Chemisorption of Al and Ga on the GaAs (110) surface

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We have studied the initial stages of the chemisorption of Al and Ga on the clean GaAs (110) surface by applying quantum chemical methods to small clusters representing Al or Ga on GaAs (110). These calculations suggest that at smallest coverages Al or Ga bind to a surface Ga atom; for higher coverages Al and the surface Ga interchange positions. We have obtained the binding energy, the chemical shifts of the Ga–3*d*, As–3*d* and Al–2*p* states, and the microscopic dipole associated with chemisorption of Al or Ga on GaAs (110). These results are compared to experimental values and further experiments are suggested.

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I. INTRODUCTION

Recently there has been a great deal of interest in the chemisorption of metals on semiconductor surfaces.[1] One system that has been studied both experimentally[2–5] and theoretically[6] is Al on GaAs (110). Here we report theoretical results for the initial stages of chemisorption of Al and Ga on GaAs (110). After a brief description of the theoretical methods, we will discuss the possible binding sites for Al or Ga on GaAs and give the results of our calculations. [Preliminary results for Al/GaAs were presented in Ref. 6(c).]

The theoretical methods we use are adaptations of well established methods of quantum chemistry. Their application to semiconductors[7] and a comparison with other approaches[8] have been discussed elsewhere. Here we only want to discuss the important features of our approach.

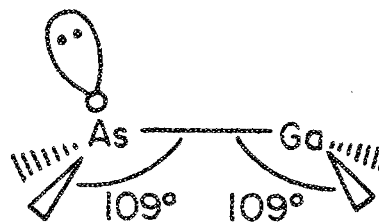
The surface chemical environment is mimicked by creating a molecular cluster representative of the surface. Atoms at the edge of this cluster, which would have been connected to further atoms in the extended system, are connected to hydrogen atoms. These hydrogens are placed such that the bond angles of the extended system are preserved, but the distance of the hydrogen atoms to their nearest neighbour surface atom is made to correspond to the same distance in the respective trihydride. This procedure insures proper hybridization of the cluster atoms and prevents artificial dangling bonds at the edge of the cluster from interfering with real dangling bonds on the surface. Figure 1 illustrates some of the clusters used in this study.

The cluster approximation 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.[8] 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 system, such as chemical shifts of the core levels or dipole moments. To make the approach feasible for clusters containing heavy atoms, we have replaced the 28 core electrons of Ga and As with *ab initio* effective potentials.[9–11] 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.[9]

The basis sets are double zeta or split valence (that is, two functions for each valence atomic orbital) and include *d* polarization functions. In the present work we have used the Hartree–Fock (HF) method, which is known to give good geometries (but not cohesive energies).

II. BONDING SITES FOR Al OR Ga ON GaAs (110)

The (110) surface of GaAs is shown in Fig. 2. It consists of zigzag chains of atoms, alternating Ga and As. Calculations show that the dangling bonds, which are broken when the surface is formed, coalesce into one lone pair of electrons located on the As site, even for the unreconstructed surface:



Furthermore, the surface reconstructs (see Fig. 2) in such a way as to give the surface Ga atom a more planar geometry (average bond angle close to 120°) and the surface As atom a more pyramidal geometry[12] (average bond angle 94°). We define the surface strain, Δz, as the z-projection (perpendicular to the unreconstructed surface) of the total displacement of the surface As relative to the surface Ga (see Fig. 2). Our theoretical value for Δz is 0.67 Å,[12] in very good agreement with the experimental values,[13–16] that range from 0.65–0.70 Å.

On the clean surface there are two sites for chemisorption, namely a $(4s)^2$ lone pair site on the As and an empty p orbital on the Ga site. If Al or Ga bind to the As site, the As lone pair will donate electrons into an empty p oribtal on Al or Ga,

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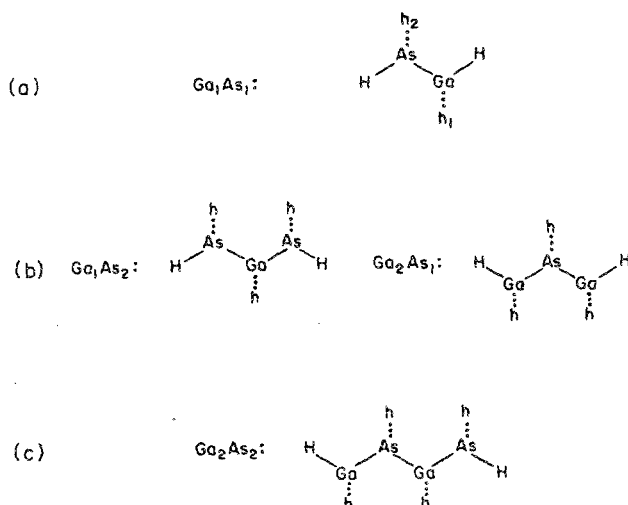
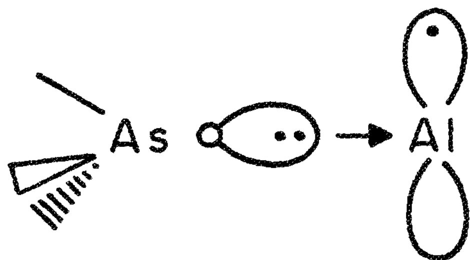


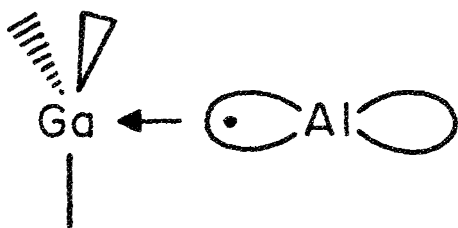
FIG. 1. Molecular models for GaAs (110). Lower case letters indicate subsurface atoms. (a) Two-site model; (b) Ga centered three-site model; (c) As centered three-site model; (d) four-site model.

forcing the singly occupied p orbital to be perpendicular to this bond,



The charge transfer in this case would be from As to Al, which is in an unfavorable direction, so we expect only a very weak bond.

On the Ga site on the other hand, we can form a one electron bond by having the singly occupied p orbital of Al (or Ga) delocalize into the empty orbital on the Ga site,



This tends to stabilize the Al and we expect a stronger bond than in the previous case.

To test out these ideas we have calculated binding energies for an Al atom attached to various sites on the GaAs (110) surface. The results of these calculations are given in the next section.

III. RESULTS AND DISCUSSION

We have studied the bonding of Al to GaAs (110) by first assuming a perfect, reconstructed GaAs (110) surface (no vacancies or broken bonds; $\Delta z = 0.67$ Å), and have examined the bonding of Al to various sites. We used the Ga centered model [Fig. 1(b)] to study the bonding of Al to the Ga site, and the As centered model [Fig. 1(b)] to study the bonding of Al to the As site. Furthermore, we have also used both models to obtain the binding energy for the case where the Al atom is equidistant from a surface Ga and a surface As atom. The results of these calculations are given in Table I. Already we find that the binding energy of the Ga site, 0.42 eV, is larger than the binding energy on the As site, 0.18 eV. Thus the Ga site is preferred over the As site.

Subsequently the surface was allowed to re-reconstruct and the position of Al on the surface was reoptimized. From the results given in Table I we see that for Al attached to the Ga site the surface does re-reconstruct (Δz decreases from 0.67 to 0.55 Å), leading to an increase in binding energy to 0.59 eV (an increase of 40%). For the case where Al is attached to a surface As however, we find that there is practically no re-reconstruction. These results can be understood on the basis of local valence considerations. On the reconstructed surface the Ga atom has a more or less planar geometry (average bond angle close to 120°). When we now bind an Al atom to the surface Ga atom, the Ga atom will prefer a more tetrahedral geometry to make more effective use of the electrons available for bonding to its neighbors, thereby increasing the bond strength of the Al atom on the surface. Therefore the surface is expected to re-reconstruct. The surface As atom on the other hand, has a pyramidal geometry (average bond angle ~94°) on the reconstructed surface, with its lone pair pointing away from the surface. This is just the optimum geometry to make

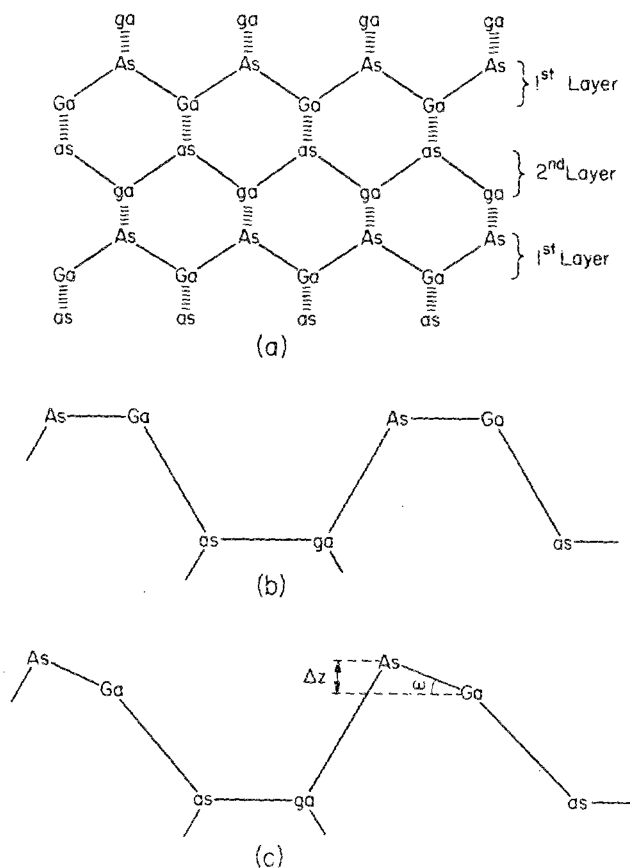


FIG. 2. (110) surface of GaAs. (a) Top view; (b) side view of projection in the ($1\bar{1}0$) plane, unreconstructed; (c) side view of projection in the ($1\bar{1}0$) plane, after reconstruction; Δz is the surface strain, ω is the reconstruction angle.

TABLE I. Geometries and binding energies for Al and Ga on GaAs (110). Δz is the projection perpendicular to the unreconstructed surface of the total displacement of the surface As relative to the surface Ga.

A. Al on reconstructed GaAs (110).

Model	Bonding site	Δz(Å)	Al–Ga Distance (Å)	Al–As Distance (Å)	Binding energy (eV)
Al/Ga_1As_2	Ga	0.67	3.04	3.97	0.42
Al/Ga_1As_2	Ga–As[a]	0.67	3.32	3.32	0.29
Al/Ga_2As_1	Ga–As[a]	0.67	3.24	3.24	0.25
Al/Ga_2As_1	As	0.67	3.13	3.13	0.18

B. Al or Ga on re-reconstructed GaAs (110).

Model	Bonding site	Δz(Å)	Metal–Ga Distance (Å)	Metal–As Distance (Å)	Binding energy (eV)
Al/Ga_1As_2	Ga	0.55	2.95	3.90	0.59
Al/Ga_2As_1	As	0.65	3.13	3.13	0.18
Ga/Ga_1As_2	Ga	0.49	2.95	4.00	0.59

[a]In these cases the Al is equidistant from the surface Ga and surface As atoms.

a donor-acceptor bond between the As lone pair and an Al atom. Therefore we do not expect the surface to re-reconstruct when the Al atom is attached to a surface As atom.

The final optimum geometry for Al on GaAs (110) is shown in Fig. 3. In this geometry the Al atom is located in the symmetry plane perpendicular to the surface and passing through the surface Ga atom. The Al atom is at a distance of 2.95 Å from the Ga and 3.90 Å from the As, while the surface strain is 0.55 Å.

For Ga on GaAs (110) we find a similar geometry, with the Ga–Ga distance equal to 2.95 Å and the Ga–As distance equal to 4.00 Å. In this case the surface strain of the re-reconstructed surface is 0.49 Å.

At these optimum geometries we have calculated chemical shifts for the Ga–$3d$, As–$3d$ and Al–$2p$ states. The bonding of the overlayer Al is such that there is a significant charge transfer from the Al to the surface. The effect of this is to shift the core levels of the Al down (greater ionization potential), and those of Ga and As up (smaller ionization potential). The calculated shifts are given in Table II. For the Ga–$3d$ level, for example, the shifts were obtained by performing calculations for both Al–GaAs (110) and clean GaAs (110) with all the Ga electrons present, although effective potentials were still used for the Al and As core electrons. In these calculations the surface was described by the Ga_1As_2 model of Fig. 1. The shift was then determined as the difference in the average ionization potentials (IP's) for the Ga–$3d$ levels of Al/GaAs (110) and clean GaAs (110). These IP's were determined using Koopmans' theorem, which is expected to be reliable for changes in IP's of core levels (but not for absolute IP's). The shift in the As–$3d$ level was obtained in a similar way, except that in this case we used the Ga_2As_1 model (Fig. 1) to describe the surface and only one surface Ga atom had an Al atom bound to it. This is expected to give a better description of the As atom than would be obtained by using the Ga_1As_2 model. We find a shift of 0.83 eV for the Ga–$3d$ level in Al/GaAs (110) relative to clean GaAs (110) and a shift of 0.39 eV for the As–$3d$ level in Al/GaAs (110) relative to clean GaAs (110). For the Al–$2p$ state we find similarly a shift of −0.11 eV for Al/GaAs (110) relative to clean AlAs (110). Unfortunately the experimental shifts of the Al–$2p$ level are all given relative to Al metal and the chemical shift of the Al–$2p$ state in AlAs (110) relative to Al metal is not available experimentally (to

TABLE II. Chemical shifts of various levels for Al or Ga on GaAs (110). All energies are in eV, positive values correspond to a lower ionization potential than the reference state.

Case	Level	Theoretical Shift (eV)
Al/GaAs	Ga–$3d$	0.83[a]
	As–$3d$	0.39[a]
	Al–$2p$	~ −1.2[b]
Ga(1)/Ga(2)As	Ga(1)–$3d$	−0.04[a]
	Ga(2)–$3d$	0.87[a]
	As–$3d$	0.46[a]

[a]Shift was calculated w.r.t. the corresponding state in clean GaAs (110).

[b]We calculate that the $2p$ level of Al on GaAs is 0.11 eV lower than the corresponding level on the surface of AlAs. Estimating the shift of AlAs with respect to Al metal to be −1.1 eV (based on GaAs versus Ga metal) leads to a value of −1.2 eV for Al/GaAs vs Al metal.

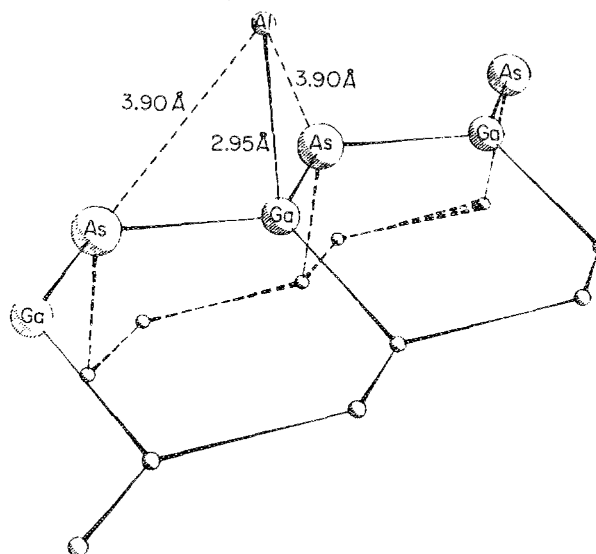


FIG. 3. Optimum geometry for Al on GaAs (110).

the authors' knowledge), nor has it been calculated. Assuming that the shift in Al-$2p$ for AlAs (110) relative to Al metal is similar to the shift in Ga-$3d$ for GaAs (110) relative to Ga metal (−1.1 eV) we estimate a shift of −1.2 eV for Al/GaAs (110) relative to Al metal. An experimental determination of the Al-$2p$ shift for AlAs (110) relative to Al metal would be very useful.

One has to be careful in comparing the theoretical values of the chemical shift to experimental values. There can be real differences between the theoretical and experimental systems; however, for a system in which there is uniformly no more than one Al per surface Ga, we expect comparison of theory and experiment to be valid. The biggest problem in comparing with experiment is the worry that the experimental system might be heterogeneous, with islands having higher Al concentrations, allowing Al–Al bonding.

First we will consider the experimental results for Al/GaAs (110). Skeath *et al.*[5] have considered the case of low coverage of Al on GaAs (110). They find that the separation between the Ga-$3d$ and As-$3d$ peaks decreases by ~0.35 eV upon the first depositions of Al. From the calculations we obtain an increase of 0.44 eV in this separation. However, for coverages of ~¼ monolayer there would be an equal number of surface As atoms that are disturbed by the presence of Al as are not disturbed. Due to the small separation between the two lines (0.39 eV) and the much greater width of these lines [the full width at half maximum (FWHM) is 1.4 eV] one would observe only one line shifted by 0.19 eV. From simulations of the spread we conclude that there would be no significant change in lineshape. One possible reason for the differences in the behavior of the Ga-$3d$ signal is that the disturbed Ga atoms experience a shadowing effect from the Al atoms bound to them. As a result, for coverages of less than ½ monolayer the observed signal may be dominated by the undisturbed Ga atoms. For example, using gaussian lines (FWHM 1.15 eV, separation 0.83 eV) and a ratio of 9 to 1 for the contribution of undisturbed Ga atoms to that of the disturbed Ga atoms we find a shift of 0.01 eV, while the lineshape changes slightly on the low binding energy side. This case then leads to a decrease in the separation between the Ga-$3d$ and As-$3d$ lines of 0.18 eV, close to the value of 0.35 eV observed by Skeath *et al.*[5]

For coverages of about a half monolayer of Al on GaAs (110), Brillson *et al.*[4] report a chemical shift of 0.95 eV for the Ga-$3d$ line, in good agreement with the theoretical value of 0.83 eV. They observe no shift for the As-$3d$ line, whereas we calculate a shift of 0.39 eV. The As-$3d$ line is not shown by Brillson *et al.*, but the spectra published by Skeath *et al.*,[5] indicate a FWHM of 1.4 eV for the As-$3d$ line. Thus the line is very broad and it may be that deconvolution of this line would produce a shift. Furthermore, given the weakness of the bond of Al to the surface, it is possible that at these coverages Al atoms are bonded to each other to form a two-dimensional network or island of Al atoms on the surface. This can lead to Al atoms located over surface As atoms, allowing the As lone pair to delocalize into the empty orbital on the Al atom. This leads to a stabilization (and hence a smaller shift) of the As orbitals.

Finally, Huijser *et al.*[17] have done experiments for the case of about one-third of a monolayer of Al on GaAs (110). They find that the Ga-$3d$ line does not exhibit a chemical shift. This is in agreement with our discussion (vide supra) for the effect of shadowing by Al atoms at low coverage. Indeed, from an inspection of the spectra obtained by Huijser *et al.*, we conclude that there is a change in the Ga-$3d$ lineshape on the low binding energy side, consistent with the argument given above.

The experimental shift for the Al-$2p$ line with respect to Al metal is observed to be 0.6 ± 0.2 eV by Skeath *et al.*[5] for the lowest coverages and increasing to 0.9 ± 0.1 eV for coverages corresponding to between a half monolayer and a full monolayer. Brillson *et al.*[4] report a shift of 0.7 eV for the Al-$2p$ line. Given the uncertainties in referencing the theoretical shift (1.2 eV) to Al metal the agreement between theory and experiment seems reasonable.

For Ga/GaAs (110) Bachrach *et al.*[18] have reported a shift of 0.6 eV to lower binding energy for the Ga-$3d$ level. This is in good agreement with the theoretical value of 0.87 eV, since in this case there are three contributions to the Ga-$3d$ line (not considering the subsurface), namely from uncontaminated surface Ga atoms, from surface Ga atoms covered with Ga and from chemisorbed Ga atoms. They find a shift of 0.15 eV to higher binding energy for the As-$3d$ level, whereas theoretically we obtain a shift of 0.43 eV to lower binding energy. Again, the As-$3d$ line is much broader than the shift (FWHM ~1.3 eV) and has additional structure, so that deconvolution of the line may lead to a different result. Furthermore, for the coverages considered in this experiment the deposited Ga atoms may bond to each other to form a two-dimensional network or island on the surface, leading to a stabilization of the surface As atoms in the same way as discussed above for Al/GaAs.

Finally for the case of Al/GaAs (110) we have investigated the occurrence of a surface dipole as reported by Brillson *et al.*[4] We find a surface dipole of 0.6 eÅ/atom, with the sign such that the Al is positive with respect to the underlying surface. In contrast Brillson *et al.*[4] have interpreted the initial slope of the surface potential versus Al layer thickness in terms of surface dipole formation and obtain a value of −0.34 eÅ/atom, disagreeing substantially with the theoretical value. Other features of the system, such as vacancies and interstitials induced by the metal overlayer,[19] may be responsible for an additional surface dipole that accounts for part of the discrepancy.

For multilayer coverages of Al on GaAs, the experimental studies show that a reaction occurs at the interface, leading to both Ga and As in the overlayer and the formation of AlAs at the interface; however, this does not mean that similar reactions occur for submonolayers. We have compared Al/GaAs (110) and Ga/AlAs (110) and do indeed find that the energy of Ga/AlAs (110) is 0.62 eV lower than the energy of Al/GaAs (110), as would be expected from comparison of bulk heats of formation. However, for a perfect GaAs (110) surface, this process would require breaking three Ga–As bonds and hence it is likely that there will be a substantial reaction barrier. Furthermore it is unlikely that the exchange reaction would lead to an ordered LEED pattern.[4] This is in agreement with the results of Huijser *et al.*,[17] who conclude from their ex-

periments for low coverages of Al on GaAs (110) that no exchange reaction occurs.

To account for the exchange reaction, Mele and Joannopoulis[6(b)] have proposed a model in which Al substitutes for a surface Ga, after which the Ga remains on the surface and binds to a nearest neighbor surface As atom. By calculating valence charges on each atom they find that the chemical shifts can be explained this way. (They performed tight-binding calculations and hence they cannot calculate the actual chemical shifts). Our calculations suggest that for submonolayer coverages the freed Ga atom should bind to the substituting Al or to another surface Ga (thus the geometry assumed in the tight-binding calculations is incorrect). Thus the exchange reaction would lead to chemical shifts opposite to those observed experimentally.

A crucial experiment would be a low temperature, submonolayer examination of Al on GaAs (110). 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.

IV. SUMMARY

Our calculation shows that the initial stage of chemisorption of Al on GaAs (110) consists of an Al atom bound to a surface Ga atom. For higher coverages it is likely that an exchange reaction between Al and the surface Ga will occur, since this reaction is exothermic. Similarly we find that in the case of Ga/GaAs (110) the chemisorbed Ga atom binds to a surface Ga. As might be expected, the geometry and chemical shifts for Ga/GaAs (110) are very similar to those for Al/GaAs (110).

Since Schottky barriers appear at submonolayer coverage,[20] we expect studies of this type to yield information on the phenomena of Schottky barrier formation.

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