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GaAs(100): Its spectrum, effective charge, and reconstruction patterns

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We have carried out self-consistent wave-mechanical calculations for the Ga-terminated GaAs (100) surface in its unreconstructed form. The calculations were done for an ideal termination geometry, for which the spacing between the Ga and As layers is 2.67, and two additional geometries, one for which the Ga surface layer was relaxed inward by 0.38 a.u., the other for which it was expanded by 0.23 a.u. The most prominent spectral features found were two bands of gap surface states, one having dangling-bond character, the other having p character within the Ga plane. The dangling-bond band is < 1.0 eV wide and lies below the 2–3-eV wide p_y band. These bands are similar to those found for Si(100). The lower band is three-quarters full. Its Fermi surface lies in a region of high electron state density and possesses an almost perfect diamond shape. The connection between the band-gap spectrum for the calculated (1×1) geometry and the experimentally realized $c(8 \times 2)$ and (4×2) structures is discussed in terms of metal-insulator instabilities. We have also calculated the effective charge on the surface Ga atoms from the change in ionization potential produced by moving the Ga layer. This number, 0.20 electrons, is close to the measured bulk value.

I. INTRODUCTION

During the last several years considerable insight has been achieved into the electronic properties of the elemental semiconductor surfaces.[1-3] Our understanding of compound semiconductor surfaces, particularly the polar surfaces, has not progressed as far and it therefore seemed appropriate to undertake a study of these materials.[4]

This paper reports the results of self-consistent wave-mechanical calculations of the GaAs (100) surface. This surface was chosen for a number of reasons. First, having completed extensive calculations for the Si (100) surface, the choice of a polar (100) surface with the same symmetry and coordination allowed us to focus on the role of polarity at the surface. Second, the surface is technologically important as a primary constituent in heterojunction devices.[5] Third, the surface occurs in a variety of structural[6,7] forms, and as such, offers a particularly rich area for the study of surface reconstruction. Fourth, some spectroscopic information is now available for this surface.[8]

While some of the information we report is specific to GaAs, many of our conclusions concerning the spectroscopy, surface-state occupancy, and surface charging are of general applicability.

GaAs(100) is prepared in its most nearly perfect form by molecular beam epitaxy.[6,7] High-energy-electron-diffraction studies of the surface reveal a variety of structural forms that it can assume. A number of these structural forms are clearly associated with nonstoichiometric surfaces; the Ga-rich $c(8\times 2)$ and (4×2) are believed stoichiometric,[7] with the latter producing the sharpest high-energy-electron-diffraction pattern. Because of the complexity of the latter two structures and our ignorance of their local atomic order we have in this paper chosen an unreconstructed Ga-terminated (100) surface to study.

Previous work on polar semiconductor surfaces falls into a number of categories. There has been work of a heuristic quality, discussing the reactivity of (111) surfaces of GaAs in terms of dangling-bond bands and their electron occupancy.[9,10] While our work is on the (100) surface, it clearly implies that there are serious misunderstandings in the literature as to the electron occupancy requirements on the dangling-bond bands necessary to ensure surface charge neutrality.

A number of spectral calculations using an empirical tight-binding or linear-combination-of-atomic-orbitals formalism exist for polar semiconductor surfaces.[11,12] These are for the (110) surfaces of GaAs and ZnSe, not (100) surfaces, so a direct comparison between our results and those calculations are not possible. Nevertheless, from our study of the effective charge state of the surface atoms compared to those in the bulk, and the modifications in the spectrum we find in going from Si(100) to GaAs(100), we are able to indicate the potential strengths and weaknesses of the empirical linear-combination-of-atomic-orbitals methods.

Work on the polar semiconductor surfaces has also focused on the reconstructions that occur on these surfaces. Work, particularly by Nosker, Mark, and Levine,[13] suggests that surface charge neutrality is achieved by having a nonstoichiometric surface, which, for GaAs(100) implies only $\frac{3}{4}$ of a layer of Ga atoms. This point of view as well as the general subject of polar surfaces has recently been reviewed by Mark *et al.*[4] By contrast, we argue in this paper that intrinsic surface-state neutralization is operative and that it is unnecessary to invoke nonstoichiometric surface compositions, either to neutralize the surface or explain the prominent reconstructed phases of Ga terminated GaAs(100).

In concluding this brief introductory survey it is appropriate to comment on the work done on the (110) surface of the compound semiconductors. This surface is not polar and its spectral properties can be expected to differ significantly from those which are. Unguarded generalizations from the (110) to other surfaces, such as (111) and (100), may well be incorrect, and care must be taken in making them. Where appropriate, we shall comment upon specific instances of this within the body of the paper.

The remainder of the paper is organized in the following way. In Sec. II we shall give a general and heuristic discussion of the GaAs (100) surface, setting forth a number of basic ideas necessary for an understanding of this surface. The detailed spectral behavior of the gap surface states and a discussion of the computational procedures used in the self-consistent calculation are discussed in Sec. III. In Sec. IV we shall focus on the effective charge of the Ga surface and its variation with bond distortions. In Sec. V a discussion of surface reconstruction will be presented in terms of metal-insulator and Fermi-surface instabilities[14] of the gap surface-state bands.

II. GENERAL DISCUSSION OF THE SURFACE SPECTRUM

We start our discussion assuming a GaAs (100) surface in its ideal unreconstructed form. To understand its spectrum we take as a working hypothesis that GaAs is basically covalent, so that two bonds per surface atom have been severed in forming the (100) surface, exactly as was the case for Si(100).[3] The spectrum of GaAs(100), especially within the gap, should then resemble that of Si(100). There will be two bands of states, one normal to the surface and dangling-bond-like, the other p_y-like, where $\hat{y}$ is along the broken bond direction (see Fig. 1). This latter band we referred to in our work on Si(100) as the bridge bond, since it acted there as a link between surface atoms. The bridge bond band should be relatively broad (2–3 eV), and the dangling-bond band narrow (≤ 1.0 eV).

The relative position of these bands of gap surface states is going to be different from that of Si. We can understand these differences if we assume that the wave functions for the gap surface states do not change dramatically in going from Si to GaAs. From an examination of their charge distributions, one notices that the bridge states are more strongly localized on the surface atoms than the dangling states, which have significant density in the vicinity of the second layer. In going from a Si to a Ga-terminated GaAs crystal, the weakening of the surface atom potential will affect the bridge band more than the dangle, which can more effectively take advantage of the increased attractive potential of the second As layer. The bridge then should be higher in energy relative to the dangle for the Ga-terminated GaAs (100) surface than for the Si (100) surface. We expect the opposite behavior on the As-terminated GaAs (100) surface.

Having argued for the qualitative similarity of the gap surface state spectra in going from homopolar Si to heteropolar GaAs, we now show that their occupancy changes in a very important way. For Si(100) the two bands of surface states shared two electrons per surface atom, equal exactly to half the Si atom's valence. If, for Ga-terminated GaAs, Ga contributes half its electrons to the back bonds and the other half to the gap or broken states, $1\frac{1}{2}$ electrons per surface atom must be accommodated in these two bands.

The fractional occupancy of the gap surface states can be understood quantum mechanically as follows. Consider a slab of GaAs with identical Ga surfaces on either end. For each $\vec{k}_{\parallel}$, the two-dimensional Bloch wave number, one finds a finite number of energy levels. Some are grouped into bands, others are separated from these by finite energy gaps. In the limit of a very large slab, this separation is always apparent. Each state which is occupied for all $\vec{k}_{\parallel}$ will clearly contain an even number of electrons (allowing for spin degeneracy), and as a consequence the completely filled set associated with the valence bands will contain an even number of electrons per surface unit cell. The total number of nuclear charges is

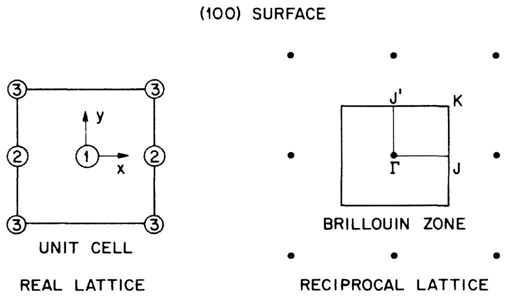

FIG. 1. Real space unit cell and Brillouin zone, with symmetry points labeled are shown for the (100) GaAs surface. The $\hat{x}$-$\hat{y}$ origin is under the surface atom, indicated by 1, and the second and third layer atoms have the obvious notation 2 and 3, respectively.

odd, though, so that one will have to place an odd number of electrons into the gap surface state bands. Since there are two surfaces per slab, the bands of gap surface states associated with a particular surface must contain a half-integer number of electrons.

The above argument can also be made for a semi-infinite crystal. From previous work, it has been shown that the total charge in a filled band from a symmetry plane within the crystal to a point in vacuum where there is no longer any charge must be integral.[15] For GaAs(100), the only appropriate symmetry planes are through the atoms (one needs a plane where the average electric field is zero). The total charge within the valence band is integral, and since there is a half-integer number of nuclear charges on the vacuum side of this plane (the plane splits an odd nuclear charge), the gap surface state bands must be occupied with a half-integer number of electrons. That this half-integral number is $1\frac{1}{2}$ follows only from the covalency assumption and a comparison of the charge within the valence bands for Si. For Si, the dangling-bond band overlapped weakly with the bridge band. On the basis of our argument that the bridge band rises relative to the dangling bond, we expect them to split for GaAs(100). This implies a $\frac{3}{4}$-filled dangling-bond band and an empty-bridge bond band. For an As-terminated GaAs (100) surface a total of $2\frac{1}{2}$ electrons must be accommodated in these two bands, implying a filled dangling bond and a $\frac{1}{4}$-filled bridge bond.

The picture that emerges from the above analysis is the following. The charge contributed to the backbonds by the surface Ga atoms is left as it is in the bulk crystal and the surface states that are derived from the broken surface bonds accommodate the remaining electrons. This is consistent with arguments advanced by Holt,[10] who, for GaAs(111), suggested that the dangling bond band was $\frac{3}{8}$ occupied.

By contrast, Gatos and Lavine[9] argued that the dangling-bond band was completely empty for GaAs(111), implying that at least the first few layers of completed bonds between the Ga and As atoms differ from their bulk limit. The reader should be aware that our quantum mechanical arguments cannot be applied directly to the GaAs (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces, since this orientation lacks the necessary mirror planes that make the arguments advanced for the (100) surface proceed so smoothly. As a consequence, we cannot directly challenge Gatos and Lavine, but since their argument requires the first few layers of completed GaAs bonds to be disturbed, we find it highly unlikely.

The situation for GaAs(110) is different. There we have a mirror plane (with respect to planar average properties) which passes through atomic layers consisting of equal numbers of Ga and As atoms. The quantum-mechanical argument applied to the semi-infinite solid now implies that the charge in the gap surface states must be integer, and is in fact completely analogous to that for Si(110). The counting argument fails to tell us whether there are two bands of Ga- and As-like dangling bonds, one above the As, the other above the Ga, both of which are partially occupied, or only a single full dangling-bond band above the As, with the Ga dangling bond empty. Both these alternatives (and, in fact, any in between) are consistent with having the completed GaAs bonds at their normal charge states.

For example, if the As dangling bond is full and if the As contributes $\frac{5}{4}$ electron to the second layer Ga atom to which it is bonded (making that a normal bond), then the As must contribute $\frac{7}{8}$ of an electron to each of the surface Ga atoms. Each surface Ga atom in turn contributes $\frac{3}{4}$ of an electron to the second layer As atom to which it is bonded (making that a normal bond) which leaves $\frac{9}{8}$ electron for each of its surface plane As neighbors. The $\frac{9}{8}$ of an electron from the Ga-surface atoms and the $\frac{7}{8}$ of an electron from the As-surface atoms leaves the surface saturated bonds identical to the bulk bonds. The same situation could have been achieved by having the As-dangling-bond state contain $\frac{5}{4}$ of an electron, the Ga-dangling-bond state $\frac{3}{4}$ of an electron. In fact, any arrangement in which the dangling bond bands share two electrons is allowed on the basis of the above reasoning.

From specific theoretical and experimental studies on GaAs(110),[16] the evidence strongly favors a filled As-dangling-bond band, and an empty Ga band. We see from the above analysis that dangling bonds on GaAs (111) and (110) surfaces are going to have different occupation numbers.

III. DETAILED SPECTRA

The potential, charge density, and spectra of the Ga-terminated GaAs (100) surface have been calculated self-consistently. The methods used are identical to those employed in the study of Si(100).[3] Model potentials for Ga and As used in this calculation were obtained by fitting self-consistent bulk calculations for the series Ge, GaAs, and ZnSe to experiment.[17] These, together with a local density approximation for exchange and correlation, and Poisson's equation for the electrostatic contributions, enables us to calculate a total electronic potential in the surface region. This surface region extended from a plane midway between the third and fourth atomic layers to a plane a number of angstroms beyond the last Ga layer where the electron density has fallen off to essentially zero.

Assuming an initial linear response potential in this region, Schrödinger's equation was solved by the transfer matrix technique for all occupied states at a number of points in the surface Brillouin zone (shown and labeled in Fig. 1). From these states a charge density was produced and a new surface potential calculated. The iterative process was repeated a number of times (~3 or 4) until 50-meV-rms agreement between input and output potentials was achieved. Charge neutrality was satisfied to within ~0.02 of an electron in the surface region, which contained the order of ten electrons. The sampling scheme used to construct the surface charge was the same as that for Si(100), i.e., the Γ amd *K* points were used for filled bands. For the three-quarter full dangling-bond band, we assumed the band completely full using the Γ and *K* points to represent its charge, and then corrected this using the *J′* point to represent the one-half of a hole present. This is a convenient and typical point lying at the center of the hole portion of the band.

Self-consistent calculations were carried out for three different positions of the Ga-surface layer. These were the ideal Ga position corresponding to a normal coordinate $d = 10.68$ a.u., relative to an origin located on a Ga atom in the fourth atomic layer, a relaxed geometry with $d = 10.30$ a.u., and an expanded geometry with $d = 11.00$ a.u. These allowed us to explore the sensitivity of our calculated spectra to geometry and to study the effect on the surface barrier of moving a polar atomic plane. The spectra found at Γ and *K* are summarized in Figs. 2 and 3. The bulk energy band spectrum is shown on the left-hand side, together with its surface point group symmetry classifications. The (100) surface possesses C_{2v} symmetry and the transformation properties of these states are summarized in Table I. In the right-hand columns of these figures we have indicated the surface states found for the three geometries studied.

The distribution of surface states within the bands bears a strong similarity to that of Si, if each state is referenced to the bulk band from

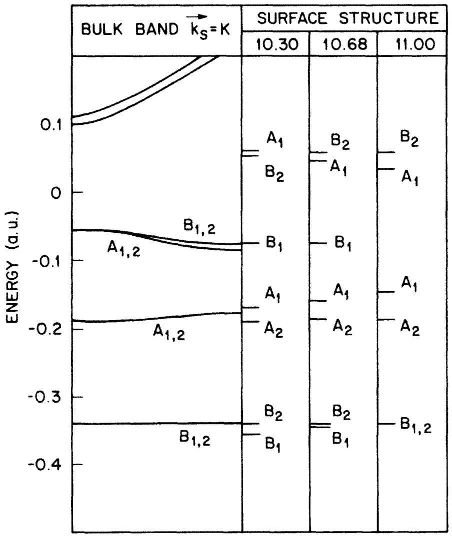

FIG. 3. Spectra of allowed energy bulk bands at $\vec{k}_s = K$ in the bulk is shown together with their symmetry labels in the left-hand portion of the figure. In the right-hand portion of the figure is indicated the location of the surface states found for the three different positions of the last Ga surface layer. The distance indicated is measured from an origin at the fifth Ga layer from vacuum.

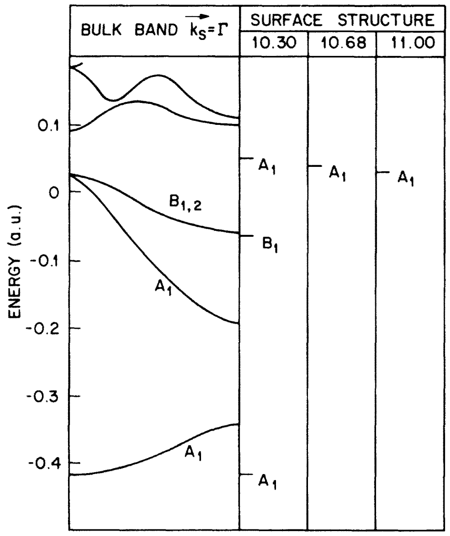

FIG. 2. Spectra of allowed energy bulk bands at $\vec{k}_s = \Gamma$ is shown together with their symmetry labels in the left-hand portion of the figure. In the right-hand portion of the figure is indicated the location of the surface states found for the three different positions of the last Ga surface layer. The distance indicated is measured from an origin at the fifth Ga layer from vacuum.

TABLE I. Character table appropriate to the point-group symmetry of the GaAs (100) surface is shown. σ and σ′ correspond to the symmetry operations $x \to -x$, $y \to y$ and $y \to -y$, $x \to x$, respectively. See Fig. 1 for the orientation of the coordinate system.

C_{2v}	E	C_2	σ	σ'
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	−1	1
B_2	1	−1	1	−1

which it is derived so as to remove bulk effects introduced by the heteropolar character of GaAs. The similarity suggests that the changes in the Madelung energy are relatively small and do not play an important role in determining the surface spectrum. Additional support for this position will be presented in Sec. IV, where the surface effective charge on the Ga is discussed.

Consider now the surface states within the gap between the valence and conduction bands. As discussed in Sec. II, and confirmed by detailed calculations here, two bands of gap surface states exist. One, whose wave functions have dangling-bond character, exists throughout the surface Brillouin zone, while the other, bridge bond in character, disperses strongly upward in energy disappearing into the conduction band in the region near the line $\vec{k}_s = \Gamma$ to J.

We have calculated the energy of the dangling-bond band at the four symmetry points, Γ, J', J, and K and have fitted it with the simple periodic function

$$\epsilon(\vec{k}_s) = \epsilon_0 + 2\epsilon_{10}\cos\pi k_1 + 2\epsilon_{01}\cos\pi k_2 + 4\epsilon_{11}\cos\pi k_1 \cos\pi k_2 , \tag{3.1}$$

$$\vec{k}_s = (2\pi/\sqrt{2}a)(k_1\hat{x} + k_2\hat{y}) . \tag{3.2}$$

The fitted dispersion relation is shown in Fig. 4.

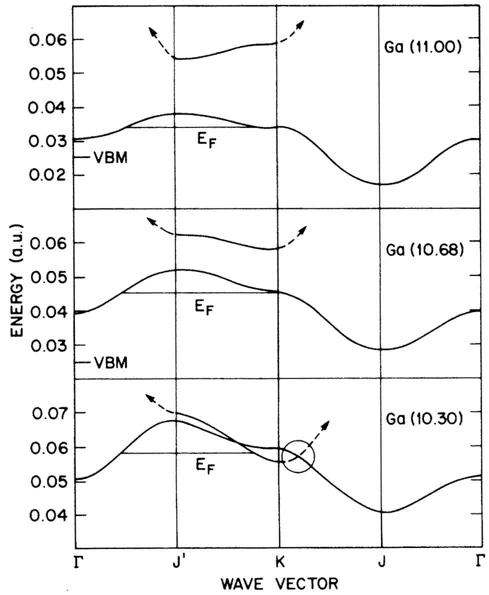

FIG. 4. Dangling-bond band and portions of the bridge bond band are plotted vs $\vec{k}_s$ along symmetry lines in the surface Brillouin zone for three different locations of the Ga surface layer. The ideal location is 10.68. The circle in the lower portion of the figure indicates the region in which we expect a hybridization gap to occur between the bridge and dangling bond bands. The position of the valence-band maximum (VBM) is shown as well as the surface Fermi level ϵ_F. The dispersion along lines other than J' to K for the bridge state is schematic (see text).

For the bridge band only the states at J' and K were calculated; those at Γ and J do not exist. The two surface bands are split by a substantial gap for the ideal and expanded geometry, while for the relaxed geometry a slight crossing occurs. We have continued to use (3.1) for this case but have indicated by a circle the region in which a small hybridization gap can be expected to develop between the two bands. Note that along the line J' to K symmetry forbids mixing of the two bands and they cross as indicated. The spatial nature of the gap surface states are indicated in Figs. 5–10. The electron density for the dangling bond band is plotted on a plane normal to the surface and passing through the back bonds as contours of constant density in Figs. 5–8. The states resemble those on Si, but are noticeably modified by the presence of the strongly attractive second layer of As. For the states that are constrained by symmetry to have nodes on the As atoms, i.e., those at $\vec{k}_s = J$ and K shown in Figs. 5 and 6, the effect is to polarize the back lobe of the dangle towards the As, but not to shift weight out of the peak above the Ga. For comparison the analogous state on Si is shown in Fig. 9 of Ref. 3. For the states at Γ and J' (Figs. 7 and 8) this is not true, and significant weight is transferred to the region about the second layer As. In fact, these states dangle at least as much over the second atomic layer as they do over the first. The states at J' and K that

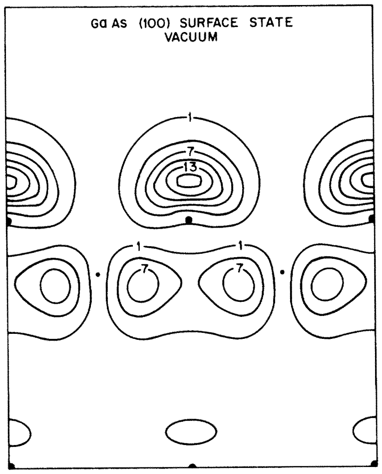

FIG. 5. Dangling-bond electron density at $\vec{k}_s = J$ is contour plotted as on a plane normal to the (100) surface and passing through the back bond between the surface Ga atoms (shown as heavy dots) and their second layer As atoms (shown as light dots). Units are atomic with the density scaled by 10^3.

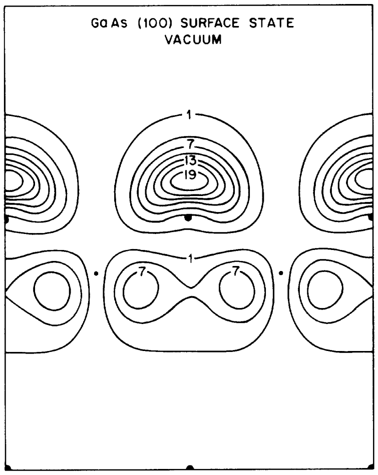

FIG. 6. Dangling-bond electron density at $\vec{k}_s = K$ is contour plotted on a plane normal to the (100) surface and passing through the back bond between the surface Ga atoms (shown as heavy dots) and their second layer As atoms (shown as light dots). Units are atomic with the density scaled by 10^3.

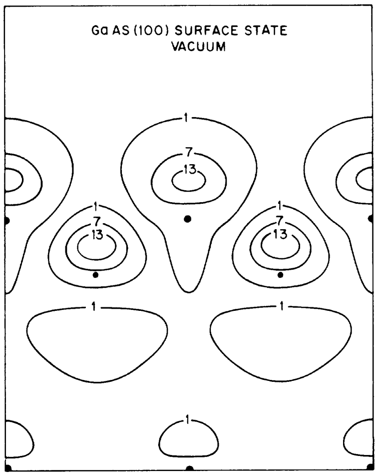

FIG. 8. Dangling-bond electron density at $\vec{k}_s = J'$ is contour plotted on a plane normal to the (100) surface and passing through the back bond between the surface Ga atoms (shown as heavy dots) and their second layer As atoms (shown as light dots). Units are atomic with the density scaled by 10^3.

were sampled from the upper-bridge band are shown in Fig. 9 and 10. They are similar to those for Si (see Figs. 9 and 10), but once again there is some transfer of charge from the Ga to As atoms. Compare Fig. 9 to Fig. 12 of Ref. 3 for confirmation of this effect. Note that because of the additional layer of atoms in the surface region for this calculation compared with that of Si (100), the surface layer has rotated by 90° with respect to the bulk based reference system used in both calculations. As a result, states at $\vec{k}_s = J$ and J' must be interchanged in comparing the two calculations.

The bridge states at Γ and J which have a node between the surface atoms were not found. These would have considerably higher kinetic energy than those at J' and K and as a consequence have moved into the conduction band. This is consistent with the Si spectrum, where the analogs of the

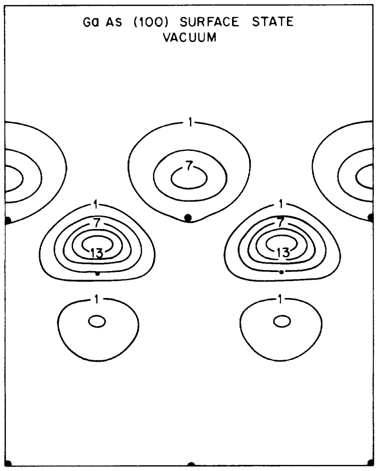

FIG. 7. Dangling-bond electron density at $\vec{k}_s = \Gamma$ is contour plotted as on a plane normal to the (100) surface and passing through the back bond between the surface Ga atoms (shown as heavy dots) and their second layer As atoms (shown as light dots). Units are atomic with the density scaled by 10^3.

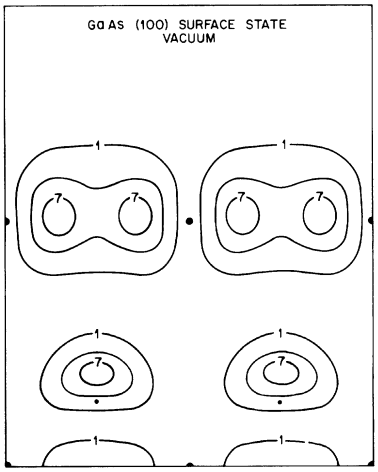

FIG. 9. Bridge-bond electron density at $\vec{k}_s = J'$ is contour plotted on a plane normal to the (100) surface and oriented in the direction of the surface broken bonds. The Ga (As) atoms are shown as heavy (light) dots and the density is scaled by 10^3 (units are atomic).

missing states on GaAs were extremely close to the bottom of the conduction band.

The behavior of the gap surface states with changing geometry is easily understood. With increasing Ga to As separation the dangling-bond band moves down in energy. This behavior is caused by the surface barrier moving out and becoming smaller with expansion—an effect that will be analyzed in Sec. IV. The wave functions, in contrast to their energies, do not change appreciably. The energy of the bridge states is not sensitive to geometry because their wave functions are located primarily on the last surface plane. On this plane, the potential is nearly independent of geometry since competing effects from the surface barrier and adjacent As layer cancel, as may be seen in Fig. 11.

IV. SURFACE POTENTIAL AND EFFECTIVE CHARGE

The behavior of the surface potential with surface planar spacing is shown in Fig. 11, where the planar average potential is plotted versus distance for the three geometries studied. As the Ga plane moves inward the potential becomes more attractive between the Ga and As plane. This is similar to what occurs for Si.[18] In addition the surface barrier appears to shift inward and become more repulsive, i.e., the ionization potential (IP) increases with decreasing spacing between the Ga and As. This is shown in Table II. For the Si surface we found that the surface barrier appeared to move almost rigidly with the surface plane, and that the IP was insensitive to geometry.

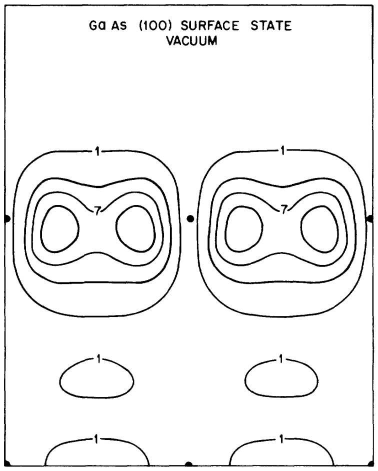

FIG. 10. Bridge-bond electron density at $\vec{k}_s = K$ is contour plotted on a plane normal to the (100) surface and oriented in the direction of the surface broken bonds. The Ga (As) atoms are shown as heavy (light) dots and the density is scaled by 10^3 (units are atomic).

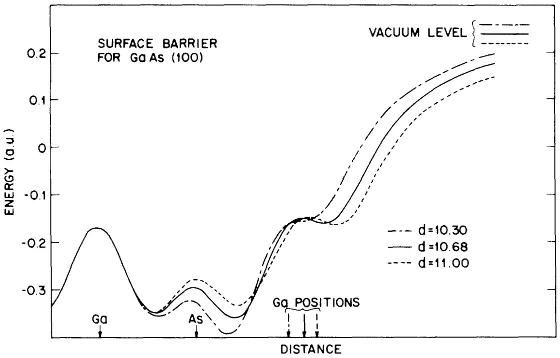

FIG. 11. Planar average potential showing the surface barrier is plotted vs distance for the three different positions of the Ga layer studied in this paper. The positions of the atomic planes are shown by arrows, and the asymptotic vacuum level indicated in the upper right-hand corner.

The IP of a surface is made up of a bulklike contribution and a surface dipole contribution. Since it is only the latter than can vary when we change the Ga-layer spacing, the change in the IP serves to determine the dynamic effective charge e^* that resides on the surface plane. The change Δ in the IP is related to the effective surface charge e^* through the relationship

$$\Delta(d) = \frac{4\pi}{A} \int_0^d dx\, e^*(x), \tag{4.1}$$

where d is the distance the surface plane has moved, A is the area of the surface unit cell, and allowance has been made for the dependence of e^* on the GaAs bond length (atomic units are used throughout). Note that (4.1) implies that e^* contains the bare Ga charge as well as its screening cloud.

From Table II we see that the IP increases with decreasing planar spacing, implying a positive sign for the effective charge e^*. The effective charge is a strong function of distance, with the average value of e^* for the expansion equal to 0.27, and for the contraction 0.11. The effective

TABLE II. Ionization potential (IP), surface-Fermi level E_F (measured from the valence-band maximum), and the Ga effective charge e^* are listed for the three geometries studied. Note that the upper (lower) e^* value quoted corresponds to an average value between the ideal geometry $d = 10.68$ and the relaxed (expanded) geometries $d = 10.30$ (11.00) in atomic units.

d	IP	E_F	e^*
10.30	0.229	0.32	0.12
10.68	0.219	0.021	
11.00	0.200	0.009	0.270

surface charge at the ideal spacing, determined by quadratic interpolation is 0.20. This is close to that found in bulk GaAs from a study of the piezoelectric and vibrational properties[19,20] of the bulk material, although the definition of bulk effective charge is usually made in such a way as to maintain constant bond length between the dissimilar atoms.[19] The dependence of e^* on Ga-As separation is also qualitatively similar to that obtained from the bulk material[19]; with increasing separation, the electronegativity difference between the Ga and As causes more charge to flow between the atoms so that their bond becomes effectively more ionic. The reverse occurs as the two atoms approach each other, tending toward the metallic limit in which there is no effective charge on either atom.

While the IP changes significantly with geometry, this is less true of the work function. The reason for this is easily understood. As the IP increases, the changing surface barrier pushes the partially occupied dangling-bond band upward in energy almost rigidly, causing the Fermi level E_F within this band to track with the IP. This has the effect of leaving the work function relatively insensitive to normal displacements of the surface atoms. The absolute value of the IP varied from 6.2 eV for the relaxed geometry to 5.4 eV for the expanded geometry, with E_F undergoing a compensating change from 0.87 to 0.24 eV. Recent measurements on the $c(8\times 2)$ GaAs (100) face[21] place the IP near 5.15 eV, with the surface Fermi level at 0.35 eV measured from the valence-band maximum. The calculated values of IP and E_F are consistent with these measurements for the reconstructed surface if allowance is made for the theoretically demonstrated sensitivity of IP and E_F to atomic motion.

V. SURFACE RECONSTRUCTION

In this final section we focus on the nature and origin of the surface reconstructions that occur on the (100) face of GaAs. An experimental survey of these structures has recently been made by Cho.[7] Some of the patterns are believed associated with partial monolayers of either Ga or As, arranged in a superlattice, others, the $c(8\times 2)$ and (4×2), are intrinsic to the defect-free or stoichiometric surface.

Why should these surfaces reconstruct? One explanation, due to Nosker *et al.*,[13] invokes electrostatic considerations. It views the crystal as composed of ionic constituents and argues that if these are arranged in alternating planes, as is the case for GaAs(100), large internal electric fields will build up. They cancel these by removing a certain fraction of the positive ions from one face and negative ions from the other [$\frac{1}{4}$ for the (111) surface], leaving a field-free interior. The superlattice is produced by having the vacancies rearrange themselves in a minimum energy configuration.

The difficulty with this argument is that the atoms are neutral entities and have ionic character only because neighboring atoms have a different electronegativity. On that basis one could equally well argue that the surface atoms on GaAs have less effective charge (fewer neighbors to donate charge to) and it is this effect that produces a field-free internal region. What happens to the surface atoms at the quantum level is that two of their bonds have been severed, and the charge that the Ga atom would have donated to the As-Ga bonds now goes into the dangling-bond surface state band. It is the charge in this band that serves to assure a neutral surface and a field-free interior region. This possibility was recognized by Nosker *et al.*,[13] but dismissed for III-V polar semiconductor surfaces for reasons that the present authors fail to appreciate.

If the surface is stoichiometric what causes it to reconstruct? We believe the reasons lie in the metallic character of the GaAs (100) surface. The system energetically would prefer to have an insulating surface, and distortions will occur in order to produce such a surface. Given this as a working hypothesis one can make a number of statements about the nature of the reconstruction. The dangling bond band is $\frac{3}{4}$ occupied. In order to accommodate these "metallic" electrons in completely filled bands the surface unit cell of the reconstructed surface must have an area $4n$ (n integer) times larger than the unit cell of the substrate. [Both the $c(8\times 2)$ and (4×2) reconstruction satisfy this criteria.] If the distortions are large, so that the surface bands derived from the dangling bond bands are completely shifted in energy, it is difficult to predict the precise form of the reconstruction. If they are relatively weak one can relate them to so-called Fermi-surface instabilities[14] such as those now known to characterize the reconstructed phases in bulk-layered compounds.[22] We consider first the possibility the distortions are weak.

The conditions favorable to Fermi-surface instabilities are an ability to achieve nesting or congruence between different portions of the Fermi surface and a high density of states there so that the energy-band distortions introduced will have an appreciable effect on lowering the surface energy. Both conditions are fulfilled for GaAs(100), as we shall see below. We focus on the ideal geometry and use the interpolation formula (3.1) to represent the E-vs-$\vec{k}_s$ relation (for the dangling-

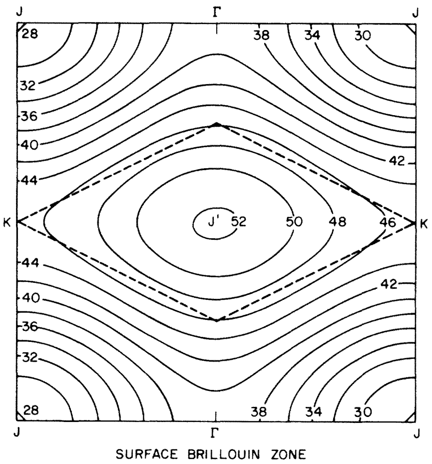

FIG. 12. Contours of constant energy for the dangling-bond band are plotted within the surface Brillouin zone. The energy of the state has been scaled by 10^3 and units are hartrees. The surface Fermi level is at contour 46, and the dashed diamond-shaped figure indicates the ideal "perfectly nesting" Fermi surface.

bond band) throughout the surface Brillouin zone. The parameters of that fit are $\epsilon_{00} = 0.0413$, $2\epsilon_{10} = 0.0045$, $2\epsilon_{01} = -0.0077$, $4\epsilon_{11} = 0.0012$. To reveal the nesting properties of the two-dimensional Fermi surface for this band we have plotted in Fig. 12 contours of constant energy for the dangling-bond band within the surface Brillouin zone. The Fermi level is located on contour 46, corresponding to $\frac{3}{4}$ occupancy of the band, and we have drawn in a dashed diamond shaped "perfectly nesting" Fermi surface. The energy scale is 0.001 hartree, and the nesting characteristic of the surface is seen to be excellent. The density of states at E_F is also high, lying essentially on a logarithmic singularity in the two-dimensional density of states. That state density is plotted in Fig. 13 on a fine-scale histogram constructed from the interpolated fit discussed above.

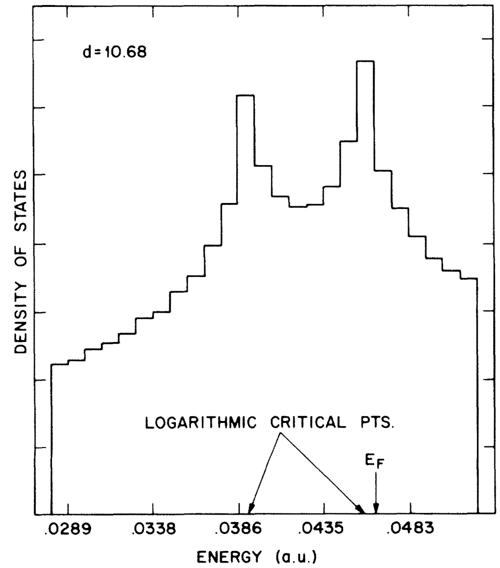

FIG. 13. Density of states for the dangling-bond band is plotted vs energy for the Ga surface layer in its ideal position. The location of analytically determined logarithmic singularities are shown by arrows, as is the position of the surface Fermi level E_F.

The nesting vector for the Fermi surface shown in Fig. 12 extends from $\frac{1}{2}J'$ to K and results in a real space oblique 2×2 superlattice shown in Fig. 14. The oblique 2×2 unit cell contains four surface atoms that have moved forming a basic unit which we shall refer to as a tetramer. The displacements shown in Fig. 14 are meant only to be suggestive of the distortions that may occur to form the tetramer.

This unit cell, which can be characterized as $c(2\times 4)$, does not, however, correspond to the experimentally attained $c(8\times 2)$ and (4×2) structures. The main problem is not the difference in size between the cell predicted on the basis of a Fermi-surface instability and that measured. That could easily be understood in terms of second layer displacements that would render adjacent tetramers inequivalent, thereby enlarging the surface unit cell. Rather, the difficulty lies in the fact that the second order reconstruction predicted by the Fermi surface instability is at right angles to that measured.

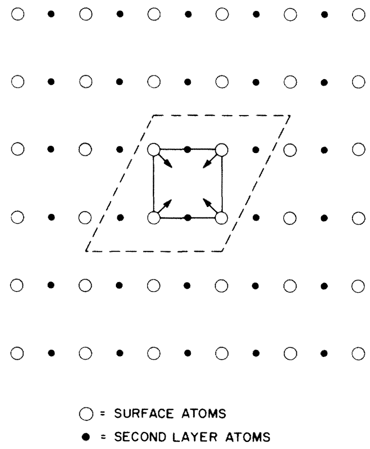

FIG. 14. Position of surface Ga atoms (open circles) and second layer As atoms (dots) are shown for the ideal unreconstructed surface. The unit cell for that surface is shown as a solid line, while the dashed rhombus is the unit cell of the oblique 2×2 or c(2×4) surface. The motion of surface atoms that would cause a c(2×4) unit cell are shown by arrows.

Consider the possibility that the distortions involved in the reconstruction are massive, in which case simple Fermi surface arguments would be inappropriate. Based on the strength of the higher-order diffraction spots (which are comparable to the primary spots in intensity), the close spectral correspondence we have found between GaAs(100) and Si(100) (which does undergo massive distortions), and the failure of the Fermi-surface argument to predict the correct structure, it is likely that GaAs has undergone structural distortions on a sizable scale.

Reasoning in analogy to Si(100), one would expect surface pairing or dimerization to occur. This causes a doubling of the periodicity along the broken bond direction, which is in accord with that seen on GaAs. However, unlike Si(100), the dimerization cannot produce a gap between the occupied and unoccupied surface-state bands. On the contrary, charge neutrality requires the surface-state bands in the now reconstructed 2 × 1 Brillouin zone to accommodate an odd number of electrons. We believe that it is this fact that accounts for the additional fourth-order reconstruction that is so prominent on GaAs(100) and that is essentially absent on Si(100).[23,24]

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