

Chemisorption of oxygen and aluminum on the GaAs (110) surface from *ab initio* theory

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(Received 2 November 1979; accepted 20 December 1979)

We have applied quantum chemical methods to the structure of the clean GaAs (110) surface and the chemisorption of oxygen and aluminum. We find that results for small clusters give geometries for the clean surface in agreement with those observed experimentally. We propose that an intermediate stage of oxidation would exist in which the O atom binds to a surface As. Our studies indicate that the initial site for Al chemisorbed on GaAs (110) has the Al bonded to the surface Ga. Geometries and chemical shifts are reported for both O and Al on GaAs (110). The chemical shifts are in agreement with recent experimental results.

PACS numbers: 73.20.Cw, 73.20. - r, 73.40. - c, 73.30. + y

I. INTRODUCTION

Diverse and valuable technical applications of GaAs and the large amount of materials research already completed for this compound semiconductor have made it a favorite subject for fundamental surface science studies.¹ Here we report progress in our theoretical study of the GaAs (110) surface. After a brief description of the theoretical methods, we will discuss our results for the structure of the clean surface, the initial oxidation of the perfect surface, and chemisorption of Al atoms on this surface.^{2,3}

The theoretical methods we use to study GaAs are adaptations of well established methods of quantum chemistry. Their application to semiconductors⁴ and a comparison with other approaches is available in the literature.⁵ In this section we wish only to highlight the important features of our approach.

Selecting a surface site or group of sites, we create a molecular cluster to mimic the surface chemical environment. Atoms at the edge of the cluster, which would have been connected to further atoms in the extended system, are connected to hydrogens in the molecular cluster. This prevents artificial dangling bonds at the edge of the cluster from interfering with real dangling bonds on the surface and insures proper hybridization of the cluster atoms. Figure 1 illustrates some of the clusters used in this study.

Having approximated the surface by a finite cluster allows the use of the powerful techniques of molecular quantum mechanics to provide a microscopic and quantitatively accurate model for the surface and its chemisorption chemistry.⁵ With these methods we can calculate the total energy of the cluster as a function of geometry and electronic configuration and so determine variationally the minimum energy atomic geometry and its electronic configuration. At the optimum geometry we can then evaluate local properties of the semiconductor system, such as chemical shifts of the core levels, microscopic dipole moments, and vibrational and electronic

spectra. Furthermore, one can accurately predict chemisorption bond energies by using the generalized valence bond (GVB) method and configuration interaction (CI).⁵

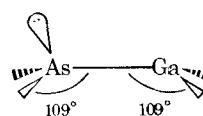
To make the approach feasible for clusters containing heavy atoms, we have replaced the filled Ga and As cores with *ab initio* effective core potentials.^{2,6,7} These are obtained in such a way that the atomic valence orbitals have the same energy and shape as the *ab initio* orbitals and such that the coulomb and exchange interactions as well as the long-range behavior are the same as for the *ab initio* orbitals.² This approach to core potentials allows us to retain *ab initio* accuracy while considering large systems.

The basis sets are double zeta or split valence (that is, two functions for each valence atomic orbital) and include *d* polarization functions unless previous calculations have shown *d* functions to be unimportant for the quantity of interest.³ Hartree-Fock (HF) and GVB wavefunctions were obtained in doing geometry searches, while GVB-CI calculations were carried out for accurate bond energies and geometries. All of the qualitative orbital diagrams are based upon the GVB wave functions.

II. CLEAN SURFACE STRUCTURE

The GaAs (110) surface consists of parallel zigzag chains of atoms, alternating Ga and As. Each surface atom has three ligands, two surface neighbors, and one neighbor in the layer below. The bulk tetrahedral bond angles about each atom are not preserved at the surface, and the surface reconstructs.⁸⁻¹³

Even with an unreconstructed surface (tetrahedral bond angles), GVB calculations show that the two dangling bonds broken at the surface coalesce into one lone pair of electrons localized on the As center,²



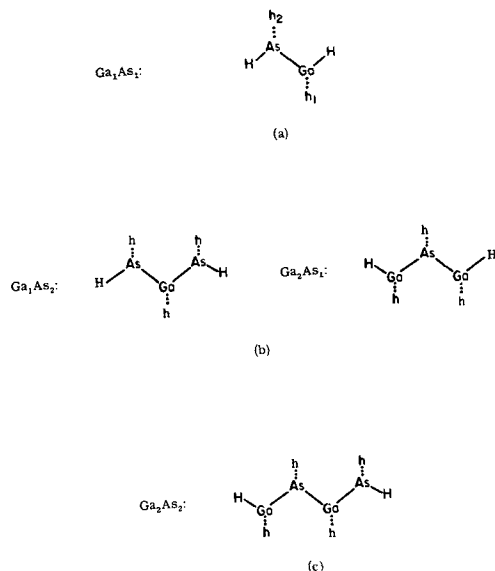


FIG. 1. Molecular models for the GaAs (110) surface. Lower case letters indicate subsurface atoms. (a) Two-site model; (b) Ga centered and As centered three-site models; (c) four-site model.

Thus the surface As has the character of a normal trivalent As with a $(4s)^2$ lone pair. Such an As atom makes bonds involving the p orbitals,²⁸ leading to bond angles near 90° (93.2° for AsH₃). Thus the surface As of GaAs (110) is expected to move so as to reduce the bond angles from tetrahedral to $\sim 93^\circ$.

The surface Ga has three bonds with no electron in the fourth valence orbital. The best configuration for such a Ga atom is planar²⁸ (e.g., GaH₃). Thus the surface Ga is expected to move toward a planar geometry (average bond angle 120°).

Indeed, our calculations, summarized in Table I.A, lead to a final reconstruction geometry quite close to that predicted by the above local valence analysis, with an average bond angle of 119.4° at the Ga and 94.9° at the As (for the Ga₂As₂

TABLE I. Surface reconstruction for GaAs (110).

A. Theoretical results				
Model	Basis functions	Δ^a (Å)	ω^b	ΔE^c (eV)
Ga ₁ As ₁	Yes	0.674	27.47°	1.250
Ga ₁ As ₁	No	0.660	26.77°	1.126
Ga ₂ As ₂	No	0.665	27.18°	1.182
B. Experimental results				
Reference	Year	Δ (Å)	ω	
9	1976	$0.64 \leq \Delta \leq 0.81$	$27^\circ \leq \omega \leq 34.8^\circ$	
10	1978	0.650	27.21°	
11	1978	0.700	26.35°	
12	1978	0.650	28.51°	
13	1979	0.650	27.34°	

^a Surface shear [difference in displacements perpendicular to the (110) surface for the As and Ga atoms].

^b Reconstruction angle.

^c Energy lowering per surface GaAs pair.

model). This confirms the dominant role of local valence hybridization in determining reconstruction. The small differences in the results for the Ga₁As₁ model and the Ga₂As₂ model (Fig. 1) indicate that the calculated quantities converge rapidly with cluster size. Comparison between the experimental results given in Table I.B and our calculations indicates that there is rather close agreement between the theoretical structure and the experimental structure as determined by low-energy electron diffraction.

III. CHEMISORPTION OF OXYGEN

Previously, we have examined the chemisorption of oxygen on the GaAs (110) surface and reported in detail the calculational results.³ In this section we reiterate the qualitative arguments to highlight the usefulness of the simple microscopic model which emerges from the calculations.

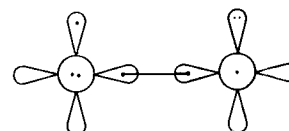
The perfect, reconstructed GaAs surface has two chemisorption sites. The Ga site has an empty $4p$ orbital over a slightly positively charged center (surrounding As ligands pull some charge off Ga). This site will tend to be an electron acceptor,



The As site has a doubly occupied lone pair and is slightly negatively charged. This site will act to donate its electron pair,

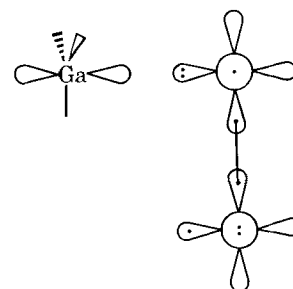


The ground state of O₂ is a triplet; in addition to the sigma bond, each atom has one singly occupied π orbital and one doubly occupied π orbital,²⁹

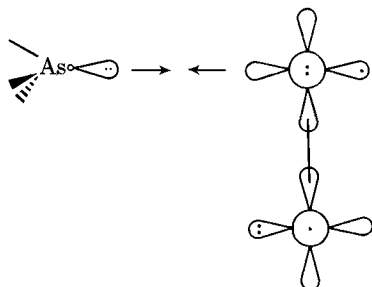


Oxygen has a high electronegativity (3.5 on the Pauling scale),¹⁴ and its appetite for electrons is not satisfied by forming dioxygen; thus O₂ is an electron acceptor. Notice, however, that O₂ can accept electrons only in its singly occupied radical orbitals, and then only one in each orbital. This restriction, resulting from the Pauli Principle, means that O₂ will generally only accept electrons from other singly occupied radical orbitals.

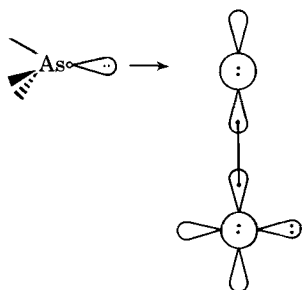
With some idea of the character of the reactants, we now consider O₂ on the GaAs surface. At the Ga site,



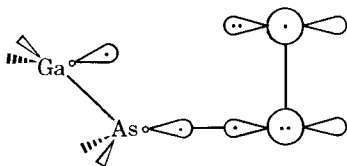
we must juxtapose two electron acceptors; this does not give a strong chemisorptive bond. At the As site,



the electron donation of As agrees with the electron accepting character of O_2 , but the Pauli Principle prevents the two electrons of the As lone pair from joining the occupied O_2 orbital. Instead, the third electron must be promoted onto the other oxygen atom,



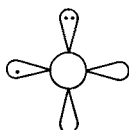
or onto the adjacent Ga,



Both of these configurations involve substantial promotion energies that are expected to be larger than the energy gained by binding the O_2 . Hence, we conclude that it is unlikely that O_2 binds to a surface As. Note that although we have only presented a chemical argument here, these ideas originate from and are consistent with the results on model systems of energy minimization of the electronic wavefunction.

From this analysis and the underlying calculations, we conclude that O_2 does not chemisorb to a perfect GaAs (110) surface. This result is consistent with the measured low sticking coefficient of O_2 on cleaved GaAs. The initial oxidation then must begin at defects, sites where O_2 may bind or be broken into atoms.^{2,3}

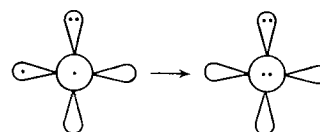
We will now consider how oxygen atoms might react with the unoxidized surface. Again, considering the perfect surface, we will examine chemisorption of O atom at the Ga and As sites but without breaking Ga-As bonds. At these sites we can bond either ground state O atom,



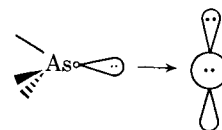
or (possibly) the first excited state of O atom,



As argued above for O_2 , the large electronegativity of O atom suggests at most a weak bond to the Ga site. In addition, the interaction of ground state O atom with As is expected to be weakly bonding since only singly occupied orbitals are available to accept electrons (just as in ${}^3\Sigma^- O_2$). However, by promoting the O atom to the singlet state we obtain a configuration with an empty p orbital prepared to accept an electron pair,



This empty p orbital can accept the electrons that As wants to donate. Our calculations show that the energy required to promote the O atom from 3P to 1D is more than compensated for by the bonding to As, leaving a strong net bond (2.2 eV for H_3AsO),



Thus, we conclude that the only way to bond oxygen to the GaAs (110) surface without disrupting Ga-As bonds involves O atom attached to As.

Experimentally, an intermediate oxidation state is observed for low exposure to oxygen.²¹ To determine if this intermediate oxide is in fact O atom bonded to As, we have computed several experimentally measurable quantities: bond length, dipole moment, vibrational frequency, and core-level energy shifts for the chemisorptive intermediate state. Note that this As=O bond is not the usual As-O single bond, as might be found in As_2O_3 . The As=O chemisorptive bond studied here has (i) a short As=O bond length, 1.63 Å (the As-O single bond length is 1.80 Å),²⁷ and (ii) a high bond-stretching frequency, ~ 125 meV (a normal As-O single bond stretch is 80 meV), and dipole moment along the As=O bond of 1.00 eÅ. These results compare favorably with the experimentally measured properties of $(H_3C)_3AsO$ which has an As=O bond length of 1.631 Å,¹⁵ a vibrational frequency of ~ 110 meV,¹⁶ and a dipole moment of 1.14 eÅ.¹⁷ Measurements of the extended x-ray absorption fine structure (EXAFS) for oxygen on GaAs yield results consistent with our value for the As-O bond length.¹⁸ An additional test would be electron energy-loss spectroscopy which should distinguish between As=O and As-O vibrational frequencies.

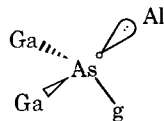
The chemical shifts, Ga ($3d$) and As ($3d$), were calculated for the As=O case. We find that the Ga ($3d$) shifts by 0.8 eV and the As ($3d$) shifts by 2.6 eV, both to higher binding energy. The experimentally reported values for the core-level shifts for the initial stage of oxidation are 0.8 eV for Ga

(3d)^{19,20} and 2.9 eV for the As (3d),^{20,21} both to higher binding energy, whereas the fully oxidized surface leads to shifts of 1.0 and 4.5 eV, respectively.²¹ This suggests that these oxidation experiments have isolated the As=O chemisorption intermediate. We have suggested several experiments³ that would examine the initial oxidation in more detail.

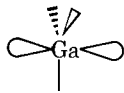
IV. CHEMISORPTION OF Al ATOMS ON GaAs

Formation of a Schottky barrier when metal is deposited on a semiconductor surface has been the center of considerable interest to experimentalists and theorists alike. Recent experimental work by Brillson *et al.*²² on submonolayer coverages of Al on GaAs has encouraged us to extend our calculations in this direction. We can report some of our results here in anticipation of the completed study to be published later.

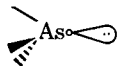
The usual assumption for chemisorption of Al (or Ga) on GaAs (110) has been^{23,24} that Al will seek unoccupied Ga lattice sites above surface As,



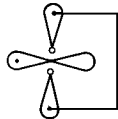
This assumption has been criticized by Goddard⁵ as inconsistent with the electronic and geometric structure of the GaAs surface revealed by our previous calculations. On the clean surface there are two sites for chemisorption, an empty *p* orbital site on Ga,



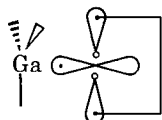
and a 4s lone-pair site on As,



We found that electronegative oxygen preferred As sites. Al, however, is not very electronegative, being 1.5 on the Pauling electronegativity scale.¹⁴ Al,



(like Ga) tends to be an electron donor, indicating that it will not be found on the electron-rich As site but rather on the Ga site, donating its 3*p* electron,



or its 3*s* electron pair

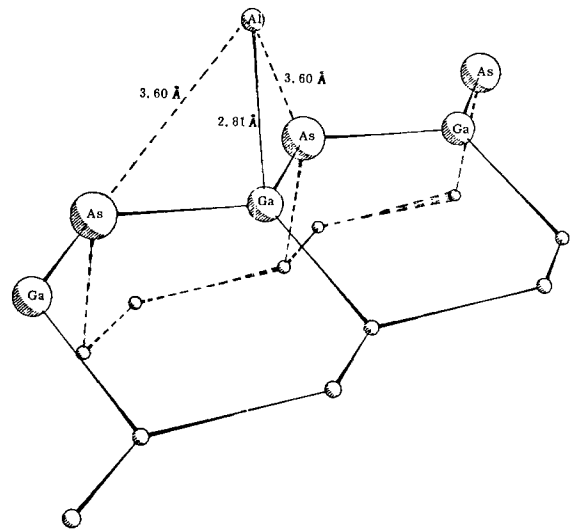
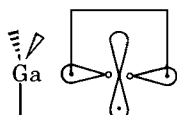


FIG. 2. Al binding to the Ga site of GaAs (110), as derived from calculations on the three-site model.

Energy minimization of the Al position over three-site models finds the Al 2.95 Å above a Ga site, tipped very slightly towards an adjacent As (3.90 Å), as shown in Fig. 2. The Al 3*p* orbital points into the Ga empty *p* orbital, as shown in Fig. 3.

Bachrach and co-workers^{22,25} have reported core-level energy shifts for room temperature deposition of small amounts of Al on cleaved GaAs samples. Their data show a state for Al on the surface with core level binding energy shifts of -0.95 eV on Ga (3*d*), +0.7 eV on Al (2*p*), and no shift²⁵ on As (3*d*). The observed charge transfer, from Al to Ga, would not be consistent with the chemisorption of Al on As, but would qualitatively be consistent with Al on Ga. Indeed, calculation of core shifts within our three-site model for Al on GaAs leads to (i) Ga 3*d* shifts to lower binding energy by 0.8 eV, and (ii) the Al 2*p* shifts to higher binding energy by 0.7 eV.³⁰ These shifts for models of Al chemisorption on GaAs agree with the experimental values for the Al deposition experiment. We calculate a 0.4 eV shifts of As 3*d* to lower binding energy, while no shift is found in the experiment.²⁵ However, the As line is much broader than the calculated shift and deconvolution of the line might lead to a shift. For multilayer coverages of Al on GaAs, the experimental studies show

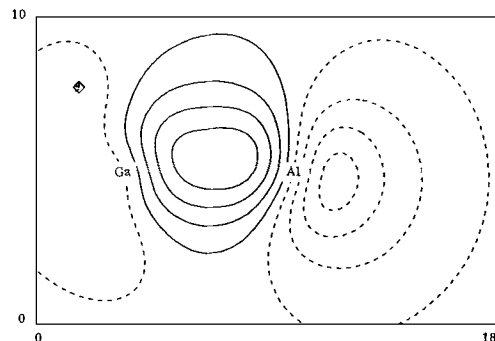


FIG. 3. The bonding state for Al binding to the Ga site of GaAs (110). The solid lines represent positive contours, the dashed lines negative contours. The contour separation is 0.03 au.

that reaction does occur at the interface, leading to both As and Ga in the overlayer; however, this does not mean that similar reactions occur for submonolayers. Mele and Joannopoulos²⁴ have proposed a particular model for the reacted surface in which the Al substitutes for a surface Ga and the displaced Ga binds tetrahedrally to a surface As. Our calculations show that this is *not* the optimum (minimum energy) geometry for the interchange reaction; the optimum geometry has the displaced Ga bonded to the interchanged Al (or to an undisplaced Ga). As a result, the interchanged configuration leads to chemical shifts (a charge shift from Ga to Al) in disagreement with experiment.²⁵

Recent experiments²² indicate that at ~ 1 monolayer the surface dipole is oriented into the surface (negative end out). Our calculations indicate that for the perfect surface, the surface dipole moment is opposite (positive end out). A possible resolution of this dilemma has been provided by Spicer who suggests^{26,31} that the measured surface dipoles can be dominated by contributions from a second dipole layer produced by charges on dopants and defects induced by the metal overlayer. A crucial experiment would be a low-temperature, submonolayer examination of Al on GaAs. By following experimentally the metallization from the initial chemisorptive states, through the monolayer stage, to the multilayer system, one should be able to provide crucial information on the nature of the monolayer and submonolayer species. Since Schottky barriers appear at submonolayer coverage,²⁶ these studies would provide information on the phenomenon of Schottky barrier formation.

V. CONCLUSION

A microscopic model of the chemistry at the GaAs (110) surface is beginning to emerge. Using methods of quantum chemistry on surface clusters, we have been able to understand the reconstruction of the clean surface. In examining the initial surface oxidation, we have eliminated O₂ as a chemisorption intermediate, but we have found a stable intermediate with O atom chemisorbed to As sites and predicted the properties of this state that would be experimentally measurable. Finally, we have begun to study the chemisorption of initial steps in forming a metal overlayer on GaAs as the start of the study of the origin of Schottky barriers.

ACKNOWLEDGMENT

This work was supported in part by a grant from the National Science Foundation (No. DMR 74-04965) and the Director's Discretionary Fund of the Jet Propulsion Laboratory.

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