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Electronic structure of the Al-GaAs(110) surface chemisorption system

J. R. Chelikowsky*
Department of Physics, Institute of Theoretical Science, University of Oregon, Eugene, Oregon 97403
and Xerox Palo Alto Research Centers, Palo Alto, California 94304

D. J. Chadi
Xerox Palo Alto Research Centers, Palo Alto, California 94304

Marvin L. Cohen
Department of Physics, University of California, Berkeley, California 94720
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
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The electronic structure of an ordered half-monolayer coverage of Al on the GaAs(110) surface is examined using a self-consistent pseudopotential approach. We find the surface geometry in which the Al adatom is chemisorbed to a substrate Ga atom is the one most compatible with experimental and theoretical considerations. Our conclusion on the chemisorption site is in agreement with recent theoretical calculations employing quantum-chemical cluster methods, but is in contrast with previous band calculations which have suggested an anion chemisorption site. In addition, we assert the surface dipole of Al chemisorbed on *intrinsic* GaAs is *positive*; some previous interpretations have suggested that this dipole is negative.

I. INTRODUCTION

The technological importance of Schottky barriers in solid-state devices has led to numerous investigations of the electronic states of metal overlayers on semiconductor substrates.[1-12] Here we will concentrate on the (110) surface of GaAs and examine the nature of the chemical bonding which occurs between the metal overlayer and the semiconductor substrate. Specifically, we hope to examine the interactions induced by one-half monolayer coverage of Al on the GaAs surface. While the electronic structure of the Al-GaAs junction has been previously examined,[13-16] certain aspects of this system remain unclear. For example, a clear description of the adatom-induced states does not exist. The chemisorption site preference has been controversial. And, the most definitive study of the surface geometry[16] yields a sign for the surface dipole which is in apparent contradiction to experiment.

Before we can address these aspects of the Al-GaAs(110) surface, we must obtain an accurate description of the surface geometry. While the clean surface of GaAs is fairly well understood, the chemisorption site for Al on GaAs is not. Low-energy-electron-diffraction (LEED) analyses for Al chemisorbed on the GaAs surface are difficult to perform and have yet to yield a definitive structure for the metal-semiconductor system. Therefore, it is fortunate that we have other means at our disposal for obtaining structural information.

One way of proceeding is to consider a specific arrangement of surface atoms[17] and perform a detailed electronic-structure calculation.[18,19] If we have reliable experimental data, we can compare the measured surface-state spectrum with the calculated one. Sometimes we may rule out structures in this fashion. However, since the method is indirect, an unambiguous determination is often not possible. Other methods, e.g., total energy calculations,[20,21] do not require experimental input and can yield results as accurate as those from the best LEED analyses.[17] Unfortunately, *ab initio* total energy calculations for solid surfaces are formidable and only a few pioneering calculations exist.[21] Hence, two different tacks have been pursued. One is a solid-state-physics approach and involves a semiempirical computation of total energies for different structures.[20] The method is highly accurate for intrinsic semiconductor surfaces, but it is nontrivial to apply it to metal-semiconductor systems. The other approach has its origin in quantum chemistry.[22] Within this approach, a cluster of atoms modeled to represent a specific surface is considered and total energies of the cluster are calculated for different adsorbate or surface configurations. While the method is applicable for the problem of determining bond lengths and bond angles, some solid-state properties cannot be obtained. These properties include all band-related features, e.g., band dispersions and bandwidths. In the present effort, we shall rely on total energy studies for structural determinations and we will concentrate on

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solid-state aspects of Al chemisorbed on the GaAs substrate.

Even with a fixed geometry, one might raise questions about obtaining information on metal-semiconductor interfaces by considering a monolayer or submonolayer coverage of the metal adatom. While this question is important in principle, in practice it has been observed for metal-semiconductor junctions that most fundamental properties of the interface are determined before multilayer coverage is achieved.[5,9] From a formal point of view, it is likely that a microscopic understanding of the monolayer or submonolayer case is necessary before multilayer overlayer properties can be understood. Moreover, in the submonolayer case we may ignore the long-range strain fields which can occur via lattice mismatch at the interface of a multilayer metallic film and a semiconductor substrate. Finally, unlike jellium-semiconductor models[13] for the interface, within our submonolayer geometry we are able to preserve the directional nature of metal–semiconductor bonds.

II. SURFACE GEOMETRY

Perhaps the earliest electronic-structure calculation for Al on GaAs was performed by Chelikowsky, Louie, and Cohen (CLC).[14] These authors considered the case of a half-monolayer of Al chemisorbed on GaAs and assumed that the Al bonded to the substrate at an anion site. The CLC work was based, in part, on the experimental work of Rowe *et al.*,[1] which suggested the anion site was preferred over the cation site for metallic adsorbates. In solving for the electronic structure of the GaAs(110)-Al system, CLC used a self-consistent pseudopotential method. The essential results of the CLC calculation are that: (a) extrinsic adatom states are introduced into the band gap, (b) the adatom states pin the Fermi level, and (c) intrinsic anion surface states are removed and strong adatom states are introduced approximately 4.5 eV below the valence-band maximum. While these results appear compatible with experimental measurements, there are some questions which remained unanswered. These questions involve the exact position of the Fermi level, the pinning mechanism, the sign of the surface dipole, and the possibility of other surface geometries.

A more recent study to address some of these questions is that of Mele and Joannopoulos (MJ).[15] In the MJ work, a parametrized tight-binding scheme was used to solve for the electronic structure. Parameters were obtained by fitting the bulk valence bands of GaAs and AlAs. Owing to the simplicity of the tight-binding approach, it was possible to consider several models for the surface geometry. Based on the observed chemical shifts, photoemission data, work-function data, and Fermi-level pinning measurements, MJ proposed that an exchange reaction would occur at the surface between Al and Ga atoms. Moreover, they suggested a "counter relaxation" of the surface which, unlike the intrinsic surface, had the cations moving outward from the surface plane and the anions inward. In their calculation, MJ attached great emphasis to the photoemission data which place an extrinsic state 4–5 eV below the valence-band maximum. MJ found that the position of this state was sensitive to the identity of the onefold-coordinated cation species on the surface. They concluded that an Al-Ga exchange reaction took place on the surface with the Ga becoming onefold coordinated. For the counter relaxed exchange geometry, MJ could account for the sign of the experimentally determined surface dipole. However, as we shall discuss in detail, we question their interpretation of the surface dipole.

In this work, we examine an alternative model for the chemisorption of Al on the GaAs surface. Instead of assuming that Al binds to an anion site, we place it over a cation site. This geometry was first suggested on the basis of a quantum-chemical calculation performed by Barton *et al.*[16] They considered a small molecular cluster to replicate the GaAs surface and were able to explore several surface geometries. Although we agree with the general features of their bonding geometry, we question some of the details of their calculation. Because of the small size of their cluster, we believe some significant Al-As interactions may have been omitted from their calculation. Explicitly, if the Ga dangling bonds are capped off by Al, their cluster does *not* contain the nearest-neighbor Al-As interactions. [For As atoms placed at the corners of the (110) unit cell, Al interactions with only half of the As atoms were considered; i.e., the dashed Al-As interactions in Fig. 1 were not considered.] Moreover, their assertion of employing a threefold chemisorption site is not precisely correct. Their calculated bond lengths place the Al slightly off the dangling-bond direction and not in a true threefold site.

With the above reservations, we have employed a cation chemisorption site for Al as suggested by Barton *et al.*[16] The chief modification we have made on their geometry is to rotate the Al to align it with the true dangling-bond direction. We have made this alteration on the basis of solid-state energy minimization calculations. In

Fig. 1, we display our geometry. It consists of an Al–Ga bond length of 2.95 Å with the Al placed along a vector which forms equal angles with the bonding directions of the substrate Ga to its three substrate As nearest neighbors. We take the substrate to be relaxed by a rotation which moves the As atoms outward and the Ga atoms inward. With respect to the surface plane, this corresponds to a 21° rotation.[16] As in the Barton *et al.*, model, we do not allow bond-length changes in the substrate. While we expect our geometry to be more optimal than the Barton *et al.* model,[16] we do not expect major modifications of the electronic structure.

III. METHOD OF CALCULATION

In order to calculate the electronic structure of Al chemisorbed on GaAs, we invoke two computational simplifications: pseudopotentials and a supercell configuration.[19,23] The supercell configuration is used to handle the lact of periodicity perpendicular to the surface. We consider a supercell consisting of a seven-layer slab of GaAs separated by five layers of vacuum from the neighboring slab. Each side of the slab exposes a (110) surface with Al chemisorbed at the cation site.

With the supercell so fixed, the remaining problem is the determination of a self-consistent pseudopotential. As in previous studies, we proceed by considering ionic pseudopotentials for Al^{3+}, Ga^{3+}, and As^{5+}. Our potentials were fixed by spectroscopic data and bulk-band calculations; they contain *no* surface information.[24] These potentials yield a bulk GaAs spectrum which is significantly more accurate than is attainable through the use of *ab initio* pseudopotentials. It is quite evident that with the deficiencies inherent in available local density expressions for the effective exchange-correlation potentials, we are forced to choose between potentials which give an accurate bulk spectrum or an accurate atomic spectrum, but not both. We feel our potentials which accurately reflect the bulk spectrum for GaAs are sufficient for the purposes of this work.

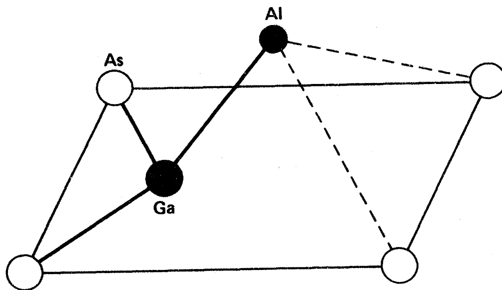

FIG. 1. Surface geometry of Al chemisorbed on the (110) surface of GaAs.

We write the total crystalline potential as

$$V(\vec{r}) = \sum_{m,\alpha} V^{\alpha}_{\text{ion}}(\vec{r} - \vec{R}_m - \vec{\tau}_\alpha) + V_{\text{scr}}(\vec{r}), \qquad (1)$$

where V^{α}_{ion} is the ionic pseudopotential for the αth atomic species, V_{scr} is the screening potential in the Hartree-Fock-Slater sense, the sum is over lattice vectors $\vec{R}_m$, and $\vec{\tau}_\alpha$ gives the position of the αth ion in the unit cell.

To solve the wave equation for this potential we find the eigenvalues of the secular equation

$$|H_{\vec{G},\vec{G}'}(\vec{k}) - E(\vec{k})\delta_{\vec{G},\vec{G}'}| = 0$$

with

$$H_{\vec{G},\vec{G}'}(\vec{k}) = (\hbar^2/2m)(\vec{k}+\vec{G})^2\delta_{\vec{G},\vec{G}'} + \sum_{\alpha} V^{\alpha}_{\text{ion}}(\vec{G}-\vec{G}')S^{\alpha}(\vec{G}-\vec{G}')S^{\alpha}(\vec{G}-\vec{G}') + V_{\text{scr}}(\vec{G}-\vec{G}'),$$

where $\vec{k}$ is the wave vector, $\vec{G}$ is a reciprocal-lattice vector, and $S^{\alpha}(\vec{G})$ is the structure factor for the αth species. $V^{\alpha}_{\text{ion}}(\vec{G})$ and $V_{\text{scr}}(\vec{G})$ are the Fourier transforms of the ionic pseudopotential and screening potentials, respectively. The Fourier transform of the ionic potential was fit to a four-parameter curve of the form

$$V_{\text{ion}}(\vec{q}) = (a_1/q^2)[\cos(a_2 q) + a_3]\exp(a_4 q^4). \qquad (3)$$

The parameters a_i are given in Table I.

As in any self-consistent calculation, we initiate the process by an approximate potential. With this potential, a charge density is calculated from the eigenfunctions. Once the valence charge density, $\rho(\vec{r})$, is known in terms of its Fourier components $\rho(\vec{G})$, the screening potentials can be easily evaluated. This potential consists of two parts: V_H, the Hartree potential and V_{xc}, the exchange-correlation local potential. V_H is defined by Poisson's equation:

$$V_H(\vec{G}) = 4\pi e\rho(\vec{G})/|G|^2. \qquad (4)$$

TABLE I. Ionic pseudopotential parameters as in Eq. (3). The normalization volume is $\Omega_a = 236.9$ a.u. The Ga^{3+} potential is valid only for $q < 3$ a.u.

Parameter	Al^{3+}	Ga^{3+}	As^{5+}
a_1	−2.4482	−0.219 96	−0.4548
a_2	0.376	1.3305	1.044 80
a_3	−0.870	0.4466	0.166 20
a_4	−0.0824	0.007 05	−0.015 12

The exchange-correlation term is of the form

$$V_{xc}(\vec{G}) = -\alpha(3/2\pi)(3\pi^2)^{1/3}e^{5/3}\rho^{1/3}(\vec{G}), \quad (5)$$

where $\rho^{1/3}$ is the Fourier transform of the cube root of the pseudo-charge-density in units of $(e/\Omega)^{1/3}$ and α is taken to be 0.8. The computational details of determining the charge densities and diagonalizing the matrix in Eq. (2) are identical to previous work on the intrinsic GaAs surface.[19]

Finally, we will make use of a local-density-of-states analysis. We define this density of states by

$$N_L(E) = \sum_{\vec{k}_{\parallel}, n} P_{\vec{k}_{\parallel}}(L,n)\delta(E - E_n(\vec{k}_{\parallel})) \quad (6)$$

where

$$P_{\vec{k}_{\parallel}}(L,n) = \int_L |\Psi_{\vec{k}_{\parallel},n}(r)|^2 d^3r, \quad (7)$$

$\Psi_{\vec{k}_{\parallel},n}$ is the eigenfunction of the nth band at $\vec{k}_{\parallel}$, L is an index referring to the region of integration. We shall concentrate on three regions: one corresponding to the bulk which we take as the center region of our slab, one corresponding to the first layer of the substrate, and one corresponding to the chemisorbed overlayer.

IV. RESULTS: SURFACE-STATE SPECTROSCOPY AND CHARGE-DENSITY ANALYSIS

In Fig. 2, we present the total pseudo-charge-density plotted in a plane perpendicular to the surface. Two planes are displayed: one plane passes through the Al adatom, the other through the outermost As atom. The latter resembles the pseudo-charge-density for the free GaAs(110) surface.[19] This results from the cation chemisorption site used in our calculations and is not surprising. With respect to the former plane, the Al-Ga charge-density configuration is difficult to characterize. Perhaps, the nature of the bonding can be best described as "weakly covalent." Analysis of the states which contribute to the density in this region support this characterization. The two states, which dominate the charge density along the Al–Ga bond, include an Al s state which places most of the charge density in a nonbonding configuration and a Ga-Al p-state interaction which places the remaining charge density in a covalent bond configuration. If the Al–Ga bond were shortened, the charge density would become more covalent. However, there is indirect evidence that our bond length is appropriate. First, the bond length used is supported by the calculations of Barton *et al.*[16] Second, we estimate from chemical arguments a bond length of about 2.85 Å in accord with our

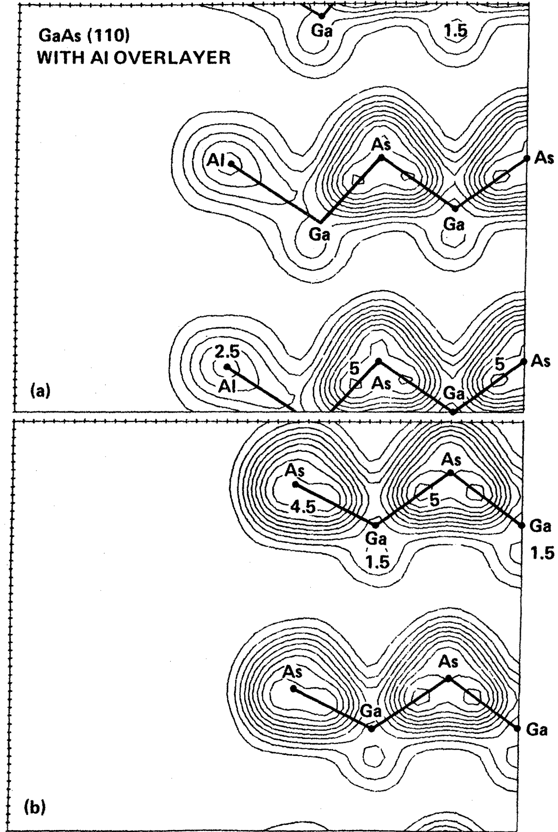

FIG. 2. Total valence pseudo-charge-density for Al chemisorbed on the GaAs(110) surface. Two planes are displayed: (a) is a $(1\bar{1}0)$ plane passing through the chemisorbed Al atom and (b) is a $(1\bar{1}0)$ plane passing through an As surface atom. The contours are spaced by units of 0.5; the normalization is one electron per unit cell. The unit cell volume is 4262.8 a.u.

model.[25] And third, we find a shorter bond length leads to a Fermi-level position in strong disagreement with experiment.

In Fig. 3, we present a projected band structure for the Al-GaAs(110) system. The prominent surface states and surface resonances are displayed. For the purposes of notation we label the anion-associated states by A_i and the cation-related states (either Al- or Ga-derived) by C_i. Not surprisingly, the anion surface features are essentially unaltered from the free GaAs surface.[19] The most tightly bound state, A_1, is s-like and derived from the lowest bulk GaAs band. The three anion-related features near the valence-band maximum, A_2, A_3, and A_4, are p-like states derived from the upper valence bands. Figuratively, we can think of these states an atomic As p states which have become nondegenerate owing to "crystal-field" effects. One set of the As-localized p states, A_2, is directed along the As–Ga

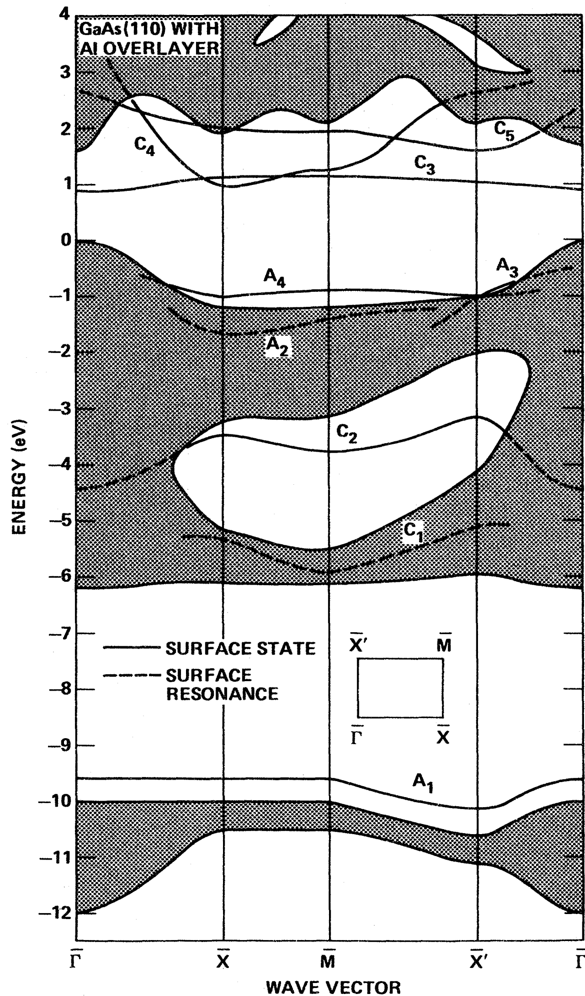

FIG. 3. Two-dimensional projected band structure for the (110) surface of GaAs. Bulk features are given by the shaded region; surface-state bands are indicated by solid lines. Resonance-surface features are indicated by dashed lines. Resonance-surface features are indicated by dashed lines. The surface bands labeled by $A_i(C_i)$ are anion (cation) localized. The energy zero is taken at the valence-band maximum.

bonds which extend inward toward the bulk. The second set, A_3, runs parallel to the surface along As–Ga bonds, and the third set, A_4, are p states which run along the As–Ga bond which has been "broken" by the creation of the surface. We do not exhibit charge-density maps for the anion-related features;they are not significantly altered from the free surface and they have been displayed elsewhere.[19]

The cation-related states can also be categorized as "s-like" or "p-like." C_1, C_2 are s-like states, with C_1 localized predominantly on the Ga and C_2 localized predominantly on the Al. We can think of the Al interacting with the substrate in a weak fashion. The Al 3s atomic state is not strongly perturbed and remains, more or less, intact to form the C_2 surface band. The Ga s-like state on the free surface is not strongly affected by the adatom and forms the C_1 band. There is some interaction between these bands, a detailed analysis indicates a "bonding-antibonding" relationship exists between them. The lower band exhibits a charge density considerably polarized along the Al–Ga bonding direction. When we shorten the Al–Ga bond length, this distinction becomes quite sharp and the charge density for the C_1 band forms a "bondlike" configuration along the Ga-Al direction. Figure 4 displays the charge-density patterns for the C_1 and C_2 bands.

The p-like cation states C_3, C_4, C_5 in the band gap are predominantly Al associated. Of the three bands, the C_3 feature is the most important as it pins the Fermi level. The C_3 band is formed by an Al–Ga bonding combination of p-like states.

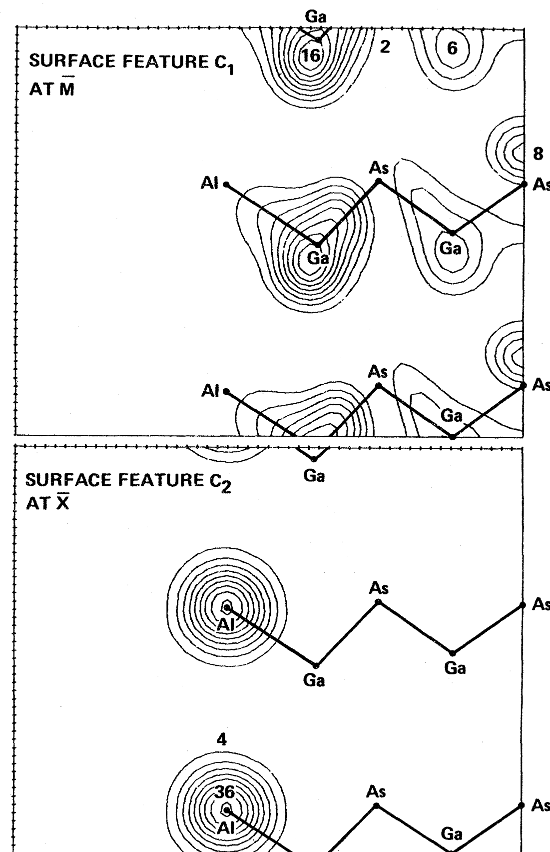

FIG. 4. Pseudo-charge-density contour maps for the cation surface features which reside below the valence-band maximum. C_1 is primarily a Ga "s-like" feature; C_2 is primarily an Al "s-like" state. Experimental measurements confirm the presence of the C_2 state (see text). Normalization of the charge is as in Fig. 2.

Essentially, an Al p state is directed along the Al–Ga bonding such that it overlaps strongly with the Ga "dangling-bond" p orbital. This is illustrated in Fig. 5. Also displayed in Fig. 5 are the charge densities for the C_4 and C_5 states. C_4, C_5 are states which correspond to p-like orbitals perpendicular to the Al–Ga bonding direction. Band C_4 actually crosses the C_3 surface band and, therefore, is partially occupied.

Figure 6 illustrates the local density of states for Al on GaAs. The bulk region is in good accord with densities of states previously calculated with bulk pseudopotentials. In addition, the convergence of the local density of states (LDOS) to a bulklike configuration[26] reassures us that our slab is suf-

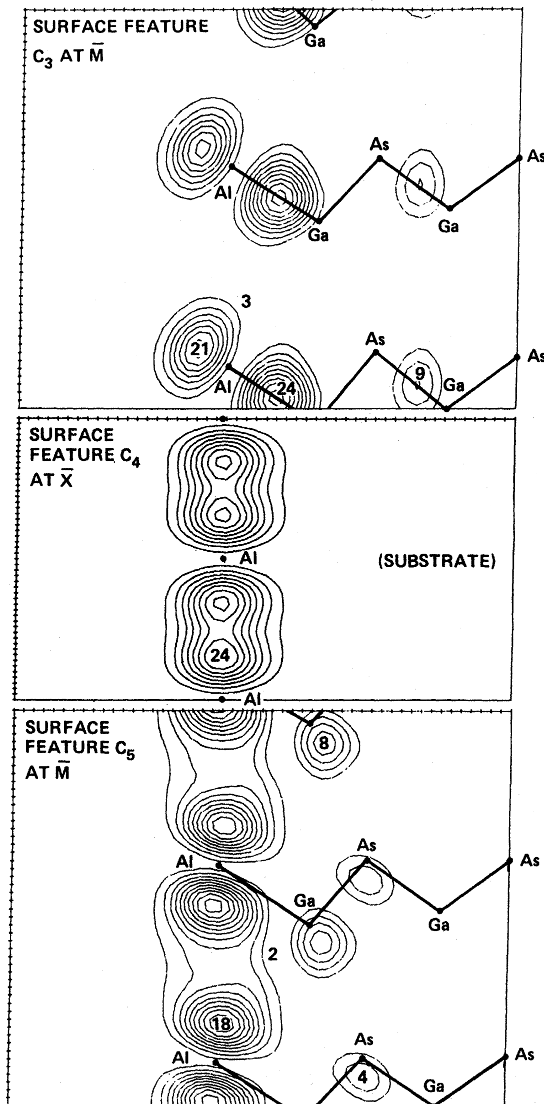

FIG. 5. Pseudo-charge-density maps for Al-induced states within the band gap of GaAs. C_3 pins the Fermi level and corresponds to an Al–Ga partially saturated bond. C_3 and C_5 are plotted in planes identical to Figs. 2 and 4. C_4 is a plane which passes through the Al atoms and is perpendicular to the plane of Fig. 2. Note the Al–Al interactions occuring for the C_4 band (also Fig. 1).

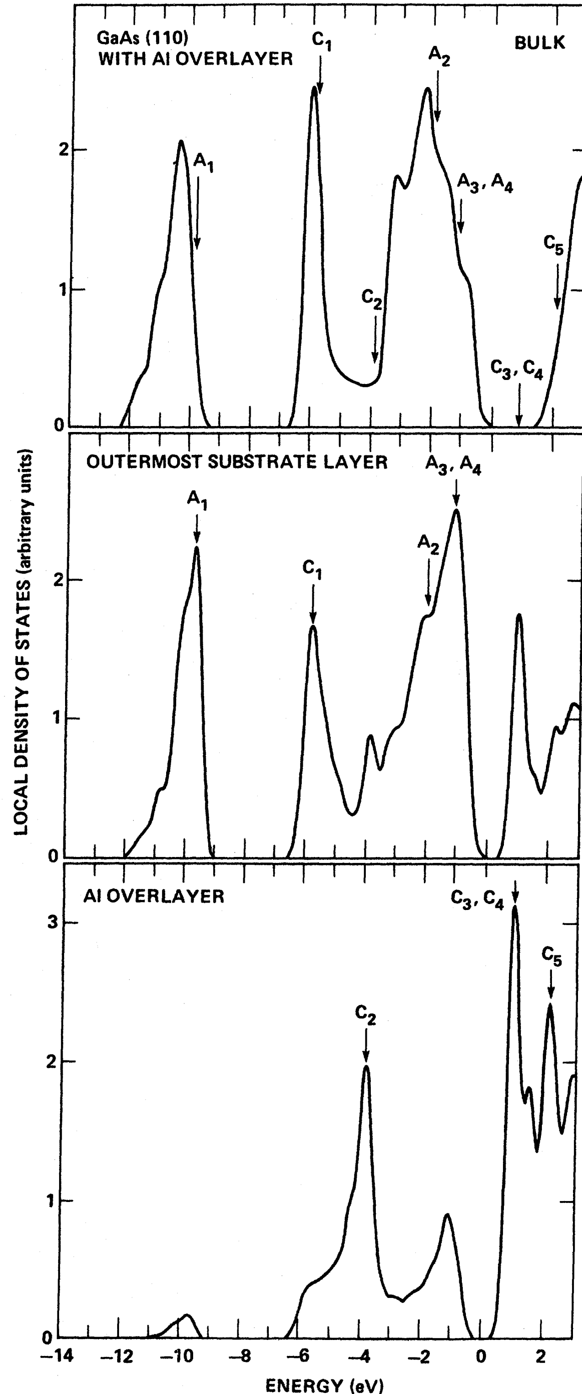

FIG. 6. Local density of states for Al chemisorbed on the (110) surface of GaAs.

ficiently thick to yield correct surface-state dispersions. The outermost layer of the substrate reflects mostly As-related features. This result is a natural outgrowth of the capping-off of only the cation dangling bonds and the rather weak interaction of the Al adatom with the substrate. The relative intensity and energy positions of the As features appear to be in good agreement with previous calculations.[19] The C_1 feature is the only significant cation feature which penetrates to the second layer. The LDOS region corresponding to the Al overlayer has a strong peak corresponding to the C_2 states below the valence-band maximum and three states within the band gap (C_3, C_4, C_5). The sharpness of the C_3 peak is a consequence of the small dispersion of this band. The Fermi level is essentially fixed by this band at approximately 1.0 eV above the valence-band maximum.

V. DISCUSSION AND COMPARISON WITH EXPERIMENT

Perhaps the strongest point we can make is fairly self-evident. Namely, the Al does not interact strongly with the substrate. If we examine our projected band structure (Fig. 3), there exist four adatom-related features (C_2, C_3, C_4, and C_5) which owe their roots to the Al 3s and 3p states. C_2, which represents the Al 3s state, is very insensitive to the Al chemisorption site. This state is not strongly altered if we place the Al adatom over the anion site, nor is it altered by small changes (~10% or less) in the Al–substrate bond-length change. In addition, the Ga 4s-like state, C_1, is not removed by the overlayer and remains intact as a surface resonance. With respect to the other adatom bands (C_3, C_4, C_5), they also retain their atomic roots. Upon adsorption, these bands appear to arise from linear combinations of $3p_x$, $3p_y$, and $3p_z$ states along and perpendicular to the Al–Ga bonding direction. If the Al interacted strongly with the GaAs substrate, we would not expect the atomic character of the Al bands to remain intact and we would expect the Ga-derived surface states to be obliterated by the Al overlayer.

Evidence for the passivity of Al adsorption on GaAs also arises from photoemission measurements. Bachrach *et al.*,[11] have examined the clean GaAs(110) surface and the surface after deposition of Al adatoms. In Fig. 7, we display the photoemission measurements and compare them to a calculated LDOS difference spectrum. The difference spectrum was obtained by subtracting the bulk LDOS spectrum from the Al overlayer LDOS spectrum. Our calculation and experiment indicate that below the valence-band

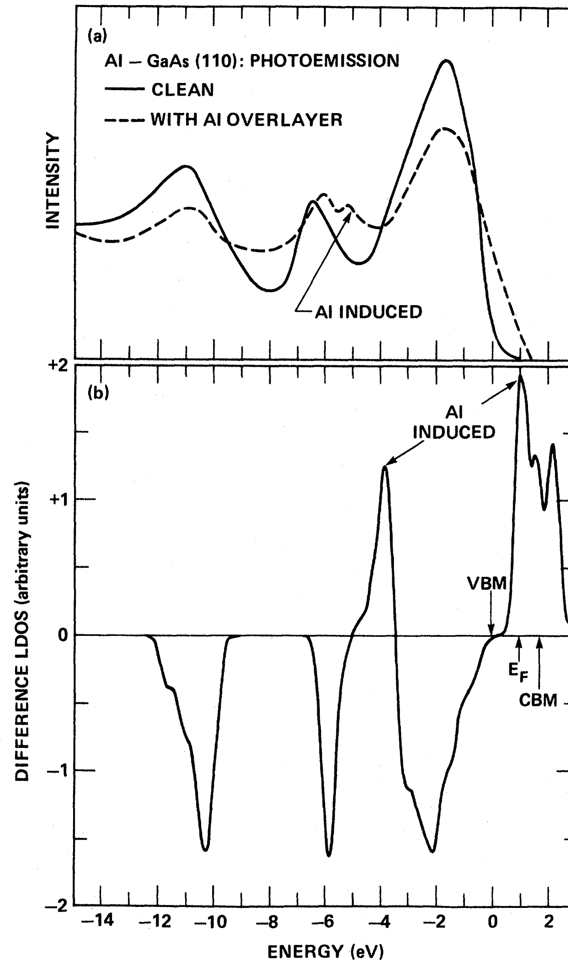

FIG. 7. (a) Experimental photoemission spectrum for the clean GaAs(110) surface and for the (110) surface after deposition of approximately one monolayer of Al from Ref. 11. (b) Calculated difference of the local density of states for Al chemisorbed on the (110) surface of GaAs. A positive contribution indicates an Al-induced feature. Only one strong Al feature occurs below the valence-band maximum. This result is confirmed by the experimental curve. Surface photovoltage measurements indicate the presence of Al-induced states within the band gap (Ref. 12). The positions of the valence-band maximum (VBM), the conduction-band minimum (CBM), and the Fermi level are indicated in the figure.

maximum, only one strong photoemission feature appears under the exposure of GaAs to Al. This feature appears approximately 5 eV below the valence-band maximum and is in accord with our calculated C_2 peak. Above the valence-band maximum we find the Al adatom p-like states. Since the Fermi level resides within the C_3 band, we might expect some contribution from this sharp level. No evidence for this assertion exists in the photoemission work and, to date, all one-

electron theories make this unfulfilled prediction. However, it is possible that matrix-element effects, which have not been included in our analysis, may play a role in the suppression of emission from the gap state. Our speculation is reinforced by a surface-photovoltage-spectroscopy study by Brillson *et al.*[12] For submonolayer coverage, they find adatom-induced states 0.6–0.7 eV below the conduction-band edge. Thus, we do have evidence for the Al-induced states (C_3, C_4) which lie above the valence-band maximum. From Fig. 7, the position of our calculated states in a LDOS difference spectrum occur approximately 0.5 eV below the conduction-band edge in good agreement with the surface-photovoltage measurements.

At this point, we should contrast our LDOS work with the anion site models of CLC (Ref. 14) and MJ (Ref. 15). In the anion model, with one notable exception, strong Al-induced features occur in the approximate positions we have calculated. The exception occurs near the valence-band maximum; here, anion site models find an Al-As adatom state. There is no experimental evidence for this spectral feature, and we feel this significant discrepancy tends to cast additional doubt on anion site geometries for the Al adatom. In our cation site model, we expect no significant contributions to the photoemission spectrum in this region and we expect no significant alteration of the anion surface spectral features from the free surface configuration.

Another feature of the photoemission which merits attention is the relative separation of the bulk peak at approximately −7 eV and the adatom-induced peak at −5 eV. Mele and Joannopoulos[15] suggest that the separation between the two peaks is a fundamental aspect in favor of an exchange reaction at the surface. However, we achieve a separation of about 2 eV without resorting to an Al and Ga exchange.[27] We note that, in the early stages of deposition, an exchange reaction appears difficult to rationalize. Since the Ga substrate atom is threefold coordinated, the exchange reaction would involve the breaking of three bonds and would be expected to have an appreciable activation barrier.

Experimental data beyond photoemission are available on the Al-GaAs(110) system. In particular, Brillson[8] has performed measurements to determine the magnitude of the surface-induced dipole. He concludes that the surface dipole is approximately $-0.34e$ Å/atom. The sign of this dipole implies that the overlayer is more negatively charged than the substrate layers below are. We find this result surprising as it disagrees with our calculation and that of Barton *et al.*[16] An examination of our charge-density map (Fig. 2) indicates that the charge density around the Al atom is polarized inward toward the substrate; the form of the charge density is imcompatible with a negative dipole.

Although we have no reason to question Brillson's measurements,[8] we do question the interpretation of his results which associate the negative dipole with the *intrinsic* properties of the Al-GaAs system. If Al were more electronegative than the GaAs substrate, then we would expect charge flow from the substrate to the Al overlayer. One common measure of electronegativity is the work function of the material; the larger the work function, the larger is the electronegativity.[28] In Brillson's study,[8] owing to the n-type sample used the work function of Al exceeds that of GaAs. If the measured dipole is not intrinsic but arises from band bending, then it is not surprising that he finds a flow of charge from GaAs to Al. However, the GaAs work function is dependent upon doping levels. We may alter the work function of GaAs by nearly 1.5 eV, if we pass from an n-type sample to a p-type sample. For a p-type sample, we expect a larger work function for GaAs than Al and we *predict* for p-type GaAs that the measured (extrinsic) surface dipole will not be negative, but will be positive. Thus, we assert that the surface dipole measured by Brillson is not an intrinsic property of Al on GaAs, but is dependent on whether the substrate is n type or p type. For an intrinsic GaAs, we expect, on the basis of our work, to find a positive dipole.

Only one theoretical study, that of Mele and Joannopoulos,[15] has achieved a predicted negative dipole. They find a charge transfer from the more electronegative As to the less electronegative Ga. This is a direct consequence of the counter-relaxed geometry used in their calculation. This geometry raises the energy of the As orbitals relative to the Ga orbital and induces charge transfer away from the As. Since the preponderance of charge in the substrate resides in As-derived orbitals, it is difficult to see how a counter-relaxed geometry could result in a lowering of the total energy of the system.

Another experimental source of information on the Al-GaAs(110) system comes from core-level measurements of the chemical shifts.[9,11] At low coverages of Al, the Al $2p$ moves to a stronger binding energy, the Ga $3d$ moves to a weaker binding energy, and the As $3d$ states move in an ambiguous fashion. These shifts can be interpreted as removing charge from the Al and increasing charge on the Ga. Within our calculation, the Al shift is fairly apparent; the Ga shift

is not. Consider the charge density in Fig. 2. The Al charge is decidedly polarized toward the substrate. On the basis of Figs. 4 and 5, we see Al charge has been transferred from the Al site to the bond site. This transfer is in accord with the chemical shift observed; however, from our charge densities it is difficult to quantify the Ga charge density. Unfortunately, by their very nature, pseudopotentials eliminate core states and, hence, prohibit a precise calculation of chemical shifts.

Finally, while we are not in a position to calculate total energies, we can make some germane comments on which chemisorption site the Al atom should find energetically favorable. Our comments are similar to those made by Barton *et al.*[16] If we examine the pseudopotential calculations for intrinsic GaAs, we find for all the geometries studied (relaxed, ideal) a doubly-occupied anion dangling bond and an empty cation dangling-bond state. Since the As dangling bonds are saturated "nonbonding" orbitals, they are basically inert. If we place an Al atom over the As orbitals, we expect the Al valence electrons to avoid overlap with the As orbitals. This is the configuration found in the pseudopotential work on anion site adsorption.[14] We find the Al $3s^2$ electrons remain inert and essentially atomiclike. The Al $3p$ electron deposits itself in a p orbital running parallel to the surface as opposed to interacting with the substrate. The charge-density configuration for these states is similar to the C_4 states found for the cation site (Fig. 5) and, in the anion-site case, they pin the Fermi level. Consequently, in the anion-site-adsorption case the pinning mechanism is inherently extrinsic to the substrate. If we place the Al over the cation site, we have empty orbitals which can form bonds with the Al adatom. Again, we expect the Al $3s^2$ electrons to remain "inert," but we expect an Al–Ga bond to be composed of the Al $3p$ electron and the Ga empty orbital. Since this bond is not saturated, the Al-Ga states (C_3) pin the Fermi level. Physically we expect the Al–Ga bond to be of lower energy than the Al-Al interaction occurring in the anion site model; this is confirmed by total energy calculations.[16]

VI. CONCLUSIONS

In summary, we believe a model of cation-site chemisorption for Al on the (110) surface of GaAs is compatible with present experimental and theoretical considerations. With respect to theory, total energy calculations based on quantum-chemical techniques[16] indicate the cation site is energetically favored over the anion site. Moreover, pseudopotential charge-density analyses suggest the Al adatom interacts more strongly with the substrate when chemisorbed at the cation site as opposed to the anion site. The saturated nature of the anion site dangling bond appears to preclude significant interaction with any "electropositive" metal adatoms such as Al.

On the basis of experimental measurements involving photoemission, surface photovoltage, and chemical shift data, we find further support for the Ga site. With respect to photoemission,[11] we find only one significant Al-induced feature. This feature has been interpreted as an induced adatom Al $3s$ state. No other features, such as an Al–As bond might induce, are observed within the valence-band spectrum by photoemission measurements. Thus, the photoemission data agrees with our calculation, but not those involving anion-site chemisorption. Surface photovoltage spectroscopy[12] predicts adatom-induced states within the band gap, a result predicted on the basis of our model. Moreover, we find these states pin the Fermi level at approximately 1.0 eV above the valence-band maximum; this position is confirmed experimentally.[9] With respect to the chemical shift data,[9,11,12] we appear to be in qualitative agreement with experiment on the basis of a pseudo-charge-density examination.

One prediction of our study is that the surface dipole for Al chemisorbed on GaAs need not be negative for the intrinsic system. We feel the negative dipole as measured by Brillson[8] is a consequence of employing n-type GaAs and is not the intrinsic dipole.

Finally, consideration of a more detailed comparison with experiment must await the elimination of some deficiencies for currently available electronic-structure calculations. As an example, we have no way of quantifying effects resulting from heterogeneous deposition of Al on GaAs. From our calculations, and as has been suggested elsewhere,[29] we expect significant Al-Al interactions. These interactions are enhanced by the weakness of the Al-substrate interaction. To the extent the Al-Al interaction results in nonuniform deposition of Al on GaAs, our surface-band analysis need not be sustained by experiment.[30]

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*Present address: Exxon Research and Engineering Co., Linden, NJ 07036.

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