Reconstruction and oxidation of the GaAs(110) surface

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Using *ab initio* methods (generalized valence bond with small clusters to represent the surface), we have studied reconstruction of the GaAs (110) surface and the initial steps of oxidation. The relaxation of the surface atoms (26° twist angle) is found to be in good agreement with the results of recent LEED experiments ($27^\circ \pm 2^\circ$ twist angle). The results indicate that the reconstruction is dominated by hybridization effects of orbitals localized at the surface. The calculations of chemisorbed O_2 and O support the following picture: (i) Molecular O_2 can bond only weakly (physisorb) to the perfect GaAs(110) surface. Chemisorption of the O_2 requires a defect site which may then catalyze decomposition of the O_2 . (ii) There is an intermediate oxidized state at low coverages (before O is inserted in the GaAs bonds) in which O atom is chemisorbed to a surface As (donor-acceptor bond). For this intermediate oxide we calculate chemical shifts of 2.6 eV (deeper) in the 3d levels of the surface As and 0.8 eV (deeper) in the 3d levels of the surface Ga, which are in agreement with recent experiments. We propose several experiments to test various aspects of the initial stages in the oxidation process.

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I. INTRODUCTION

Recently there has been a great deal of interest (experimental¹⁻³ and theoretical⁴⁻⁸) in the reconstruction of the (110) surface of GaAs and in the initial steps of oxidation of this surface.⁹⁻¹⁶ Recent experimental and theoretical studies of the reconstruction seem to agree; however, there has been controversy concerning whether the oxidation proceeds initially at the Ga^{9,10} or As^{5,8,11,12} site and whether the initial chemisorbed species involves O_2 ^{13,14,16} or O atoms.^{5,8,11,15} Much of this discussion is inconclusive because neither theory nor experiment has been capable of giving a definitive statement about the reacting species and their location on the surface.

In this paper we present the results of a theoretical study of the reconstruction and the initial stage of oxidation. Our approach applies *ab initio* (first principles) calculations to finite complexes designed to model the system of interest. Our calculations use methods developed for and tested on chemical systems, and they include these features: (i) replacement of the inner-core electrons with angular-momentum-projected effective potentials⁵ or all-electron calculations when core ionization potentials are to be determined, (ii) calculation of the electronic structure and total energy without approximating the exchange terms and including the dominant electron correlations self-consistently [generalized valence bond (GVB) method], and (iii) inclusion of further electron correlation in a configuration interaction calculation¹⁷ (GVB-CI) when quantitative bond energies are calculated.

We have studied the initial oxidation of the GaAs(110) surface with all-electron calculations. Using the calculated electronic structure, geometries, bond energies, vibrational frequencies, dipole moments, and core level ionization potentials (core shifts), we find additional support for the model

of GaAs oxidation presented last year,⁵ namely, that the initial form of oxidized GaAs(110) involves a donor-acceptor-type As=O bond to the 4s lone pair characteristic of the reconstructed GaAs(110) surface,

Section II contains our new theoretical results with comparison to previous experiments, and Sec. III presents a series of proposed experiments to test for various aspects of the oxidation process. A summary is presented in Sec. IV.

II. CALCULATIONS AND RESULTS

A. Reconstruction

The unreconstructed (110) surface of GaAs is illustrated in Fig. 1(a). In modelling this surface we consider that a finite portion of the surface is sliced out of the solid and every Ga-As bond so cut is replaced by a bond to an H atom.⁵ In this way the proper hybridization is retained at each atom and there are no spurious radical centers. Thus the minimal complex for studying reconstruction of the GaAs surface is model 0 [see Fig. 1(b)] consisting of $Ga_1As_1H_4$, where the Ga and As are both surface atoms. A more complete complex is model 1 [see Fig. 1(c)] where the original Ga or As is bonded to three As or Ga neighbors, respectively. Here we will report only calculations with model 0.

The geometric variations were carried out as follows:

- (i) All second-layer atoms were fixed.

FIG. 1. Cluster models for the (110) surface of GaAs. (a) Top two layers of the full surface, viewed from above. (b) Cluster model 0, AsGaH_4 . (c) Cluster model 1, $\text{As}_3\text{Ga}_3\text{H}_{10}$.

(ii) The surface Ga and the surface As were moved independently but with the constraint that the bond length to the (virtual) second-layer atoms be fixed and that there be no lateral displacements of this bond (that is, the surface atom remains in the yz plane defined by this AsGa interlayer bond and the normal to the surface).

(iii) The virtual surface atoms being represented by H atoms [H_3 and H_4 in Fig. 1(b)] are moved by the same amount as the real surface atoms of item (ii).

With the above constraints there are two independent parameters remaining, one for the Ga and one for the As. These will be written as δz_{Ga} and δz_{As} , referring to the projection of the displacement upon the normal to the surface (positive δz is away from the surface); of course, $\delta z \neq 0$ implies that there is also motion in the y direction as defined in Fig. 1.

Previously⁵ we carried out similar calculations using an effective potential to replace the 28 core electrons of Ga and of As. Since one experimental probe of the surface atoms is the chemical shift in the 3d levels of the Ga and As, we have included all electrons in the current calculations.^{18,19} The previous calculations led to

$$\delta z_{\text{Ga}} = -2\delta z_{\text{As}}$$

within 0.01 Å, and the current calculations have assumed this relationship. The resulting potential curve for reconstruction is given in Fig. 2 (the energies are tabulated in Table II). The optimum displacement is calculated as

$$\begin{aligned} \delta z_{\text{Ga}} &= -0.44 \text{ Å}, & \delta y_{\text{Ga}} &= 0.48 \text{ Å} \\ \delta z_{\text{As}} &= +0.22 \text{ Å}, & \delta y_{\text{As}} &= 0.37 \text{ Å} \end{aligned}$$

with a total energy drop of 1.1 eV resulting from the reconstruction.²⁰ The experimental results are often cast in terms of an angle ω corresponding to the angle between the unreconstructed surface (110) plane and the line connecting a surface Ga to a surface As, measured in the (110) plane perpendicular to the surface plane. The calculated ω is 25.6°,

which is in good agreement with the best experimental results of $27^\circ \pm 2^\circ$.^{1,2,21}

The close correspondence between calculated and experimental geometries indicates that the surface reconstruction is dominated by rehybridization or atomic valence effects of orbitals localized at the surface. This validates our use of finite clusters for calculation of reconstruction geometries. Indeed, the bond angles subtended at the As are 90°, 90°, and 108° for an average of 96°, close to the value of 92° found²² for free AsH_3 . The bond angles at the Ga are 125°, 125°, and 108°, leading to an average of 119°, close to the value of 120° expected for free GaH_3 . Thus the surface atoms come close to the valence angles expected for isolated trivalent molecules.

The orbital character and charge on the surface Ga and As atoms is different from that of the bulk atoms; the valence distribution on these surface atoms is quite asymmetric. This suggests that in dynamic LEED calculations, one should be cautious about using spherically symmetric, muffin-tin potentials for these surface atoms. However, the good agreement between our calculated reconstruction and the experimental value based on dynamic LEED calculations suggests that the usual approach does not lead to errors affecting the geometry.

The core ionization potentials shift as the surface distorts from the purely tetrahedral position to the optimum reconstructed position (see Table II). The 3d-level on As shifts to higher binding energy by 0.24 eV and the 3d level on Ga shifts to lower binding energy by 0.19 eV. These shifts would be too small to resolve with current photoemission experiments. The empty orbital localized above the Ga center becomes more p-like during reconstruction and moves up in energy (less bound) by 1.2 eV.²³ Recent band structure calculations⁶ have

FIG. 2. Relaxation energy (see Table II) for cluster models of clean surface (solid line) and of donor-acceptor oxide (dashed line). Referenced to the state in which all bonds are tetrahedral. The reconstruction angle ω is defined in the text. In the oxide the $\text{As}=\text{O}$ bond length is taken as 1.72 Å (from $\text{H}_3\text{As}=\text{O}$), and the $\text{As}=\text{O}$ is oriented at equal angles from the other three bonds to the As.

FIG 3. Donor-acceptor oxygen bond energies versus bond length for H_3AsO (solid line) and H_3GaO (dashed line). Plotted energies are differences in total energies of the GVB-CI wavefunctions (see Table III).

also shown that the relaxation moves empty Ga-derived surface states up (and out of the band gap).

B. Oxidation of the surface

1. Studies of small molecules

In order to obtain quantitative information relevant for understanding the initial steps in oxidation of GaAs (110), we carried out *ab initio* calculations^{17,18} on H_3As , H_3AsO , H_3Ga , H_3GaO , and H_3AsO_2 .

Figure 3 gives the total energy of H_3AsO and H_3GaO as a function of As-O and Ga-O bond length, respectively (these energies are tabulated in Table III). Our results for H_3GaO (upper curve of Fig. 3) show that the O atom is not bound to the Ga.²⁴ However, for the case of $\text{H}_3\text{As=O}$, our calculations indicate a strong bond (2.2 eV).

In Table I, we summarize the properties of $\text{H}_3\text{As=O}$

TABLE I. Properties of arsine oxides.

Property	H_3AsO (theory)	$(\text{H}_3\text{C})_3\text{AsO}$ (experiment)
Oxygen bond strength (eV)	2.21	---
As-O bond length (Å)	1.63 ^a	1.631 ^d
Dipole moment (eÅ)	1.00	1.14 ^e
As-O vibrational frequency (meV)	124 ^b to 136 ^c	107 ^f to 112 ^g

^a From spline fit to minimum of potential curve. See Fig. 2.

^b Using reduced mass = 16 amu.

^c Using reduced mass for H_2AsO = 13.27 amu.

^d C. J. Wilkins, K. Hagen, L. Hedberg, Q. Shen, and K. Hedberg, *J. Am. Chem. Soc.* **97**, 6352 (1975).

^e R. Carlson and D. W. Meek, *Inorg. Chem.* **13**, 1741 (1974).

^f H. Rojhtantalab, *Spectrochim. Acta, Part A*: **32**, 947 (1976). This bond vibration is very nearly a normal mode.

^g Reference 41.

FIG. 4. Probability amplitudes for self-consistent orbitals. For correlated pairs (GVB) the first natural orbital is plotted. Long dashes represent zero, solid lines indicate positive amplitude, and dashed lines are negative amplitudes. The increment between contours is 0.05 au. All plots are in the plane defined by one of the hydrogens, the As (or Ga) atom, and the oxygen atom. (a) As lone pair of H_3As . Note the slight *p* character. (b) As lone pair (or AsO bond orbital) of $\text{H}_3\text{As=O}$. Note the strong O *2p* character indicating charge transfer. (c) Oxygen *2pπ* pair of $\text{H}_3\text{As=O}$. Note the slight delocalization of O *2p* onto As (back bond). (d) Oxygen *2pσ* bond pair of H_3GaO . (e) Oxygen *2pπ* orbital (singly-occupied) of H_3GaO . Note the lack of delocalization.

computed at the minimum in the total energy. While H_3AsO is not known experimentally, we can compare (see Table I) our results with a known system $(\text{H}_3\text{C})_3\text{AsO}$, which should have similar properties. The agreement is quite good. For the As=O bond, we find a bond length of 1.63 Å, in good agreement with the value (1.63 Å) for $\text{Me}_3\text{As=O}$ and considerably shorter than the 1.80 Å typical of an As-O single bond (from As_4O_6).²⁵ This result is consistent with the P-O bond lengths in P_4O_{10} , where the donor-acceptor bond P=O is 1.39 Å and the single bond P-O is 1.62 Å (see Table IV).

Since the GVB orbitals (see Fig. 4) are localized in the bond region, we can calculate²⁶ unique bond dipole moments as an aid to understanding the electronic structure and bonding. The lone pair of H_3As leads to a moment of $-1.26 e\text{Å}$ (electron-Å) with As atom positive and the lone pair negative. This gives an average distance of the lone-pair electrons from the As of 0.63 Å. For the As-O in H_3AsO , the bond dipole moment is $-2.32 e\text{Å}$, with the O negative with respect to the As. The O *2pπ* dipole moment is $+0.26 e\text{Å}$, with the As negative and the O positive. The sum of these two bond dipole moments indicates that approximately one electron has been transferred from the As to O. Also note that the O *2pπ* dipole moment indicates some back bonding [delocalization of O *2pπ* onto the As, see also Fig. 4(c)].

Since it has been suggested¹⁶ that O_2 might chemisorb onto the As of the GaAs surface as O_2 , we also carried out calculations on a model molecule H_3AsO_2 analogous to that assumed in Ref. 16,

The result was (i) an energy 1.6 eV *higher* than free O₂ (no bonding) and (ii) a chemical shift between the two O 1s orbitals of 3.4 eV. Since no splitting in the O 1s level is observed,²⁷ we consider this as strong evidence against chemisorption of molecular O₂ onto the perfect surface.

Previously^{5,28} we have presented evidence that O₂ *does* chemisorb onto the cleavage surface (111) of Si, and it is relevant to review the differences in these two cases. The ground state of O₂ has the character⁵

with singly occupied (antibonding) orbitals in both the *xz* and *yz* planes. These orbitals are spin-paired to form the triplet ground state of O₂. Bonding of O₂ to a species *R* is favorable if *R* has a singly occupied orbital that can be paired up with one of the single occupied orbitals of the O₂ to form an RO bond,

This leads to a singly occupied orbital perpendicular to the ROO plane that may lead to an ESR signal (close to that of superoxide, O₂⁻). Since the Si(111) surface has singly occupied dangling bond orbitals at the surface, this peroxy radical state is favorable and probably observed on Si.

However, GaAs(110) does not have such singly occupied orbitals and the bond of Eq. (5) is not favorable. Forcing the

O₂ to the As position changes the state of the O₂, leading to (the electron in the single occupied orbital pointing toward the As is excited into the π -like single occupied orbital). Consequently, the two oxygen atoms are quite different, leading to the large differential O1s chemical shift.

The Joannopoulos and Mele assignment¹⁶ of the initial observed species of oxygen on GaAs as molecular O₂ bonded to As was based on the agreement between the calculated photoemission structure (tight binding approximation) with the experimental spectrum,¹¹ the key feature being a second peak not expected for O atom. Of course tight binding calculations do not give total energy and hence it was not possible to use bond energy as a criterion for plausibility. On the other hand, comparing calculated and experimental photoemission spectra is risky since the analysis may depend on small features. Indeed, the extra small peak on which Joannopoulos and Mele based their proof of molecular O₂ chemisorption does not appear in more recent spectra.^{27,29}

2. Calculations on oxidized surfaces

We have carried out calculations¹⁹ for O bonded to model 0 (see Fig. 1) as a donor-acceptor complex leading to the potential curves in Fig. 2 (the numbers are tabulated in Table II). Thus, upon oxidation, the GaAs relaxes from a twist angle ω of 25.6° back to a twist angle of 18.6°.

From our theoretical studies we expect the As=O bond length of the donor-acceptor oxide to be 1.63 Å (recall that the As-O single bond is 1.80 Å) oriented at 56° with respect to the normal of the original unreconstructed surface. Preliminary results from EXAFS studies¹⁵ on the initial oxide layer on GaAs (110) also indicate a short AsO bond length, ~1.5 Å. Extracting such bond lengths from EXAFS requires phase shifts for scattering of the As x-ray electron by the neighboring O. Generally this phase shift is obtained from EXAFS studies of compounds with known geometries. This is a problem for the As=O donor-acceptor bond since this bond is much shorter than a normal As-O bond and is quite different electronically. Probably an effective experimental approach would be to determine the As-O phase shift from EXAFS studies on As₂O₃ and then using this phase shift for

TABLE II. Theoretical Results for GaAs Surface Clusters.

Twist angle (ω) (degrees)	Total energy ^a (hartrees)	Orbital energies (hartrees) ^a			
		Ga3 <i>d</i> (average)	As3 <i>d</i> (average)	Empty Ga4 <i>p</i>	As lone pair
H ₄ GaAs ^c					
0.0	-4159.3761	-1.2441	-2.0998	-0.0244	-0.2936
14.3	-4159.4079	-1.2382	-2.1063	0.0030	-0.3137
19.3	-4159.4135	-1.2364	-2.1077	0.0109	-0.3192
27.0	-4159.4162	-1.2367	-2.1086	0.0204	-0.3253
H ₄ GaAsO ^{b,c}					
0.0	-4234.1600	-1.271	-2.196	—	—
14.3	-4234.1834	-1.2673	-2.2009	-0.0185	—
19.3	-4234.1850	-1.2675	-2.2018	—	—
27.0	-4234.1795	-1.2677	-2.2005	-0.0032	—

^a 1 hartree = 27.2116 eV.

^b Energy of O atom in same basis is O(3P) = 74.8006*h*, As-O bond length was 1.72 Å.

^c Hartree-Fock wavefunctions.

TABLE III. Theoretical Energies for H₃AsO and H₃GaO near equilibrium.

	$r_{\text{x-O}}(\text{\AA})$	Energy (h)	$r_{\text{x-O}}(\text{\AA})$	Energy (h)	$r_{\text{x-O}}(\text{\AA})$	Energy (h)	$r_{\text{opt}}(\text{\AA})$ Optimum E_{opt} (h)
H ₃ AsO ^a							
Hartree-Fock (valence double zeta) ^b	1.59	-2310.4596	1.69	-2310.5062	1.80	-2310.5030	1.74 -2310.5118
Hartree-Fock (valence double zeta plus <i>d</i> polarization)	1.56	-2310.6073	1.61	-2310.6095	1.64	-2310.6085	1.61 -2310.6095
GVB-CI (valence double zeta ^c plus <i>d</i> polarization)	1.59	-2310.6660	1.61	-2310.6677	1.69	-2310.6651	1.63 -2310.6686
H ₃ GaO							
GVB-CI (valence double zeta ^d plus <i>d</i> polarization)	1.59	-1999.5507	1.72	-1999.5932	1.85	-1999.6075	— -1999.6156

^a Angle between hydrogens is 101.6°, $r_{\text{As-H}} = 1.52 \text{ \AA}$.

^b Energy of AsH₃ for same wavefunction is 2235.7315h; O atom ³P is 74.8006h.

^c Energy of AsH₃ for same wavefunction is 2235.7852h; O atom ³P is 74.8006h.

^d Energy of GaH₃ for same wavefunction is 1924.7749h; O atom ³P is 74.8407h.

the three As–O bonds to determine the As=O phase shift from EXAFS studies on As₂O₅.³⁰

We can also compare our core ionization potential shifts with photoemission. These calculations indicate that a donor–acceptor As=O bond shifts the As 3*d* orbitals by 2.6 eV and the Ga 3*d* by 0.8 eV, both to higher binding energy. Thus, even though the O is bonded only to the As, it has a large effect upon Ga. The reason is that bonding the O to As (i) causes the As lone pair to rehybridize (become more *p*-like) and to delocalize onto the O to form a sigma bond, (ii) this rehybridization affects the other three bonds to the As (less *p*) and causes the geometry to distort toward tetrahedral, (iii) the delocalization of the As lone pair toward the O shifts the As core orbitals to deeper energy and polarizes the surface GaAs bonds, moving some charge from Ga to As, and (iv) this latter effect causes the Ga core orbitals also to shift to deeper energy. The experimental core shifts are ~2.9 and ~1.0 eV for the As and Ga, respectively.^{27,28} These values are in good agreement with our calculated values, supporting our suggestion that the initial observed state of oxygenated GaAs(110) corresponds to the donor–acceptor oxide.

Upon bonding the O to the As of H₄GaAs we find that the empty orbital on the Ga shifts down (higher binding energy) by 0.8 eV.²³ Such a large shift downward is consistent with the observed pinning of the Fermi energy upon oxidation of *n*-GaAs.

3. Thermochemistry

Previously⁵ we argued that the initial stage of oxidation is one in which an O atom is attached to the lone pair of a surface (denoted as As=O). We refer to this stage of oxidation as the *donor–acceptor oxide*. This bond between O and As results when As lone pair donates electron density to the empty *p* orbital of a singlet O atom. The donor–acceptor complex provides an energetically accessible intermediate between the

reactants (clean GaAs and O₂) and the products (O atom inserted in a GaAs bond) as illustrated below.

First, consider the strength of this donor–acceptor bond. For *X* = P, As, and Sb, there are crystalline forms of the composition X₂O₃ having three X–O single bonds per *X* (and two X–O bonds per O).²⁵ In these forms the valence *s* pair is not effectively involved in bonding. In all three cases there are also crystalline forms of the composition X₂O₅ having bonding similar to X₂O₃ but with an additional donor–acceptor X=O bond on each *X* (this O bonded only to the *X*).³⁰ The experimental heats of formation lead to the effective bond energies³¹ shown in Table IV. We see that the P=O bond is very strong, 6.1 eV, while the As=O and Sb=O bonds are 4.0 eV. Unfortunately, these numbers need not apply to a donor–acceptor bond on a III–V surface. For example, the P=O bonds of R₃P=O are ~5.3, 5.4, and 5.6 eV³² for R=Br, Cl, and F, respectively. There are no relevant experimental data for the As=O bond with more electropositive elements such as R=Ga.

From extensive GVB–CI calculations, we calculate an As=O bond energy of $2.2 \pm 0.2 \text{ eV}$ for H₃As=O. However, the HAs bond is much less polarizable than the GaAs bond at the surface, and hence 2.2 eV is a lower limit for the surface As=O bond. A plausible bond energy for O bound to a surface As is ~3.0 eV. Since the bond energy of O₂ is 5.2 eV, it is exothermic by ~0.8 eV to form two donor–acceptor As=O bonds from O₂.

TABLE IV. Comparisons of oxide bond parameters.

<i>X</i>	Bond energies (eV)		Bond lengths (Å)	
	<i>X</i> -O ^a	<i>X</i> =O ^b	<i>X</i> -O	<i>X</i> =O
P	3.79	6.06	1.62	1.39
As	3.47	3.99	1.80	—
Sb	3.42	3.95	2.0	—

^aAverage bond energy based on crystalline X_2O_3 having infinite nets with three O bonded to each *X* (Ref. 32).

^bBased on comparison of crystalline X_2O_3 and X_2O_5 , where X_2O_5 is an infinite net with three *X*-O single bonds and one *X*=O donor-acceptor bond. For *X* = As and Sb, the crystal structures of X_2O_5 are *not* shown.

Assuming no broken Ga-As bonds, the bonding of an O atom to a surface Ga of GaAs (110) is expected to be very weak²⁴

since Ga has no nonbonding electrons to donate to the O and it is not favorable for O to donate electrons into the empty Ga orbital. Consistent with this assignment, we found no bond for H_3Ga-O .

Of course the donor-acceptor oxide is not the final stage of oxidation of the surface. With attack of oxygen upon the Ga-As bonds, much more stable oxides are formed. The experimental results are complicated. It is generally accepted that anodic oxidation leads to formation of Ga_2O_3 and As_2O_3 (but complicated by loss of As_2O_3 to the electrolyte and formation of metallic As at the GaAs/oxide interface).³³ However, because of the higher temperatures used, thermal oxidations lead to vaporization of an arsenic-oxide, leaving the crystalline oxide rich in Ga_2O_3 . The oxide formed under UHV conditions shows chemical shifts^{11,27} consistent with Ga_2O_3 and As_2O_3 .

One should also consider the possibility that GaAs forms a mixed oxide, $GaAsO_4$, isomorphous with GeO_2 , in which each group IV element is tetrahedrally coordinated to four oxygen atoms (each of which is bonded to two metal atoms). Our estimate of the energy of this species is compared with other possibilities in Table V. Although there are considerable uncertainties in such estimates, it would appear that formation of such a mixed oxide might be energetically favorable. Of course we can say nothing about the *kinetics* for formation of the mixed oxide.

The experimental evidence on the oxidation state of the Ga and As in the oxide of GaAs is partly based on the Ga and As 3*d* chemical shifts, which are consistent with Ga_2O_3 and As_2O_3 . Since the average oxidation number of the mixed oxide is 4, one might have guessed that the chemical shift at the Ga would be greater than that of Ga_2O_3 , with the shift at the As intermediate between As_2O_3 and As_2O_5 . However, the O coordination in the mixed oxide is tetrahedral, whereas it is a mixture of tetrahedral and octahedral³⁴ in Ga_2O_3 and trigonal²⁵ in As_2O_3 . This should tend to decrease the chemical

TABLE V. Energetics for oxidation of GaAs.

	ΔH_f (eV)
$(GaAs) + 2O_2$	-0.74 ^a
$(GaAs=O) + \frac{3}{2}O_2$	-1.13 ^b
$\frac{1}{2}Ga_2O_3 + \frac{1}{2}As_2O_3 + \frac{1}{2}O_2$	-9.04 ^a
$\frac{1}{2}Ga_2O_3 + \frac{1}{2}As_2O_5$	-10.44 ^a
$(GaAsO_4)_2$	-9.8 to -11.2 ^c

^aBased on Ref. 32.

^bBased on estimate of 3 eV for the donor-acceptor oxide bond.

^cUsing the average As-O single bond energy of 3.5 eV from As_2O_3 (see Table IV) and a Ge-O single bond energy of 3.7 eV from GeO_2 , we estimate a Ga-O single bond energy as 3.9 eV. Then for the mixed oxide we consider four bonds to each As to be three parts As-O and one part As=O (estimated at 4.0 eV, see Table IV) and the four bonds to the Ga as three parts Ga-O and one part Ga···O=As. This latter bond is estimated between O and Ga at 1.4 eV (based on $R_3Ga\cdots NH_3$).

shift and might lead to values close to that of Ga_2O_3 and As_2O_3 .

Perhaps EXAFS studies on the final oxide could be used to determine the O coordination at both the Ga and As. Use of EXAFS to determine whether the metal neighbors are similar or different would be difficult for GaAs (similar phase shifts) but should be feasible for GaP or GaSb.

III. SUGGESTED EXPERIMENTS

One problem in the experimental study of the initial steps in the oxidation of GaAs is that (for good cleaves) the sticking coefficient of O_2 is extremely small,^{8,35} requiring very long exposures for observable oxidation. The alternative to long exposures has been to leave on the ion gauges leading to an excited form of O_2 (probably O atom but possibly the singlet excited state of molecular O_2); this leads to rapid oxidation but perhaps too fast to observe the initial steps. Based on our model of the oxidation, we suggest the following experiments.

(1) With the sample cooled to at least 77 K, expose the surface to O_2 (ion gauge off). At this temperature, one should observe the physisorbed O_2 (bonded weakly to the surface) or weakly bound O_2^- .¹³ Photoemission should indicate the characteristic O_2 spectrum and temperature-programmed desorption studies could provide the data on the energy of bonding. Such studies as a function of surface temperature (with submonolayers of O_2) might provide thermochemical data on the process of converting physisorbed O_2 into chemisorbed O.

(2) A problem with using O_2 as the source of O atom is the large strength of the O-O bond, 5.2 eV. This requires strong bonding (chemisorption) of the O_2 with the surface in order to weaken the O-O bond sufficiently for subsequent oxidation. An alternative is to break the O_2 bond in gas phase and expose the surface to free O atoms (probably the process when the ion gauge is on). Unfortunately the resulting O atom is very reactive, releasing ~ 5.7 eV upon forming a bond:

As a result, one may not see the sequence of intermediate states that characterizes usual oxidation of the surface. Thus, we suggest alternative sources of O atom that may be useful

in examining the sequence of stages in oxidation of the surface and that might also be useful in practical controllable, low-temperature oxidation of GaAs (and other semiconductors) in device fabrication. Two appropriate oxidants are ozone

and nitrous oxide, $\text{N}=\text{N}=\text{O}$. The energy to break the O–O bond of ozone is only 1.0 eV,³⁶ and the energy to break the N–O bond of nitrous oxide is 1.7 eV.³⁶ In each case, this produces a single O atom on the surface plus a rather unreactive molecule (ground state O_2 or N_2). Thus, one can be fairly sure that the initial chemisorbed state has a single O atom on the surface.

(3) Of additional interest is the possibility that the O atom oxidation from O_3 and N_2O might behave differently. The spin-allowed dissociation of O_3 (a singlet state) leads to a ground state O_2 (a triplet) plus ground state O (a triplet, ^3O). However, the spin-allowed dissociation³⁷ of N_2O (a singlet state) leads to ground state N_2 (a singlet) plus the excited singlet state of O atom (^1O). Since the ^1O is much more reactive than ^3O and since ^1O can attack both the lone pair of a surface As and the GaAs bond (without spin-flip), it is possible that ozone might lead to a different series of intermediate states of oxidized GaAs than would N_2O .

(4) To establish the nature of the species responsible for the increased oxidation when the ion gauge is involved, experiments can be carried out in which the two most likely species (a) singlet molecular oxygen, $^1\text{O}_2$, and (b) triplet oxygen atom, ^3O , are deliberately produced. Chemists have developed procedures³⁸ for using microwave discharges of O_2 to separately produce both $^1\text{O}_2$ (up to 15%) and ^3O atom, and other techniques³⁹ have been producing for free ^3O .

(5) Starting with a surface that has been exposed to oxygen to produce a low coverage, one could possibly deoxygenate it with PCl_3 .⁴⁰ If O has not inserted in the Ga–As bonds, this procedure should produce OPCl_3 and remove oxygen from the surface, perhaps with restoration of the LEED pattern. Further, PCl_3 is a strong electron donor and could bind associatively to surface Ga, resulting in a relaxation of the surface structure back toward the unrelaxed geometry.

(6) The arsenic–oxygen donor–acceptor bond has a characteristic vibrational frequency around 110–125 meV (see Table I), whereas the AsO single bond is typically at 80 meV.⁴¹ Thus, electron energy loss spectroscopy could be used to detect this vibration for low oxygen coverages.

(7) We have suggested⁵ that defect sites act as initial binding centers for O_2 . Halogen atoms could be used to tie up these defect sites. Hence, clean GaAs exposed to halogen atoms (under conditions such that surface bonds are not disrupted) should have a dramatically reduced initial rate of oxidation.

(8) The strength of the donor–acceptor bond between oxygen and Group V elements increases in the sequence $\text{Sb} < \text{As} < \text{P}$; bond strengths to III–V surfaces should be approximately independent of column III elements. Hence, we would expect the initial oxygen uptake to be more rapid for

the phosphides, than arsenides, than the antimonides. Some evidence for this effect has already been reported.⁴²

From these suggested experimental studies, it should be possible to gather sufficient data to provide a more detailed microscopic mechanism of the oxidation of GaAs (110). This particular system is an excellent one for such studies because of the rather low rate of oxidation for $^3\text{O}_2$. Similar studies of other surfaces of GaAs might then provide a test of the model and complete our picture of oxidation of this material. Perhaps at this point we would be armed to examine the more complicated processes at semiconductor–electrolyte interfaces where the thermal oxidation and photocatalytic production of O_2 are of interest.

IV. SUMMARY

Our new theoretical results and recent experiments are consistent with our previous model⁵ that the initially observed form of oxidized GaAs (110) involves O atom bonded to As. We conclude that (i) molecular O_2 bonds only weakly (physical adsorption) to the perfect GaAs (110) surface, (ii) defect sites with a broken Ga–As bond are required to form a strong bond to molecular O_2 , (iii) such sites may catalyze the dissociation of O_2 into chemisorbed O atoms, (iv) these O atoms may then attack nearby Ga or As atoms even though O_2 would not, (v) this O atom may then bond to As atoms of the perfect surface as in configuration (1) or may attack the AsGa bonds of the surface to form the oxide, (vi) consequently, perfect (110) surfaces of GaAs should show a low sticking coefficient for $^3\text{O}_2$ but higher values for $^1\text{O}_2$ or O atom, and (vii) bonding the O to the As as in configuration (1) also affects the geometry of the Ga (moving it toward the unreconstructed position). As a result, the empty orbital of the Ga is affected (changed from a nearly pure p orbital to tetrahedral and shifted down in energy) even though the O atom has attacked the As. Our model is consistent with the available experimental evidence, and we have suggested a series of experiments that should provide a detailed microscopic model of the steps in oxidation of GaAs.

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