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Self-consistent pseudopotential calculation for the relaxed (110) surface of GaAs

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The electronic structure of the (110) surface of GaAs is analyzed using a surface-relaxation model as determined by recent low-energy-electron diffraction studies. A self-consistent pseudopotential calculation based on this model yields *no* intrinsic surface states within the fundamental band gap: a result not achieved in previous pseudopotential calculations. The calculations appear to be in good accord with recent photoemission measurements and we present an analysis of the surface-state energy spectra. In addition, our studies suggest that pseudopotential calculations coupled with angle-resolved photoemission measurements can be a sensitive probe of surface structural properties.

I. INTRODUCTION

The compound semiconductor surface most studied, both theoretically and experimentally, is the (110) surface of GaAs. This is a surprising fact since GaAs is an extraordinarily important material for technological applications. In fact, it has been so widely studied that, with the possible exception of Si and Ge, its properties are more extensively understood than any other semiconductor. While this statement is rigorously correct for the bulk properties of GaAs, there still remain fundamental questions to be answered with respect to the *surface* properties of GaAs. In particular, studies on the cleavage plane of GaAs, the (110) surface, have been quite controversial. While the *recent* experimental work on the (110) surface of GaAs may be characterized as thorough and consistent,[1-19] the theoretical effort may not be so characterized.[7,20-27] Indeed, the theoretical efforts have not been in accord with one another, nor have they been completely consistent with certain well-established experimental measurements.

The most widely publicized conflict between experiment and theory has been the question of whether intrinsic surface states exist within the fundamental band gap of GaAs. Initial experimental data[6,23] convinced many workers that intrinsic surface states existed within the band gap; the data seemed to unequivocally place intrinsic surface states away from the bulk band edges near the center of the fundamental gap. Fermi-level pinning studies[6] and partial yield spectroscopy seemed quite consistent on this point.[23] However, now it is almost universally accepted that the interpretations of the Fermi-level studies and partial yield work were *incorrect*. Today we know that the early Fermi-level studies were in error because of the presence of defect states which pinned the Fermi level near midgap.[1,2] When good cleaves are achieved, the (110) surface exhibits *no* pinning of the Fermi level within the band gap.[1-5] With respect to the partial yield measurements, another problem was experienced. These measurements did reveal intrinsic surface states, but the energy placement of these states within the band gap was erroneous. The currently held explanation of this observation is the neglect of rather strong excitonic interactions between an electron in the band-gap surface state and a hole in the initial core state.[28,29]

At first, theoretical efforts, both tight-binding calculations and pseudopotential calculations, appeared to be in accord and to place intrinsic surface states within the band gap.[20,21,23,24] These early electronic structure calculations employed an *ideal* surface geometry which is now known to be incorrect. Thus it should not be surprising, especially in retrospect, that these calculations are in strong disagreement with the currently accepted picture. Unfortunately, when more realistic surface geometries were used in the calculations, the results were not made more consistent. For example, parametrized tight-binding calculations using the *same* geometry have yielded intrinsic states within the fundamental gap or outside the fundamental gap depending on the parameters used.[7,25-27] This strange situation arises from the fact that parametrized tight-binding schemes do not reproduce the bulk conduction bands of GaAs very well, and different workers may use different interaction parameters to describe the bands. Since it has been demonstrated that the surface states in question are conduction-band derived, the energy placement of these states depends crucially on the interaction parameters used.[25]

Self-consistent pseudopotential calculations,[21,22] which do not suffer from the aforementioned problem, have to date not yielded a fundamental gap free of intrinsic surface states. This is a rather distressing situation since it is generally accepted that pseudopotential calculations are the most reliable means for describing semiconductor surfaces. Moreover, the pseudopotential calculations have disagreed with tight-binding calculations for the *same* geometry with respect to the placement of gap-related surface states. This situation raises fundamental questions with respect to the merits of tight-binding versus pseudopotential methods; it even raises a general question as to the accuracy of electronic structure calculations for surface properties.

The (110) surface of GaAs is an almost ideal surface for theoretical investigations into such questions. Besides the abundant amount of experimental data on this surface, the surface possesses the very desirable feature of *not* reconstructing. Owing to its primitive surface symmetry configuration, the (110) surface of GaAs has been the subject of several low-energy-electron diffraction (LEED) studies.[16-18] This is a fortunate situation; the problem of determining the surface atom coordinates relative to the bulk atom coordinates remains one of the most fundamental problems for performing electron structure calculations. While we will rely on these studies to provide a description of the surface structure, we note that it may be possible to extract structural information directly by comparing our electronic structure calculations to experiment, e.g., angle-resolved photoemission measurements.

II. METHODS OF CALCULATION

Our methods of calculating surface properties with self-consistent pseudopotentials have been extensively discussed in the literature.[21,22,30] We review only the basic ideas here. The key step in our procedure is to consider an artificially periodic system of GaAs slabs. Each slab has a (110) surface exposed on both sides and is isolated from its neighboring slabs by a large region of vacuum. In our calculation we examine a nine-layer slab of GaAs surrounded by six layers of vacuum from neighboring slabs. By introducing the artifact of periodicity perpendicular to the surface plane, we may then employ bulk band-structure techniques to solve for the surface electronic properties.

TABLE I. Ionic and empirical pseudopotential parameters for Ga and As. The form of the potentials is given in Eqs. (1) and (3). The potentials are normalized to an atomic volume of 152 a.u. and the unit of potential energy is Ry if q is entered in a.u.

	Ionic potentials			Empirical potentials	
a_1	−0.3416	−0.7726	b_1	1.22	0.35
a_2	1.33	1.07	b_2	2.45	2.62
a_3	0.452	0.171	b_3	0.54	0.93
a_4	0.0071	−0.015	b_4	−2.71	1.57

There are two inputs to our calculation: One is the potential; the second input is the geometry. With respect to obtaining a self-consistent pseudopotential for our slab, we first construct ionic pseudopotentials for Ga^{3+} and As^{5+}. These ionic potentials are obtained from model potential calculations and bulk band-structure calculations. We express these potentials in reciprocal space as

$$V(q)=a_1[\cos(a_2 q)+a_3]\exp(a_4 q^4)/q^2\,, \tag{1}$$

where the parameters a_i are given in Table I. We screen these ionic potentials within a Hartree-Fock-Slater scheme to obtain the final self-consistent potential. These ionic potentials, when screened, will yield a bulk band structure in good accord with the best available local pseudopotential band structures for GaAs. The local approach does not produce the high-precision accuracy of nonlocal pseudopotential calculations,[31] but should prove satisfactory for our purposes. Moreover, the potentials we employ here are identical to previous calculations on the (110) surface of GaAs. This will allow us to assess differences in the present work from previous efforts solely in terms of surface geometry changes.

The ionic potentials given in (1) are screened by using the valence charge density to compute Hartree and exchange potentials. The self-consistent process is initiated from an empirical potential of the form

$$V(\vec{r})=\sum_{\alpha,G} V^a_\alpha(G)S_\alpha(\vec{G})\exp(i\vec{G}\cdot\vec{r})\,, \tag{2}$$

with

$$V^a(q)=b_1(q^2-b_2)/\{\exp[b_3(q^2-b_4)]+1\}\,, \tag{3}$$

where $\vec{G}$ corresponds to the reciprocal-lattice vectors of the superlattice, $S_\alpha(\vec{G})$ is the structure factor, $V^a(q)$ is an empirical atomic pseudopotential, and α labels the species. The values of the parameters b_i for both Ga and As are listed in Table I. These parameters are chosen by bulk considerations alone. With the initiating potential and a specified geometry, the wave functions are expanded in terms of the reciprocal-lattice vectors. The eigenvalues and wave functions are determined through a diagonalization of the secular equation. Using the resulting wave functions, the total charge density can be calculated in terms of its Fourier coefficients, $\rho(\vec{G})$. A Hartree potential can then be formed from Poisson's equation:

$$V_H(\vec{G}) = 4\pi e^2 \rho(\vec{G})/\Omega_c G^2 , \tag{4}$$

where Ω_c is the unit cell volume of the superlattice. The exchange-correlation potential used is of the form

$$V_{xc}(\vec{r}) = -\alpha \frac{3}{2\pi} (3\pi^2)^{1/3} e^2 [\rho(\vec{r})]^{1/3} , \tag{5}$$

where $\alpha = 0.8$. The calculation of the Fourier transform of $V_{xc}(\vec{r})$ requires an evaluation of $\rho(\vec{r})$ throughout the unit cell. For this purpose $\rho(\vec{r})$ was evaluated on a grid of approximately 10^4 points throughout the unit cell. The cube root was computed at each grid point and the result transformed back into a Fourier coefficient. To accurately compute the valence charge density required, a special point scheme was employed.[32]

The sum of $V_H(\vec{G})$ and $V_{xc}(\vec{G})$ was then added to the ionic pseudopotential coefficient from (3) to form the total potential:

$$V_T(\vec{G}) = \sum_{\alpha} V^i_\alpha(G) S_\alpha(\vec{G}) + V_H(\vec{G}) + V_{xc}(\vec{G}) . \tag{6}$$

This potential was then made self-consistent. We used this potential to calculate new eigenvalues and wave functions, and from the new wave functions we calculated a new screening potential. By a systematic alteration of the input and output potentials, it is possible to obtain accurate agreement between the input and output potentials. This self-consistent procedure allows the valence charge to respond to fixed ion cores in a manner which involves *no* adjustable surface parameters.

Upon completion of the self-consistent loop, the various states near the semiconductor-vacuum interface are analyzed in terms of a local density of states (LDOS) and individual charge densities. The LDOS displays the density of states in real space near the interface and, for a given region in space, it is given by

$$N_\Omega(E) = \sum_{\vec{k}_\parallel, n} \int_\Omega |\psi_{n,\vec{k}_\parallel}(\vec{r})|^2 d\vec{r}\, \delta(E - E_{n,\vec{k}_\parallel}) , \tag{7}$$

where $\vec{k}_\parallel$ is the wave vector parallel to the interfacial plane, n is the band index, $\psi_{n,\vec{k}_\parallel}$ is the wave function, and Ω is the volume of interest. The physical significance of $N_\Omega(E)$ is that it gives the probability that an electron with energy E will be found in a volume Ω.

With respect to the computational details of the calculation, the criterion for self-consistency was that the rms difference between input and output potentials differ by no more than 0.1 eV when averaged perpendicular to the surface plane. The largest matrix we diagonalized was on the order of 420×420. A reflection plane perpendicular to the interfacial plane gives us a useful symmetry operation. Since this operation exists for all $\vec{k}_\parallel$ wave vectors, we may decompose our secular determinant into two determinants of half the size of the original: E.g., instead of diagonalizing a 420×420 matrix, we diagonalize two 210×210 matrices. In addition to the plane waves treated directly, we include approximately 500 additional plane waves via Lowdin's perturbation technique. To construct densities of states and determine the dispersion of surface bands we solved the secular equation at 15 $\vec{k}_\parallel$ points within the two-dimensional irreducible Brillouin zone.

III. SURFACE GEOMETRY

Since an important aspect of our calculation is the surface geometry, we shall employ LEED work[16-18] in our calculations. The most recent LEED studies appear to be consistent and favor the following model for the (110) surface of GaAs: The GaAs (110) surface does not reconstruct, but retains a primitive 1 × 1 configuration. In accord with ideas first put forth over ten years ago,[15] the As atoms are believed to move outward from their ideal positions and the Ga atoms inward. Chemically this model is to be expected, as it lowers the energy of the occupied As dangling-bond states while raising the energy of the empty Ga dangling-bond states. This general description of Ga and As movements seems to be well accepted but the detailed motions have been controversial.

Initially it appeared as if the Ga atoms relaxed inward until the Ga atoms were coplanar with the neighboring As atoms.[16] This model involved no bond-length changes and a rotation angle of 34.8° relative to the ideal surface plane. We shall refer to this model as "fully relaxed." However, more recent studies have suggested a smaller angle of rotation. At present, the angle of inward rotation of the Ga atom appears to be approximately 27°. What we believe to be the most accurate LEED studies (those of Kahn *et al.*[17] and Tong *et al.*[18]) appear to be in accord on this point. There are some differences between these two analyses, but the angle rotation seems to be similar in both. We have used the model of Tong *et al.*[17] because it involves only first layer relaxation and is thus easier to interpret. In addition, tight-binding calculations with either model appear to yield similar results.[26]

In the Tong *et al.* model the bond lengths in the surface plane and between the surface atoms and substrate are not required to be equal to the bulk bond lengths. In fact, the bond lengths from the surface atoms to substrate are slightly contracted by a few percent.

IV. RESULTS

In Fig. 1 we display the total self-consistent potential averaged parallel to the surface and plotted as a function of distance from the slab center to deep within the vacuum region. To indicate the accuracy of our self-consistency we show both the averaged "input" and "output" potentials. Since a small change in the input potential from self-consistency can result in a large change in the output potential,[30] we believe the self-consistency indicated in the figure is adequate. We have also indicated the positions of various layers of the GaAs slab: Layer 1 is the surface layer; layer 5 is the slab center. The individual displacements of the surface Ga and As atoms are indicated. In the Tong *et al.* LEED analysis the Ga surface atoms move inward a significant fraction (~0.25) of the interlayer separation; however, the As surface atoms are only slightly displaced outward from the surface plane (~0.1 of the interlayer separation). These individual movements result in a slight net contraction of the surface layer's center of mass relative to the substrate. A consequence is that the potential minimum occurring in the interlayer spacing between the surface atoms and the substrate is slightly deepened relative to the bulk minimum. This subtle change can have important consequences on the energy positions, and even the existence, of surface states on the (110) surface.

One traditional concern with slab calculations is convergence of the surface-state spectra and potentials with slab size. Our previous calculations,[21,22] together with our present results, suggest that nine layers of bulk is sufficient for the state of the art accuracy, e.g., ~0.2 eV, with respect to surface-state energies. We find by the third layer that the potential appears to be converged to the bulk configuration so that the thickness of the slab seems quite satisfactory.

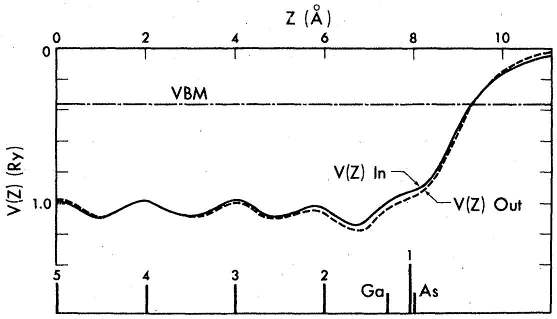

FIG. 1. Total potential for the GaAs relaxed (110) surface. The potential has been averaged parallel to the surface and plotted as a function of distance from the slab center to a point deep within the vacuum region. The degree of self-consistence is indicated by displaying the " input" and " output" potentials. Indicated is the position of the valence band maximum (VBM) and the positions of the GaAs layers: Layer 1 is the surface layer; layer 5 is the slab layer. The relaxed positions of the surface atoms are also displayed.

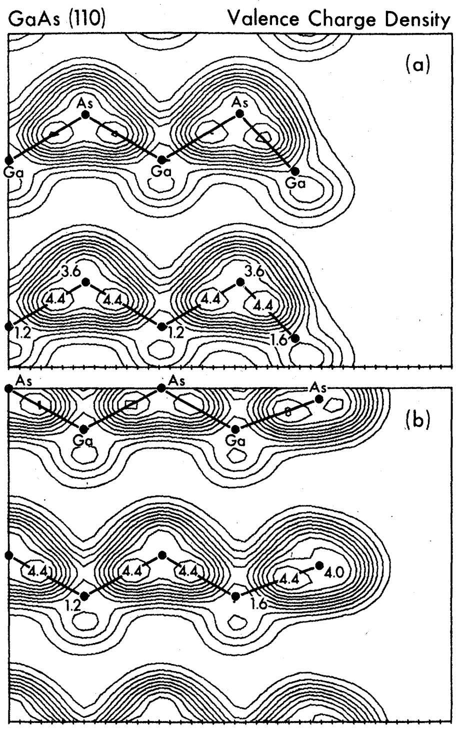

FIG. 2. Valence charge-density contour plots for the (110) GaAs surface. Two planes are displayed; (a) is a (110) plane passing through a Ga surface atom and (b) is a (110) plane passing through an As surface atom. The contours are spaced by units of 0.4; the normalization is one electron per unit cell.

In Fig. 2 we display the total valence charge density for the (110) surface of GaAs. The planes illustrated are (110) planes which pass through either a Ga surface atom or an As surface atom. While these figures are useful in determining the general features of the valence charge density as a function of distance from the vacuum to the bulk, they are of limited use in examining surface-state properties. The bulk features dominate the density configuration and obscure the surface-state features. One possible use of the total density which might prove quite valuable is to use the valence density directly to determine surface structural information. From energy considerations a bulklike configuration for the charge density is optimal and the surface should respond to this fact. In other words, we expect that when we have the correct surface geometry, the surface perturbation of the charge density will be less than for an incorrect geometry. We have evidence for this speculation in the present calculations. If we examine the bond maxima in the charge-density plots we observe that this value does *not* change from the outermost bond inward (i.e., it retains a value of 4.4 units throughout the slab). This is *not* the case for an unrelaxed surface geometry.[21] There the charge-density bond maxima vary by ~10% from the outermost bond to the slab center.

In Fig. 3 we display the projected band structure for the (110) surface of GaAs. We have also indicated the energy position and dispersion of various surface states and resonances. The experimental angle-resolved work of Huijser, van Laar, and van Rooy is also displayed in the figure.[19] For the purposes of notation we label surface features by A_i or C_i depending on whether the feature is localized on the anion or cation, respectively. Overall, the comparison between experiment and theory is fairly good. There are, however, some notable discrepancies. Perhaps the most serious discrepancy occurs in the −4- to −2-eV energy region. Here experiment seems to indicate the presence of two states; however, our calculation yields only one surface state in this region. We note that there appears in our calculation a very weak surface resonance in this region. (It is so ill defined that we do not place it on our figure.) In addition, we note that a similar state is found in the tight-binding work of Chadi.[26] It is intriguing and encouraging that such an "ill-defined" state should appear in both calculations.

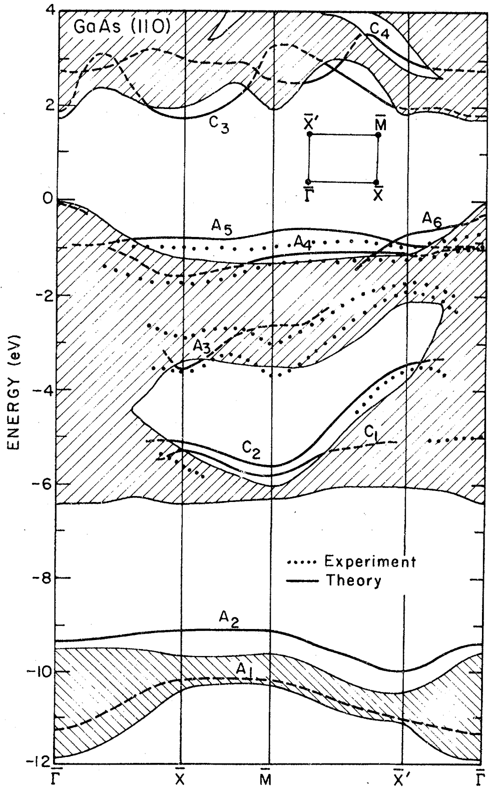

FIG. 3. Projected band structure for the GaAs relaxed (110) surface. Bulk features are indicated by the shaded regions. Calculated surface bands are shown by solid lines. If the surface band becomes resonant, then a dashed line is displayed. The experimental features are indicated by a dotted line. The experimental work is from Huijser, van Laar, and van Rooy (Ref. 19).

TABLE II. Energy positions of calculated surface features. The notation is as in Fig. 3. The calculated positions are compared to experimentally determined positions. All energies are in eV.

Surface feature	Theory	Experiment
C_4	2.6	...
C_3	2.1	1.9[a]
A_5, A_6	−0.6	−0.8,[b] −1.1[c]
A_4	−1.3	−1.5,[b] −1.9[c]
A_3	−3.2	−3.7[b,c]
C_2	−4.0	−4.2[b]
C_1, C_2	−5.5	−6.5[a,c]
A_2	−9.3	−9.7,[d] −11.0[c]
A_1	−10.7	−12.0[e]

[a] Reference 2.
[b] Reference 19.
[c] Reference 33.
[d] Private communication, J. van Laar.
[e] References 35 and 36.

In Table II we have compiled a list of experimental data[2,19,33,35,36] for the approximate energy positions of prominent surface states. Considering the difficulty of both the experiments and calculations we view the agreement as quite good. With respect to our choice of experimental data we have selected only the most recent data: earlier efforts appear to be compatible with the tabulated measurements. At this point we should emphasize that some of the discrepancy between experiment and theory does not arise from an incorrect geometry, but rather from some deficiency in the local pseudopotential. That is, some *bulk* features are misplaced by ~1 eV from experiment; this is especially true near the bottom of the valence bands. An example of this is the placement of the (C_1, C_2) complex. The bulk peak in this region disagrees with experiment by ~1 eV and as a consequence so does the surface peak in this region.

One very encouraging aspect of our calculation concerns the energy placement of the A_1 states. When our preliminary results[34] were published, there existed no experimental evidence for this state. Most recently, however, this state has been observed in x-ray photoemission spectra by Ludeke and Ley[35] and elsewhere.[36] The tight-binding calculations of Chadi[26] also predicted the existence of this state before the experimental data confirmed its presence.

Before discussing the character of individual surface features, we present our local density of states calculations in Figs. 4 and 5. We also present difference curves which emphasize the presence of surface states. In the difference LDOS spectrum we subtract from the total density of states for the slab the density of states of the slab-center layer appropriately normalized. The center layer is bulklike and thus any positive contribution in the LDOS difference curve represents the presence of a surface feature. For most purposes this is a satisfactory concept, but in some cases the surface feature is localized in the second or third surface layer and does not appear prominent in the difference curve. With respect to the integrated volumes in Eq. (7) we choose the volumes as follows: Layer 1 consists of the volume from the midpoint of the ideal interlayer spacing between the surface layer and second layer to the center of the vacuum region. Layer 2 encompasses the volume from the midpoints of the interlayer spacings between the first and second layers and the second and third layers. Layer 3 encompasses the volumes between the midpoint spacings between the second and third lay-

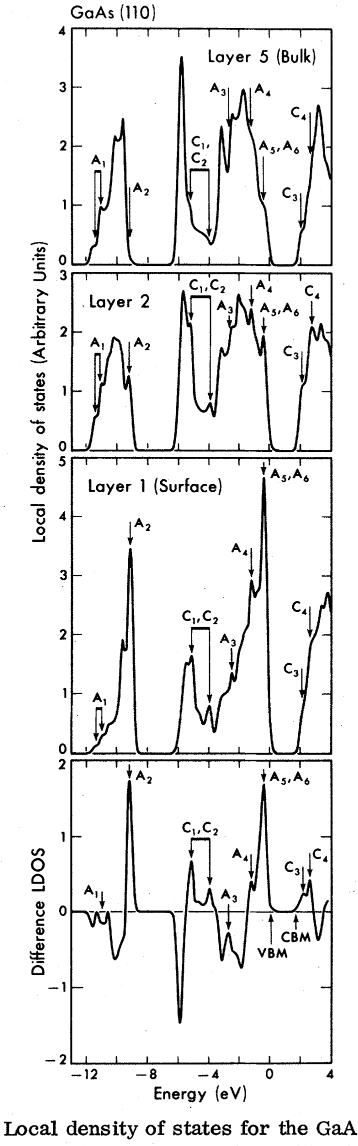

FIG. 4. Local density of states for the GaAs (110) surface. Surface features are indicated by A_i or C_i depending on whether the state is localized on the anion or cation. In the difference curve, a positive contribution indicates a surface feature.

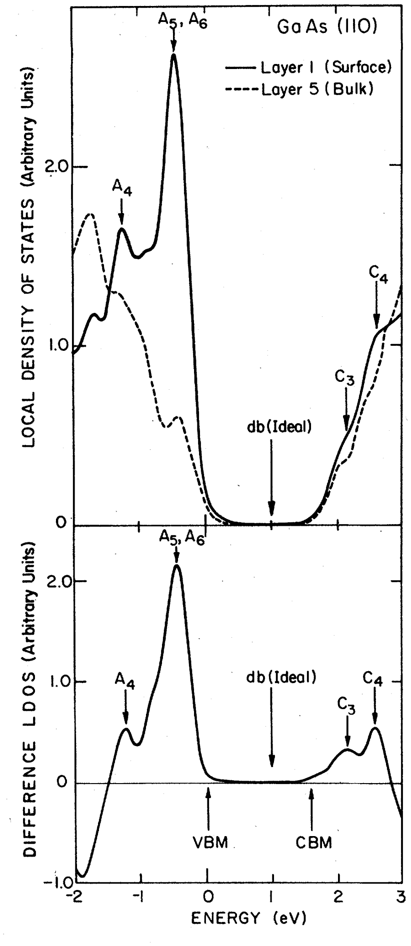

FIG. 5. A local density of states analysis for the fundamental gap region of GaAs. The ideal surface has dangling-bond (db) surface states located in the position marked by the arrow. For our relaxed model these states are swept from the gap.

ers and the third and fourth layers, and so on. We do not include any matrix elements so a direct comparison with experiment is not possible. However, we may make some conclusions which are of general interest. Most importantly, the band gap is free of surface states. We emphasize this in Fig. 5. The positions of the dangling-bond (db) states for the ideal geometry are indicated in the figure. Upon surface relaxation these db states are swept from the gap to a position on the order of 0.5 eV above the conduction-band minimum (CBM). With respect to other calculations using the same geometry, the tight-binding work of Chadi[26] yields a similar LDOS. In particular, the most prominent surface features in the LDOS are the (A_4, A_5, A_6) states. With respect to relative intensities we find that there are some differences between Chadi's results and ours, but the origin of this discrepancy is most likely involved with our LDOS definition as opposed to any fundamental differences. We note that while our valence-band LDOS agrees with the tight-binding calculations,[26] this is *not* true of the conduction band's LDOS. As mentioned earlier, in general, tight-binding calculations do not yield accurate conduction-band configurations.

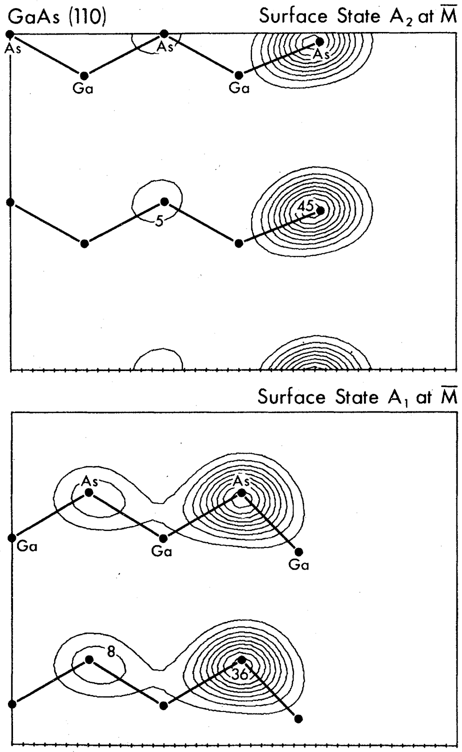

FIG. 6. Surface-state (A_1, A_2) charge density distributions on the GaAs surface (see Fig. 3). State A_1 is sensitive to bond-length changes, and detection of it (Refs. 35 and 36) provided evidence for bond-length changes on the (110) surfaces.

We will now proceed to discuss the individual surface states. The most tightly bound surface states (A_1, A_2) are localized on the anion and are predominantly s-like in character. The charge densities for these states are displayed in Fig. 6. A_1 is an interesting state. It is not observed for the ideal geometry. The small bond-length changes in the Tong *et al.*[17] model and the consequent strengthening of the potential between the first and second layers result in the creation of this state. Owing to the fact that A_1 is localized not on the first surface layer but the second layer, this state is not prominent in the LDOS curve (Fig. 4). As pointed out in our preliminary discussions,[34] the detection of A_1 states would provide direct evidence for a bond-length change occurring between the first layer and the substrate. Its subsequent detection[35,36] gives us confidence in our calculations and the LEED analyses. A_2 has also been observed experimentally, but its detection does not yield any conclusive structural data, as it appears in both the ideal and fully relaxed geometry in approximately the same energy position.[21,22]

A similar situation occurs with the surface states (C_1, C_2). These states are localized on the cation and are predominantly s-like. They are displayed in Fig. 7. The C_1 state is localized on

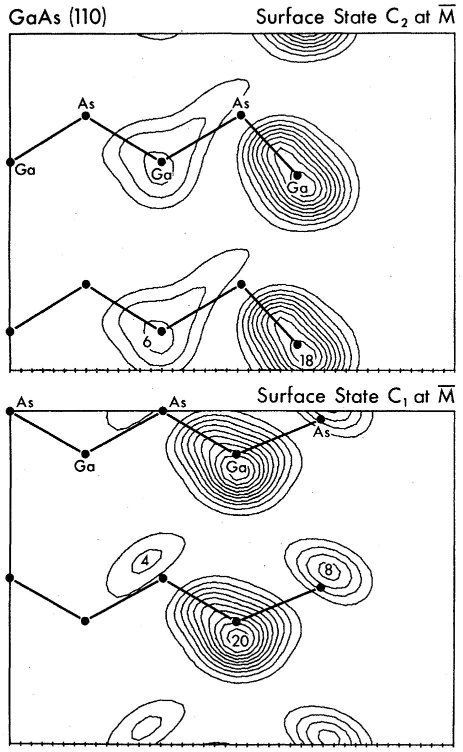

FIG. 7. Surface states $(C_1.C_2)$ charge-density distributions on the GaAs (110) surface (see Fig. 3).

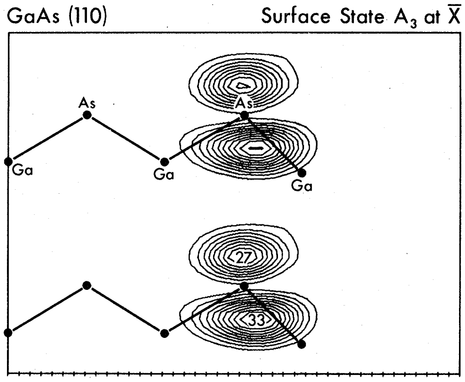

FIG. 8. Surface-state-A_3 charge-density distribution plot.

the second layer and is sensitive to surface relaxation; it is not observed for the ideal geometry. The splitting of states C_1 and C_2 has not been observed experimentally. Considering the that the splitting here is on the order of ~0.2 eV compared to the ~1.4-eV splitting observed for the (A_1,A_2) complex, the lack of experimental confirmation of our calculated splittings is not distressing.

A_3 is p-like and localized on the second layer anions. Its charge distribution is presented in Fig. 8. This state is analogous to A_1 and C_1 in several respects. First, it is localized on the second layer and is absent for an ideal or a fully relaxed surface geometry. Second, A_3 is similar to energetically nearby surface states which unlike A_3 are localized on the surface layer. With respect to the absence in the theory of a well-defined partner to A_3 which is indicated from experiment, it is interesting to speculate about our structural model. Since experiment[19] indicates two states with similar dispersion in this region, it is likely that they are of similar character, e.g., p-like and localized in the second layer. Owing to the sensitivity of A_3 to bond-length changes, it might be possible that a more severe bond-length change could create another p-like state in this region.

Near the valence-band maximum (VBM) (−0.5 to −1.5 eV) we find two strong surface states (A_4,A_5) and a weak, mostly resonant, state A_6 near the zone center. These states are p-like and are localized on the surface anions. We display the densities for (A_4,A_5) in Fig. 9. We do not display A_6; it is not localized in a $(1\bar{1}0)$ plane, but rather runs parallel to the surface plane along the Ga-As surface bonds. In addition, it is well defined only along the $\bar{\Gamma}$-$\bar{X}'$ direction and thus does not contribute significantly to the LDOS in Fig. 4. A_4 corresponds to a "back bond" surface state; A_5 corresponds to a "dangling bond" surface state. All of these states (A_4,A_5,A_6) have been observed on the ideal surface and the fully relaxed surface model.[21,22] Experimental results and our calculations appear to be in good agreement in this region except for one possible flaw, namely, the ordering of these states at $\bar{X}'$. The experimental work of Williams, Smith, and Lapeyre[33] finds three states at $\bar{X}'$ at −0.9, −1.4, and −1.6 eV. The −0.9- and −1.6-eV states respond similarly to polarization changes and oppositely to the −1.4-eV state. This would be compatible with an (A_5,A_6,A_4) ordering or an (A_4,A_6,A_5) ordering, but not our calculated ordering. Since (A_4,A_5,A_6) at $\bar{X}'$ all fall within an energy interval of ~0.5 eV, we do not view the error as serious, but this situation presents evidence that small structural errors in the LEED model of Tong *et al.*[17] may exist. In particular, it may be necessary to include second or third layer relaxations as has been suggested.[18]

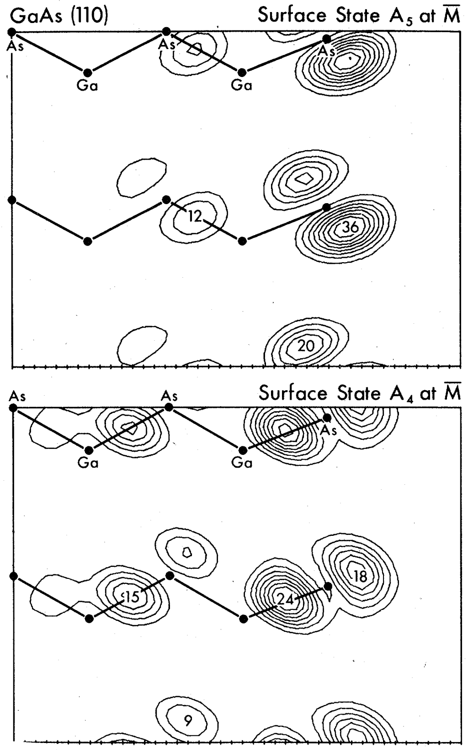

FIG. 9. Surface states (A_4,A_5) charge-density distributions for the (110) surface of GaAs. These states have been detected by angle-resolved photoemission (Refs. 19 and 35) and are the most prominent occupied surface states on the (110) surfaces.

We find empty surface states (C_3,C_4) which occur above the conduction-band minimum. These states are, perhaps, the most important surface states on the (110) surface. *Only* if certain structural criteria are met will the energy positions of these

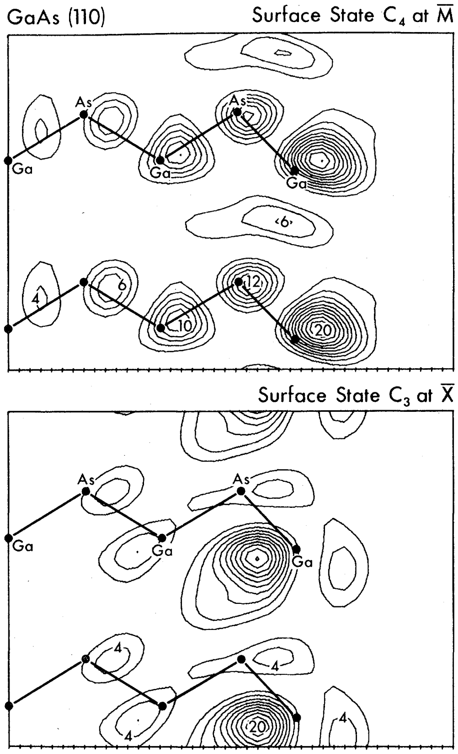

FIG. 10. Empty surface states (C_3, C_4) charge-density distributions. The energy positions of these two states are crucial in obtaining a fundamental gap free of surface states. (See Figs. 3 and 5.)

states be such that a gap free of surface states will exist. For the ideal geometry, C_4 lies in the center of the band gap while C_3 lies above the CBM. For the fully relaxed model the roles are reversed: C_3 lies in the gap; C_4 lies above the CBM. In Fig. 10 we display the charge densities for the two states (C_3, C_4). The states C_3 and C_4 are primarily *p*-like and localized on the surface cations. C_3 may best be described as an "anti-back" bonding state. It has been observed in previous pseudopotential calculations[22] and in tight-binding calculations.[26] C_4 is a "dangling-bond" surface state.

Both C_3 and C_4 are very sensitive to the angle of rotation of the Ga atoms with respect to the surface plane. As the Ga atoms are rotated inward C_4 moves *upward* in energy and C_3 moves *downward* in energy. The opposite movements of C_3 and C_4 with rotation means that only a small window of rotation angle will result in a gap free of surface states. By examining the movements of the two states with respect to rotation angle, we can put limits in the angle of rotation. Our calculations suggest the rotation angle cannot be more than ~28° or less than ~20° for a gap-free state to exist.

Finally with respect to the empty states we may obtain a rough estimate for the surface excitonic interaction proposed to explain partial yield spectroscopy. Partial yield work places a surface state near midgap.[6] If we shift the threshold of the C_3 state to correspond to this position we obtain an energy of about 0.5 to 0.7 eV. This estimate appears to be in accord with other estimates for the exciton binding energy.[29]

V. CONCLUSIONS

In summary we would like to emphasize the strong interplay between experimental measurements, the LEED studies and the pseudopotential calculations. Pseudopotential calculations[21,22] when based upon an ideal surface model or a fully relaxed surface model were not in agreement with experimental results: I.e., intrinsic surface states were found to exist within the band gap. However, when we employ the best LEED analyses available, the pseudopotential calculations are in good accord with experiment.

With respect to other computational tools, e.g., tight-binding methods, the same statements cannot be made (at least with respect to the question of intrinsic surface states within the band gap). Some of the best tight-binding studies for the GaAs (110) surface have yielded gaps free to states for the fully relaxed model and for the 27° rotation model.[26] This suggests that tight-binding techniques cannot distinguish between these two models with respect to the question of gap states. While the tight-binding approaches are extremely useful and flexible, especially with respect to the occupied surface states, it is questionable that they can achieve the accuracy of pseudopotential calculations with respect to conduction band derived surface states.

In summary, we feel that the sensitivity of pseudopotential calculations to surface structure strongly suggests that our techniques accompanied by photoemission spectroscopies can be used as a test for LEED studies or can be used without LEED studies to obtain information of surface geometries.

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[1] J. van Laar and J. J. Scheer, Surf. Sci. 8, 342 (1967); A. Huijser and J. van Laar, *ibid.* 52, 202 (1975).

[2] J. van Laar and A. Huijser, J. Vac. Sci. Technol. 13, 769 (1976); J. van Laar, A. Huijser, and T. van Rooy, *ibid.* 14, 893 (1977).

[3] W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta, and P. W. Chye, J. Vac. Sci. Technol. 13, 233 (1976); P. E. Gregory and W. E. Spicer, Phys. Rev. B 13, 725 (1976).

[4] W. E. Spicer, P. Pianetta, I. Lindau, and P. W. Chye, J. Vac. Sci. Technol. 14, 885 (1977).

[5] W. Gudat and D. E. Eastman, J. Vac. Sci. Technol. 13, 831 (1976).

[6] D. E. Eastman and J.L. Freeouf, Phys. Rev. Lett. 33, 1601 (1974); 34, 1624 (1975).

[7] K. C. Pandey, J. L. Freeouf, and D. E. Eastman, J. Vac. Sci. Technol. 14, 904 (1977).

[8] G. J. Lapeyre and J. Anderson, Phys. Rev. Lett. 35, 117 (1975).

[9] G. M. Guichar, C. A. Sebenne, and G. A. Garry, Phys. Rev. Lett. 37, 1158 (1976).

[10] J. A. Knapp and G. J. Lepeyre, J. Vac. Sci. Technol. 13, 757 (1976).

[11] R. Ludeke and A. Koma, J. Vac. Sci. Technol. 13, 241 (1976).

[12] H. Froitzheim and H. Ibach, Surf. Sci. 47, 713 (1975).

[13] J. E. Rowe, S. B. Christman, and G. Margaritondo, Phys. Rev. Lett. 35, 1471 (1975).

[14] R. S. Bauer, J. Vac. Sci. Technol. 14, 899 (1977).

[15] A. U. McRae and G. W. Gobeli, in *Semiconductors and Semimetals*, edited by X. Willardson and Y. Beer (Academic, New York, 1966), Vol. 2, p. 166.

[16] A. R. Lubinsky, C. B. Duke, B. W. Lee, and P. Mark, Phys. Rev. Lett. 36, 1058 (1976).

[17] S. Y. Tong, A. R. Lubinsky, B. J. Mrstik, and M. A. van Hove, Phys. Rev. B 17, 3303 (1978).

[18] A. Kahn, E. So, P. Mark, and C. B. Duke, J. Vac. Sci. Technol. 15, 580 (1978).

[19] A. Huijser, J. van Laar, and T. L. van Rooy, Phys. Lett. 65A, 337 (1978).

[20] J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B 10, 2075 (1974).

[21] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 13, 826 (1976).

[22] J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B 14, 4724 (1976).

[23] P. E. Gregory, W. E. Spicer, and W. Harrison, Appl. Phys. Lett. 25, 511 (1974).

[24] C. Calandra and G. Santoro, J. Phys. C 8, L86 (1975); J. Vac. Sci. Technol. 13, 773 (1976).

[25] E. J. Mele and J. D. Joannopoulos, Surf. Sci. 66, 38 (1977).

[26] D. J. Chadi, J. Vac. Sci. Technol. 15, 1244 (1978); Phys. Rev. B 18, 1800 (1978).

[27] C. Calandra, F. Manghi, and C. M. Bertoni, J. Phys. C 10, 1911 (1977).

[28] P. W. Chye, I. A. Babolola, T. Sukegawa, and W. E. Spicer, Phys. Rev. Lett. 35, 1602 (1975).

[29] R. D. Sole and E. Tosatti, Solid State Commun. 22, 307 (1977).

[30] M. Schlüter, J. R. Chelikowsky, S. Louie, and M. L. Cohen, Phys. Rev. B 12, 4200 (1975).

[31] K. C. Pandey and J. C. Phillips, Phys. Rev. B 9, 1152 (1974) and J. R. Chelikowsky and M. L. Cohen, Phys. Rev. Lett. 31, 1582 (1973).

[32] D. J. Chadi and M. L. Cohen, Phys. Rev. B 8, 5747 (1973).

[33] G. P. Williams, R. J. Smith, and G. J. Lepeyre, J. Vac. Sci. Technol. 15, 1249 (1978).

[34] J. R. Chelikowsky and M. L. Cohen, Solid State Commun. 29, 267 (1979).

[35] R. Ludeke and L. Ley, unpublished.

[36] D. Denley, private communication.