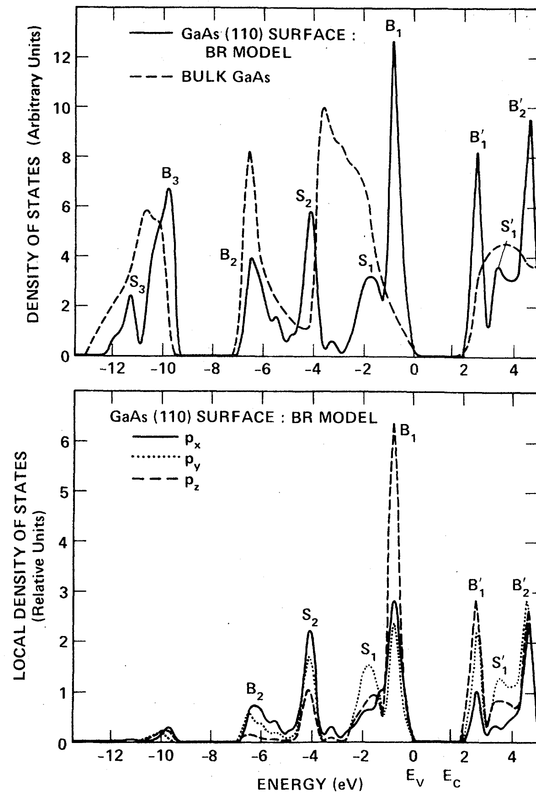

FIG. 6. Upper part of the figure gives the local density of surface states (solid line) for the bond-relaxation model of the (110) surface of GaAs. Electronic states localized on the first two layers of Ga and of As atoms at the surface are shown. The bulk density of states (dashed line) is also shown for comparison. The energies E_v and E_c denote the bulk valence-band maximum and conduction-band minimum, respectively. Only strongly localized surface states are shown. The densities of state have been Gaussian broadened. The bulk density of states is in arbitrary units. The surface density of states is shown in relative units to facilitate comparison with other figures. The p_x, p_y, and p_z derived orbital characters of the surface density of states for the BR model are shown in the lower part of the figure.

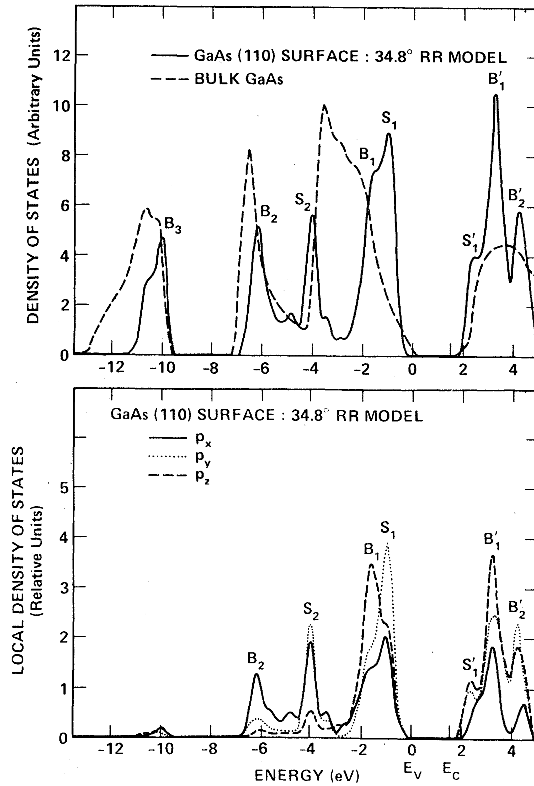

FIG. 7. Surface electronic density of states for the 34.8° rotational-relaxation model. See also caption for Fig. 6.

tronic spectra. The s-derived local density of states can be easily obtained from a comparison of the upper and lower parts of Figs. 6–8. The surface calculations were done for a 25-point grid in the irreducible zone and the results were smoothed out using 0.3-eV-wide Gaussians. In some cases this resulted in a small overlap of the surface states with the band gap; there is actually no such overlap. The bulk density of states was calculated at 308 points in the irreducible zone and has been similarly broadened.

The surface densities of states are plotted in relative units such that the strength of the surface states for different relaxations can be directly compared. To remove background noise (coming mainly from the contribution of bulk states at the surface) and to prevent weak resonances from appearing in the density of states, only those surface states for which at least 40% of the total charge is concentrated on the first two Ga and As layers (at each end of the slab) were used in the calculations. Calculations for which this figure is reduced to 30% or to 20% show the main surface peaks to remain at the same positions.

The differences in the orbital symmetries of surface states at the $\bar{X}'$ point of the Brillouin zone for the three different relaxation models are shown in Fig. 9 and discussed in Sec. V. The surface states have been broadened for better clarity.

When a very simple description of the upper filled and lowest empty surface states is needed, these states are usually referred to as being, respectively, As or Ga derived. In Fig. 10 we show the contributions of the first two layers each of Ga and As atoms to the surface density of states for the BR and RR models. Figure 10 shows that there is an appreciable mixing of Ga and As orbitals for all states except for B_3. In particular, it should be noted that the B_2 state is predominantly Ga derived. The mixing of Ga and As states in the

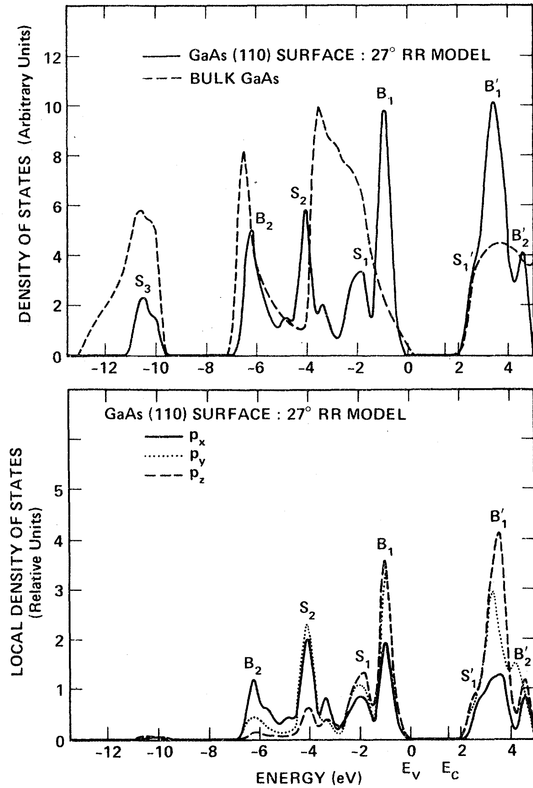

FIG. 8. Surface electronic density of states for the 27° rotational-relaxation model. See also caption for Fig. 6.

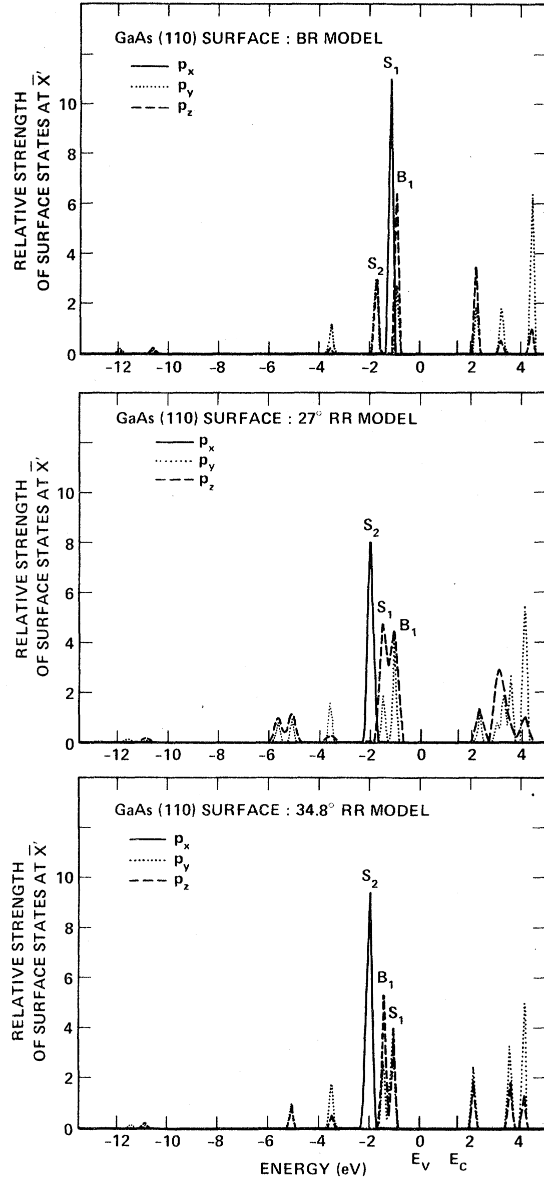

FIG. 9. Surface states at the $\overline{X}'$ point of the Brillouin zone and their p_x, p_y, and p_z derived orbital character for the BR, 34.8° RR, and 27° RR models. The states have been Gaussian broadened for clarity.

empty surface states is also appreciably larger for RR models than for the BR model.

Recent partial-yield photoemission measurements[20] on As-$3p$ core transitions to empty surface states show that these transitions have an intensity comparable to that found previously[10] for Ga-$3d$ core excitations into the same final states. This is also an indication of the mixing between Ga- and As-derived states that occurs in these states.

The degree of surface localization of the surface states is also of experimental interest. In Fig. 11 we show the local density of states for (Ga+As) surface and (Ga+As) subsurface atoms for the BR model. It can be seen that the B_2 and S_3 states are more localized on the subsurface layer than on the surface layer. There is no S_3-type state in the RR models, but the surface localization for the B_2 state is the same as in the BR model.

V. DISCUSSION OF RESULTS AND COMPARISON TO EXPERIMENTAL DATA

A. Surface states in the band gap

Our calculations show that there are no filled or empty surface states in the band gap of GaAs when the surface is relaxed. This is consistent with recent experimental data[5-9] that indicate an absence of intrinsic surface states within the forbidden band of GaAs. Intragap empty and filled states, when present, lead to Fermi-level pinning near the surface-state band edge for n- or p-doped samples, respectively. A number of measurements show no such pinning for *defect-free and clean* (110) surfaces of GaAs, GaSb, and InAs. The experimental results are very sensitive[7,9,13] to surface defects, impurities and to cleavage.[13]

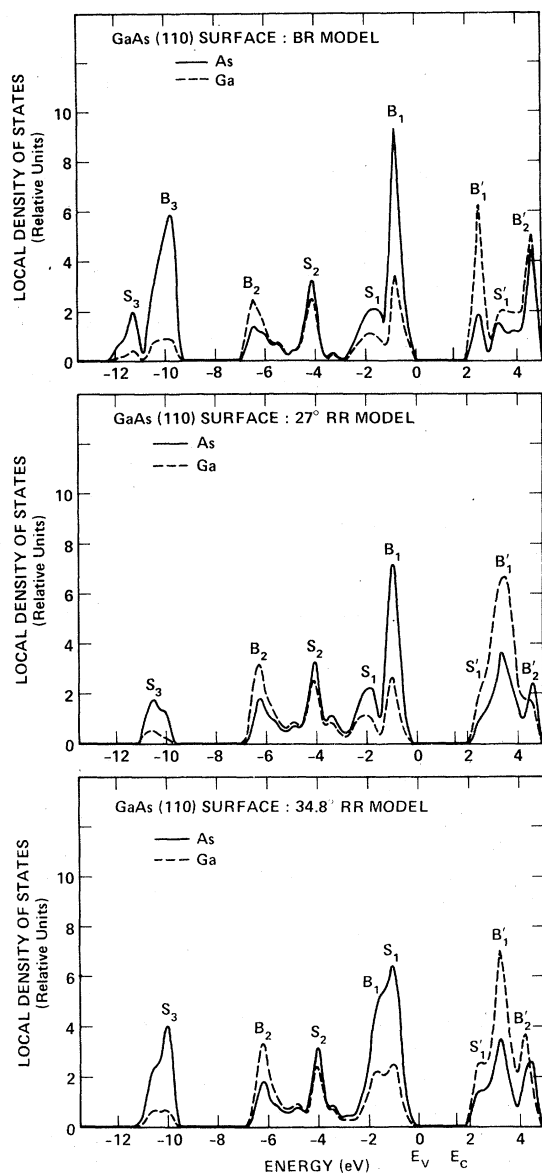

FIG. 10. Ga- and As-derived local density of surface states for the (110) surface of GaAs. Two layers each of Ga and As atoms were included in the calculation.

Because of this, some earlier experiments had indicated the presence of intrinsic states in the gap. The cleavage dependence of the experimental results has clearly been demonstrated by photoemission-total-yield spectroscopy measurements.[13] These measurements also seem to indicate the presence of a small number ($\ll 10^{14}/\text{cm}^2$) of empty states in the band gap of GaAs. It has been suggested[41(a)] that band-bending effects near the surface could give rise to the latter result.

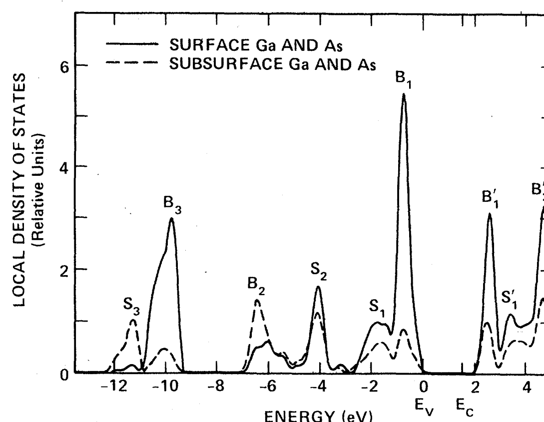

FIG. 11. Local density of states of surface and subsurface layers for the BR model.

B. Filled surface states

Excluding the weak S_3 state that occurs near the bottom of the valence bands for only the BR model, our calculations indicate five major surface-related structures in the density of states lying below the valence-band maximum at E_v, as shown in Figs. 6–8. Photoemission measurements[7,11,14-16] show the upper filled surface states to be at least 0.5 eV below E_v. Angle-resolved[14-16] and angle-integrated[11] photoemission measurements strongly indicate the presence of two surface-related structures near E_v, in agreement with theoretical calculations. Our calculations show both the B_1 and S_1 states to be primarily As surface derived. The difference between the two states is in their electronic charge density distributions. The B_1 state has a dangling-bond character with a charge distribution that projects out into the vacuum region, whereas the S_1 state has a back-bond character with the charge distribution that is directed towards the bulk layers.

Evidence for an S_2 state lying about 4 eV below the valence-band maximum at E_v has been previously[15] seen in angle-resolved measurements. More recent measurements have demonstrated with greater certainty[16] the surface sensitivity of this state. In the unrelaxed surface geometry, this state is only very weakly surface localized; surface relaxation changes S_2 into a very strongly localized surface state, particularly at $\bar{M}, \bar{X}$, and along the $\bar{M} \rightarrow \bar{X}$ direction of the Brillouin zone. The S_2 state has not been explicitly identified in previously published work, although self-consistent pseudopotential calculations[23,24] do, in fact, also show extra surface structure (absent in the bulk density of states) for energies between 3.5 and 4 eV below E_v for a 34.8° RR model. Our calculations show (Figs. 6–8) a density-of-states

maximum for the S_2 state at 4.1 eV below E_v, in good agreement with experiment.[15]

The B_2 state is seen in photoemission measurements.[14,15] The calculations indicate that the bonding for B_2 is $sp\sigma$ type with Ga s states bonding to As p states and with the predominant orbital character being Ga derived. Near the $\overline{M}$ point of the BZ, there are two B_2-type states, both of which are strongly localized. The higher-energy state corresponds to surface Ga atoms bonded to nearest-neighbor As atoms, and the lower state corresponds to subsurface Ga atoms bonded to their nearest neighbors. The small peak in the density of states on the higher-energy side of the B_2 peak arises from states at the $\overline{X}$ point of the BZ. For the BR model the peak in the density of states of B_2 occurs 6.5 eV below E_v, which is also in good agreement with experiment.[14,15]

The B_3 state is seen as a weak peak at 11 eV below E_v in ultraviolet-photoemission measurements.[9,11] The most surface localized B_3-type states occur at the $\overline{X}'$ point of the BZ. In the unrelaxed and RR surface geometries, the B_3 states near the zone center are more concentrated on the subsurface As atoms than on the surface As atoms. In the BR model the B_3 state is predominantly surface As derived, while the S_3 state is subsurface derived. The splitting between the S_3 and B_3 states results from the variation with bond length of the interaction parameters at the surface. The S_3 state may provide another way of distinguishing between RR and BR models on the basis of electronic properties. Surface states with wave vectors along the $\overline{M}$ to $\overline{X}$ direction of the zone give rise to the main density-of-states peak of B_3 at 9.8 to 10 eV (Figs. 6–8) below E_v, while states near $\overline{X}$ give rise to the shoulder at around -10.5 eV.

C. Surface states at $\overline{X}'$ and surface structure

We have labeled the surface state near E_v with the largest amount of p_z character (with $\hat{z}$ normal to the surface) as the B_1 state (see Figs. 6–8). In this way the S_1 state lies below the B_1 state for the BR and 27° RR models but above it for the 34.8° RR model. The density of states for the B_1 and S_1 states in the BR and 27° RR models are very similar. As mentioned above, in previous photoemission work,[14,15] a surface state with a doublet structure near the valence-band maximum at E_v has been observed.

At the $\overline{X}'$ point of the Brillouin zone, the calculations actually show three filled surface states within about 2 eV of the valence-band maximum (see Fig. 9). This occurs as a result of the dispersion of the S_2 band (Figs. 4 and 5) which at the $\overline{X}'$ point brings it close in energy to the B_1 and S_1 surface states. Figure 9 shows the combined cation plus anion p_x, p_y, and p_z derived orbital symmetries of the three surface states at $\overline{X}'$ and near E_v. As can be seen, the ordering of p_x and (p_y+p_z) character states is different for the BR and the RR models. This suggest that angle resolved measurements with polarized radiation can be used to distinguish between the BR and RR models.

In the dipole approximation the matrix element for the transition between an initial surface state φ and a final state ψ is proportional to the square of M given by

$$M=\langle\psi|\vec{A}\cdot\vec{\nabla}|\varphi\rangle . \quad (5)$$

Since the upper filled surface states are of predominantly p character we need to consider only final states ψ with s or d symmetry.

When ψ is a state of s symmetry, the only nonzero matrix element occurs when φ is a p function oriented in the direction of $\vec{A}$. For $\vec{A}$ along the $\hat{x}$ direction, one surface state, and for $\vec{A}$ along the $\hat{y}$ direction, two surface states would therefore be expected for states at $\overline{X}'$ and near E_v. If only emission normal to the surface is considered then transitions into final states of d_{xy}, d_{xz}, and d_{yz} symmetry should not be observed since these orbitals have vanishing charge densities in the z direction. Transitions into d_{z^2} orbitals would be observable but would be indistinguishable from transitions into s states since they involve identical selection rules. For normal emission, therefore, the relative positions of p_x and p_y symmetry states at $\overline{X}'$ can be unambiguously determined. These results are consistent with the more general group theoretical discussion given by Hermanson.[41(b)] For emission away from the surface normal transitions from p_x to d_{xy} and p_y to d_{yz} states would occur for $\vec{A}=A\hat{y}$ and similarly transitions from p_y to d_{xy} and p_z to d_{xz} would occur for $\vec{A}=A\hat{x}$. These transitions could be superimposed on those from p to s states. When the emission is confined to a mirror symmetry plane the symmetry of the initial state can be shown[41(b)] to be the same as that of the dipole operator causing the transition. Angle-resolved photoemission measurements using polarized radiation can therefore be used to determine the symmetry of surface states along the $\overline{\Gamma}-\overline{X}'$ direction. Such measurements have recently been done by Williams, Smith, and Lapeyre.[16] For initial states near the valence-band maximum having wave vectors along the $\overline{\Gamma}$ to $\overline{X}'$ direction they find (for states $\frac{2}{3}$ of the way from $\overline{\Gamma}$ to $\overline{X}'$) two surface states with (p_y+p_z) symmetry and one surface state with p_x character. The ordering of these states is observed to be the same as that

shown in Fig. 9 for the BR model at $\bar{X}'$. However, because of surface band dispersion the experimental results are also in agreement with the 27° RR model when states away from $\bar{X}'$ are examined.[28]

D. Empty surface states

We find that surface relaxation completely removes the B_1' state from the band gap of GaAs and causes a weakening of the surface localization of B_1'. Relaxation also gives rise to a new surface state labeled S_1' in Figs. 6–8. This state occurs below the B_1' state in the RR models but above it in the BR model. Because of the overlap of the B_1' and S_1' states in the RR models, the effective width of the "first" empty surface state is nearly three times larger than its value for an unrelaxed surface. The large increase in the width of this state with relaxation is in good agreement with self-consistent pseudopotential[23,24] calculations for a 34.8° RR model. These calculations show that the B_1' state is moved to higher energy with relaxation; however, a tail of empty states which we would identify as the S_1' states overlaps the band gap. Pseudopotential charge-density calculations[22,23] for the (110) surface of GaAs show the states that we have identified as B_1' and S_1' to have distinctly different charge-density distributions.[42] The B_1' state (calculated for unrelaxed surfaces, but same result also holds for relaxed surface) has a localized Ga dangling-bond-type charge-density distribution,[22] whereas the new S_1' state that results from surface relaxation has a back-bond type of charge distribution.[23] In the RR models the S_1' (back-bond) state is lower in energy than the B_1' (dangling-bond) state, but in BR models the reverse situation prevails. Because of the similarity and correspondence between the surface states obtained by the TB and pseudopotential methods, we would predict on the basis of our results that for a BR model a self-consistent pseudopotential calculation will show no overlap of the empty surface states with the band gap. This is because the S_1' states in the BR model lie much above the bulk conduction-band minimum.

Partial-yield photoemission data for Ga-3d core states into the B_1' state show[10] this state to be 1 eV above the valence-band maximum. Measurements showing an absence of empty states in the gap indicate that these transitions involve large (≥0.5 eV) excitonic binding energies. If the threshold of around 2 eV for the empty surface states obtained in our calculations is assumed to be correct, we would obtain an excitonic binding energy for these transitions of 1 eV. Experimentally, the corresponding *bulk* excitonic binding energy has been estimated to be 0.75,[43] 0.4–0.6,[10] and[44] 0.3 eV. Sole and Tosatti[45] have shown that surface excitonic binding energies of 0.5 eV or larger can be obtained for reasonable values of the parameters in their theory.

For the BR model the calculations indicate the B_1' state to be most surface localized at the $\bar{X}$ point of the BZ. At this point nearly 70% of the character of this state is surface Ga derived, while only 16% is As surface and subsurface derived. The Ga-derived character is about 83% p-like and 17% s-like. At $\bar{M}$ the B_1' state has a relatively weak surface localization, with only 43% of the "charge density" of this state being confined to the Ga and As surface and subsurface layers. The threshold for the B_1' state occurs near the $\bar{X}'$ point. At this point the wave function is also strongly surface localized.

In addition to the B_1', S_1', and B_2' empty surface states shown in Figs. 6–8, our calculations indicate a very strongly surface localized state (particularly at $\bar{X}'$) of antibonding p character with a peak at about 5.8 eV above E_v.

E. Transition energies

Electron-loss spectroscopy (ELS) is very useful in providing information on the transition energies between filled and empty surface states. For the (110) surface of GaAs, the ELS data show[17,46] surface-related structure at 3.1, 8.5, and 12.3 eV and weaker structure at 9.1, 14.6, and 18.1 eV. The ELS also shows bulk-related structure at 3.7 and 6.0 eV and a surface plasmon mode at 10.4 eV. The 3.1, 8.5, and 12.3 eV loss peaks have been assumed[46] to represent transitions from the B_1, B_2, and B_3 states into the B_1' empty state. For the BR model we find corresponding peak-to-peak energy differences of 3.3, 8.9, and 12.3 eV, in fairly good agreement with the ELS data. The 12.3-eV structure in the ELS could also arise from B_2 to S_2' transitions. The ELS data do not seem to show any structure for transitions from the S_1 band to empty surface states. The weaker structures in ELS probably arise[46] from transitions to empty surface states, such as to B_2'. ELS also shows[46] a structure at 1.9 eV whose interpretation is not clear. If this structure is genuine, it would require the B_1 and B_1' states or a portion of these states to be closer to the valence-band maximum and the conduction-band minimum, respectively. There is no indication at present from angle-resolved photoemission measurements for the presence of such states.

VI. CONCLUSIONS

We have studied the effects of three different surface relaxation models on the (110) surface

states of GaAs. All three surface relaxations were found to remove filled and empty surface states from the band gap of GaAs, in agreement with experimental results showing an absence of Fermi-level pinning within the band gap. The rotational-relaxation models push the empty Ga dangling-bond B_1' state into higher energy than is the case for the BR model. However, unlike the BR model, they give rise to a new Ga back-bonding state (S_1') which lies below the B_1' state. The ordering of As-derived dangling-bond and back-bond states near the valence-band maximum was also found to be dependent on surface structure. The calculated positions of surface states are in relatively good agreement with photoemission[7-9,11,14-16] and ELS[17,46] data. From the calculated position of the B_1' empty surface state and partial-yield photoemission data[10] on Ga-3d core state to B_1' transitions, we estimate a surface excitonic binding energy of about 1 eV. We find the filled and empty surface states to contain an appreciable mixing of Ga and As character, as shown in the decomposition of the surface local density of states into Ga- and As-derived components. This result is consistent with the observation[20] that the intensity for As-3p core transitions into the empty surface state is comparable to that for Ga-3d core transitions.[10] Finally, the results found for GaAs on the number and symmetry of the various surface states should be valid for most other III-V compounds. Angle-resolved measurements with polarized radiation along other directions of the Brillouin zone would provide more stringent tests of the accuracy of the theoretical results for the surface structure as well as for the electronic structure of the (110) surface of zinc-blende semiconductors.

ACKNOWLEDGMENTS

I would like to thank Professor G. J. Lapeyre and Dr. G. P. Williams for useful discussions.

---

[1]See, for example, CRC Crit. Rev. Solid State Sci. 5, Nos. 2 and 3 (1975); and Refs. 2–4.
[2]J. Vac. Sci. Technol. 13, No. 1 (1976).
[3]J. Vac. Sci. Technol. 13, No. 4 (1976).
[4]J. Vac. Sci. Technol. 14, No. 4 (1977).
[5]J. van Laar and J. J. Scheer, Surf. Sci. 8, 342 (1967); A. Huijser and J. van Laar, *ibid.* 52, 202 (1975).
[6]J. van Laar and A. Huijser, Ref. 3, p. 769; J. van Laar, A. Huijser, and T. van Rooy, Ref. 4, p. 894.
[7]W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta, and P. W. Chye, Ref. 3, p. 780; W. E. Spicer *et al.*, Ref. 1, p. 233; P. E. Gregory and W. E. Spicer, Phys. Rev. B 13, 725 (1976).
[8]W. E. Spicer, P. Pianetta, I. Lindau, and P. W. Chye, Ref. 4, p. 885.
[9]W. Gudat and D. E. Eastman, Ref. 3, p. 831.
[10]D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 33, 1601 (1974); 34, 1624 (1975).
[11]K. C. Pandey, J. L. Freeouf, and D. E. Eastman, Ref. 4, p. 904.
[12]G. J. Lapeyre and J. Anderson, Phys. Rev. Lett. 35, 117 (1975).
[13]G. M. Guichar, C. A. Sebenne, and G. A. Garry, Phys. Rev. Lett. 37, 1158 (1976).
[14]J. A. Knapp and G. J. Lapeyre, Ref. 3, p. 757.
[15]J. A. Knapp, Ph.D. thesis Montana State University, 1976) (unpublished).
[16]G. P. Williams, R. J. Smith, and G. J. Lapeyre, J. Vac. Sci. Technol. (to be published).
[17]R. Ludeke and A. Koma, Ref. 2, p. 241.
[18]H. Froitzheim and H. Ibach, Surf. Sci. 47, 713 (1975).
[19]J. E. Rowe, S. B. Christman, and G. Margaritondo, Phys. Rev. Lett. 35, 1471 (1975).
[20]R. S. Bauer, D. J. Chadi, R. Z. Bachrach, and J. C. McMenamin, Bull. Am. Phys. Soc. 22, 363 (1977); *Proceedings of the Seventh International Vacuum Congress and Proceedings of the Third International Conference on Solid Surfaces* (IAEA, Vienna, 1977), p. A2699; R. S. Bauer, Ref. 4, p. 899.
[21]J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B 10, 5075 (1974).
[22]J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 13, 826 (1976).
[23]J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B 14, 4724 (1976).
[24]S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, Ref. 3, p. 790.
[25]P. E. Gregory, W. E. Spicer, S. Ciraci, and W. Harrison, Appl. Phys. Lett. 25, 511 (1974); C. Calandra and G. Santoro, J. Phys. C 8, L86 (1975); and Ref. 3, p. 773.
[26]E. J. Mele and J. D. Joannopoulos, Surf. Sci. 66, 38 (1977); and Phys. Rev. B 17, 1816 (1978).
[27]D. J. Chadi and R. S. Bauer, Abstract M2.5 presented at the Thirty Seventh Annual Conference on Physical Electronics, Stanford, California, June 20–22, 1977 (unpublished).
[28]D. J. Chadi, J. Vac. Sci. Technol. (to be published).
[29]C. Calandra, F. Manghi, and C. M. Bertoni, J. Phys. C 10, 1911 (1977).
[30]A. U. McRae and G. W. Gobeli, *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic New York, 1966), Vol. 2, pp. 166–212.
[31]For a recent review of semiconductor surface structures as obtained via analyses of elastic low-energy electron diffraction, see C. B. Duke, Critical Review of Solid State Sciences, Proceedings of the Third International Summer Institute in Surface Science, Milwaukee, Wisc., August 1977 (unpublished).
[32]A. R. Lubinsky, C. B. Duke, B. W. Lee, and P. Mark, Phys. Rev. Lett. 36, 1058 (1976).
[33]S. Y. Tong, A. R. Lubinsky, B. J. Mrstik, and M. A. Van Hove, Phys. Rev. B (to be published).
[34]A. Kahn, G. Cisneros, M. Bonn, P. Mark, and C. B.

Duke, Surf. Sci. 71, 387 (1978).
[35]P. Mark *et al.*, Ref. 4, p. 910.
[36]C. B. Duke, Ref. 4, p. 870.
[37]D. J. Chadi, Phys. Rev. B 16, 790 (1977). Spin-orbit interactions are ignored in our present calculations. The atomic p energies have, therefore, been shifted upward by $\frac{1}{3}\Delta_0$, (where $\Delta_0 \simeq 0.35$ is the spin-orbit splitting at Γ) to keep the band gap equal to 1.51 eV.
[38]J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 14, 556 (1976).
[39]L. Ley, R. A. Pollak, F. R. McFeeley, S. P. Kowalcyzk, and D. A. Shirley, Phys. Rev. B 9, 600 (1974).
[40]R. M. Martin and D. J. Chadi, *Proceedings of the Thirteenth International Conference on the Physics of Semiconductors*, edited by F. G. Fumi, (Rome, 1976), p. 187; D. J. Chadi and R. M. Martin, Solid State Commun. 19, 643 (1976).
[41](a) A. Huijser and R. S. Bauer (private communication); (b) J. Hermanson, Solid State Commun. 22, 9 (1977).
[42]See Ref. 22, Fig. 5(a) and Ref. 23, Fig. 3 for a comparison of the pseudocharge densities of the cation-derived empty surface state for unrelaxed and 34.8° RR surfaces.
[43]P. Thiry, Y. Petroff, R. Pinchaux, J. R. Chelikowsky, and M. L. Cohen, Solid State Commun. 20, 1107 (1976).
[44]D. E. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. B. 12, 2527 (1977).
[45]R. D. Sole and E. Tosatti, Solid State Commun. 22, 307 (1977).
[46]J. van Laar, A. Huijser, and T. L. van Rooy, Ref. 4, p. 894.