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Chemisorption of aluminium on GaAs(110)

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Abstract. We have performed total-energy pseudopotential calculations for a variety of structures for Al adsorbed on the GaAs(110) surface. For the coverage of one monolayer we find only very small differences of the adsorption energy for a number of competing structures. In contrast to recent LCAO calculations, we find all these structures to be either metallic or to have only a very small band gap. Total energy calculations are also made for a Ga–Al exchange reaction and for different structural models for half a monolayer coverage including a 2×1 reconstruction. In all cases we find the adsorption energy to be less than the cohesive energy of bulk Al in FCC structure or the energy gain due to an exchange reaction, indicating the tendency for cluster formation, as observed experimentally, or penetration into the substrate. By means of density-of-states calculations it is shown that the Schottky barrier is already formed for the ordered half-monolayer case and is completed for one monolayer of Al on GaAs. The band gap is found to open for an asymmetric dimer in a 2×1 reconstruction which may explain recent experimental observations.

1. Introduction

Aluminium adsorption on GaAs and InP has in the past, as well as recently, received attention in order to understand the formation of the Schottky barrier as a function of the coverage (Bachrach *et al* 1979, McKinley *et al* 1982, Ortega *et al* 1992). Over a decade ago Zunger (1981) examined in detail a wide body of experimental and theoretical information pertaining to the adsorption of Al on GaAs. He predicted an Al–substrate bond length of about 3 Å and found that the Al–Al interaction exceeded the Al–substrate interaction, thus promoting the growth of metallic clusters. Ihm and Joannopoulos (1982) used a total energy approach to determine possible adsorption sites and structures for half-monolayer and one-monolayer (ML) coverages of Al on GaAs(110). They found that the most stable structure was the long-bridge-bond position in the case of the half-monolayer coverage, but the adsorption energy was found to be higher for a coverage of one monolayer in the epitaxially continued layer structure (ECLS). They also found the binding energy of Al to be twice as large and the Al–substrate bond length considerably shorter than was predicted by Zunger (1981). Both for half- and one-monolayer coverages of Al, a finite density of states (DOS) pinning the Fermi level in the gap region was reported. In addition they stressed that exchange reactions and clustering are favourable at room temperature. Indeed, at room temperature, diffusion of Al into GaAs and formation of stable Al–As bonding has been observed by atom-probe mass spectroscopy (Nishikawa *et al*, 1984), thus confirming the predictions of Ihm and Joannopolous. In an earlier experimental work (Prinz *et al*,

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1982) reported that a successful epitaxial growth of Al on GaAs(110) was achieved only after cooling the substrate down to liquid nitrogen temperature. From synchrotron-radiation experiments at ultralow coverages Daniels *et al* (1982) concluded that the Al/GaAs(110) interface formation occurs in *three* different stages corresponding to different Al adsorption states. In particular, at coverages between 0.1 and several monolayers they also found direct evidence of replacement interactions between the adatoms and the substrate.

Recently using a self-consistent tight-binding LCAO technique Ortega *et al* (1992) have reported the long-bridge-bond position and the ECLS to be the most stable adsorption sites of Al in the case of the half- and one-monolayer coverages, respectively. In contrast to the earlier work by Ihm and Joannopolous (1982), they found for ECLS a bandgap of about 1.2 eV. In other words, they found no finite DOS appearing near the semiconductor charge neutrality level for one monolayer. Ortega *et al* seemingly found their calculated semiconducting nature of the system to be in accordance with STM measurements by Suzuki and Fukuda (1991). However, it is important to note that Suzuki and Fukuda deposited about three monolayers of Al on the GaAs(110) surface at room temperature and observed the formation of Al clusters, together with the existence of single Al atoms located over Ga sites. In particular, they found that one cluster, consisting of about 200 Al atoms, and not correlating to the crystallographic direction of the substrate, had non-metallic characteristics with a band gap of 1 eV. These workers also observed very small clusters consisting of several atoms, located over Ga sites with an atomic corrugation of about 1 Å above the GaAs surface. Once again, both occupied and unoccupied states were observed, but there is no report of the band gap for the small clusters.

Very recently Yi and Bernholc (1992) have performed total-energy calculations for a variety of adsorption geometries in the range of 1/8 to 1 monolayer. In contrast to Ihm and Joannopoulous (1982) and Ortega *et al* (1992), Yi *et al* found, for one-monolayer coverage, an irregular chain structure (IRC) to be more favourable than the ECLS. The work of Yi *et al* also suggests that for the half-monolayer coverage, single Al atoms should reside at the centre of a triangle of one Ga and two As atoms rather than in a long-bridge-bond position as reported by Ihm and Joannopolous (1982) and Ortega *et al* (1992).

From the above discussion it is clear that, despite the great deal of work that has been done to clarify both the atomic and electronic structure of this system, no unique picture exits up to now. The aim of the present work is to contribute to a clearer understanding of Al adsorption on GaAs(110). We apply accurate self-consistent total-energy calculations to determine the adsorption energy for different adsorption-geometries and to study the DOS for the most probable ones. Additionally, we examine the nature of the bonding between Al and the substrate, and present a comparison with the adsorption of group V and group I elements on GaAs(110) to gain some insight into the chemical trend.

2. Theory

We performed state-of-the-art electronic structure, total-energy, and force calculations based on the density-functional theory (DFT) (Hohenberg and Kohn 1964, Kohn and Sham 1965). The electron–ion interaction was treated by using norm-conserving, *ab initio*, fully separable pseudopotentials (Kleinman and Bylander, 1982) as given in Stumpf *et al* (1990) and the many-body electron–electron interaction was treated within the local-density approximation (LDA) and the Ceperley–Alder scheme (Ceperley and Alder, 1980) as parametrized by Perdew and Zunger (1981). We used the repeated-slab method to simulate the semiconductor surface. The system is periodic parallel to the surface and we introduced an artificial periodicity perpendicular to the surface, defining a large three-dimensional unit cell. Our

slab contained eight layers of GaAs(110) (1×1 and 2×1 surface periodicities as discussed later), both sides covered with Al, and a vacuum region equivalent in thickness to six such layers. For the plane wave basis set we used an energy cutoff equal to 8 Ryd. The k-space integration was replaced by a sum over four special points (Evarestov and Smirnov, 1983) in the irreducible part of the surface Brillouin zone. The choice of the number of plane waves corresponding to the energy cutoff of 8 Ryd was found to be adequate for the present study. This was confirmed by extending the energy cutoff to 15 Ryd, and Brillouin zone summation over 20 uniformly distributed k-points, for some of the calculations, as discussed later in the text.

The GaAs lattice constant was optimized for a GaAs(110) (1×1) slab using the above-mentioned parameters. All results reported hereafter were obtained with the theoretical lattice constant of 5.5 Å (the experimental value is 5.65 Å). In order to determine the equilibrium atomic positions the three outermost substrate layers and the adatoms were relaxed to geometries given by the minimum of calculated total energy and forces. Proceeding with an assumed starting geometry, the single-particle wavefunctions were brought to self-consistency within a global minimization scheme of the total energy functional (Car and Parrinello, 1985), using the analytical expression of Payne *et al* (1986). Using the resulting Hellmann–Feynman forces, a steepest descent method was employed to move the ions. The new structure was the starting configuration to relax the wavefunctions again until the next ionic movement could take place. The procedure was repeated until the ions were fully relaxed towards the nearest local minimum on the total energy surface and the wavefunctions were fully self-consistent.

The adsorption energy was calculated as the difference between the total energies of the aluminium covered surface and the clean relaxed surface plus the free Al atom. It was taken as positive when adsorption was favourable. The total energy of the free atom was calculated with the same energy cutoff and exchange-correlation functional as applied to the surface and overlayer calculations. The calculated adsorption and cohesive energies were found to be somewhat higher than experimental results, due to the application of the LDA. However, the results provide a fully consistent comparison between the different geometrical models considered in this work.

3. Results

3.1. The ordered half-monolayer coverage

The two earliest self-consistent calculations of the Al/GaAs(110) system were made for an ordered half-monolayer coverage of Al, using semi-empirically determined local pseudopotentials (Chelikowsky *et al* 1976, 1981). The first of these two works did not have the capability of optimizing atomic geometry, as until that time the pseudopotential total energy method had not been developed. That work considered Al bonded to the GaAs substrate at an anion site. While the results of their work appeared compatible with available experimental work, some questions remained unanswered. The second of these works examined an alternative model for the chemisorption of Al on the GaAs surface. Using total energy calculations of Barton *et al* (1980), based on quantum-chemical techniques as a guide, the chemisorption site for Al was considered to be along the true dangling bond direction of a cation. This geometry consisted of an Al–Ga bond length of 2.95 Å with Al placed along a vector which formed equal angles with the bonding directions of the substrate Ga to its three substrate As nearest neighbours. A relaxed geometry for the GaAs(110) surface was considered, with a surface tilt angle of 21°. No attempt was made

to relax bond lengths in the substrate. The Fermi level, lying at 1.0 eV above the bulk valence band maximum, was found to be governed by an Al–Ga bonding combination of p-like states. The position of the Fermi level was found to be in agreement with experiment (Skeath *et al*, 1979). Furthermore, in agreement with photoemission experiment (Bachrach *et al*, 1978) a strong feature in DOS was observed at approximately 5 eV below the valence-band maximum. While it was claimed that the calculated electronic band structure for this geometry was compatible with available photoemission results, it was fully realized that a more detailed comparison with experiment needed elimination of deficiencies in the then available methods of electronic structure calculations.

In the present study we have considered four different chemisorption geometries. The Al atom placed in the dangling bond directions of Ga and As respectively, the overlayer atom in a long-bridge-bond position bound both to As and Ga, and the Al atom on top of the Ga atom as suggested by Suzuki and Fukuda (1991) in evaluation of their STM images. A top view of these geometries is given in figure 1. In contrast to the findings of Ihm and Joannopoulous (1982) and Ortega *et al* (1992) we find that the position in front of the As atoms (chemisorption energy 3.49 eV per adatom) is more favourable than the long-bridge-bond position (chemisorption energy 3.30 eV). The positions in front of and on top of the Ga atoms are far less favourable, with adsorption energies 3.17 and 2.20 eV respectively. The difference between our results and that of Ortega *et al* is more likely due to the simpler approach used in their work. On the other hand, the results of Yi *et al* (1992) for low coverages are not comparable with our geometries due to the larger unit cell used in their work, which allows a different substrate relaxation and interaction with the substrate. It is interesting at this point to note that Na (group I) adatom is found to lie halfway between neighbouring Ga atoms along [001] (Hebenstreit and Scheffler, 1992), while Sb (group V) finds its equilibrium at the long-bridge-bond position (Schmidt *et al*, 1993).

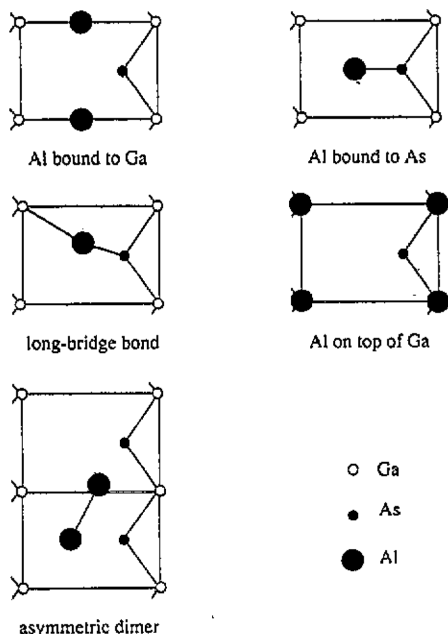

Figure 1. Top view of different structures for 0.5 ML coverage of Al on GaAs(110). The denotation of the atoms is valid throughout the paper.

The large chemisorption energy for the position of Al in front of As is not only due to the saturation of the broken As dangling bond but arises also from a weak interaction of Al with the two oppositely situated Ga atoms. This becomes evident from an inspection of the

charge density plot in figure 2. The maximum pseudocharge-density between Al and Ga is approximately 0.03 $e\times$ Bohr^{-3}, whereas we find a value of 0.08 $e\times$ Bohr^{-3} between Al and As. Caused by the larger electronegativity of both substrate atoms with respect to Al we find a charge transfer towards the substrate. The equilibrium atomic distances are 2.82 Å (Ga–Al) and 2.61 Å (As-Al). Clearly, our calculated value of the Al–Ga distance is much smaller than that used in the work of Chelikowsky *et al* (1981). Our calculated distances Al–Ga and Al–As are also much smaller than those obtained in the work of Zunger (1981). On the other hand, our calculated values of Al–substrate bond lengths are larger than those obtained in the work of Ihm and Joannopoulous (1982) (namely 2.35–2.40 Å for Al–As and 2.45–2.50 Å for Al–Ga).

As can be seen from the DOS calculation in figure 6, the Schottky barrier is already formed for this geometry. The calculated DOS curve was superimposed onto the bulk DOS curve for determining the Fermi level pinning with respect to the bulk band edges. The Schottky barrier height, as a measure of the difference between the Fermi level and the bulk conduction band edge, of approximately 0.6 eV was obtained. For the half-monolayer coverage the good agreement between our calculated Schottky barrier height and the synchrotron-radiation photoemission measurement of Daniels *et al* (1982) is encouraging but somewhat fortuitous, since we have considered an ordered overlayer structure whereas they have direct evidence of replacement interactions between the adatoms and the substrate.

In order to discuss the nature of Schottky barrier formation we note that recently Hebenstreit and Scheffler (1992) have discussed the case of Na adsorption on GaAs. The Na atom at the half-monolayer coverage is placed in front of Ga, donating its 3s electron into the Ga dangling bond. The state arising, although only half occupied, is highly localized and should therefore, as discussed by the authors, not contribute to surface metallization. The situation for Al adsorption is somewhat different. We have shown the orbital character of the highest occupied state in figure 3. This state arises not only from the bonding of Al with As but is also localized around Ga and, in addition, we find a non-vanishing overlap with the Al in the neighbouring unit cell. Thus we think that this state already gives rise to surface metallization in the half-monolayer case.

3.2. *The one-monolayer coverage*

For the one-monolayer coverage we considered different structures, some of which have been proposed in the past. These are the ECLS, the IRC (Yi *et al*, 1992), Al dimer bonded to either As or Ga, the epitaxially overlapping chain structure (EOCS), the epitaxial on top structure (EOTS), another model as discussed by Ortega *et al* (1992) corresponding to one Al atom bonded to Ga and another Al atom located on top of As, and finally the p^3 model. The EOTS, EOCS and p^3 models have been discussed by LaFemina *et al* (1990) and Skeath *et al* (1983) for Sb adsorption. A top view of all these structures is given in figure 4.

The adsorption energies per adatom are given in table 1, together with the nearest atomic distances in equilibrium. To our surprise all these structures yielded nearly the same adsorption energy. The difference in energy between the most favourable IRC model and the least but one (the EOTS model) is less than 1/4 eV. All the structures were found to be either metallic or to have only a very small band gap of about 1/10 eV . This behaviour is quite different from the one found for Sb/GaAs (Srivastava 1992,1993; Schmidt *et al* 1993). The GaAs(110)–Sb(1 ML) system has been found to clearly favour the ECLS over the other structures, and to be semiconducting. The reason for the completely different behaviour of the Al coverage lies in the fact that only weak covalent bonds exist within the overlayer and between Al and Ga. In contrast, we find a strong bond between Al and As (figure 5).

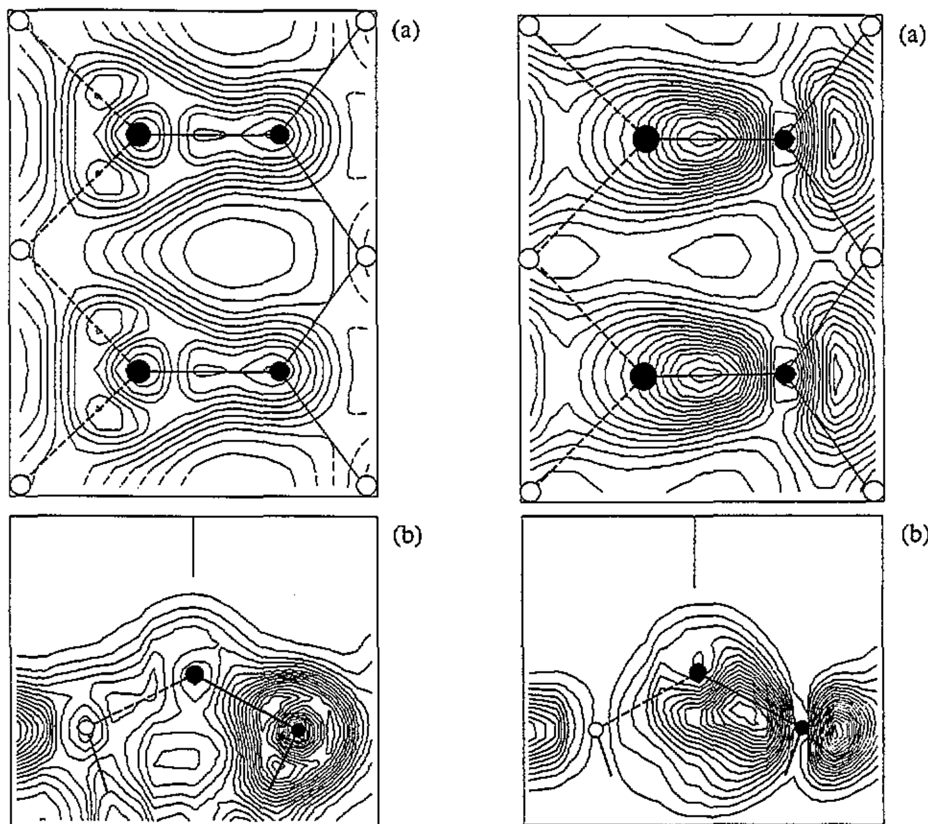

Figure 2. Contour plots of the total valence pseudocharge density for 0.5 ML with Al bonded to As (a) drawn along a horizontal plane 0.4 Å above the Al atoms and (b) drawn along a folded plane containing both the Al–As and Al–Ga bonds. The contours are spaced by 0.0025 and 0.005 $e\times$ Bohr^{-3}, respectively.

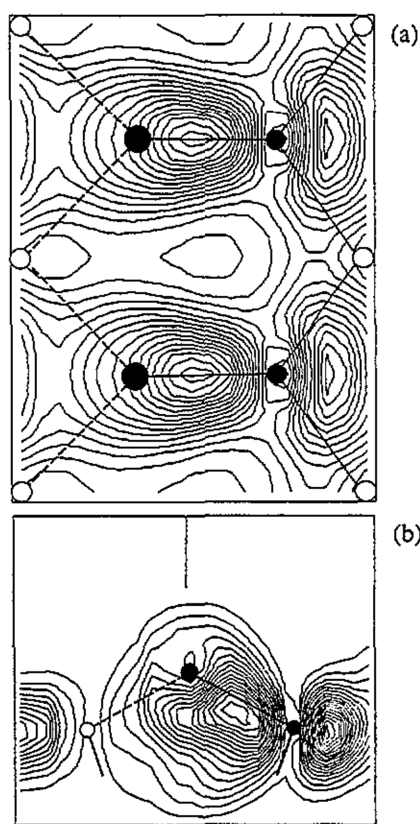

Figure 3. Orbital character of the half-occupied state pinning the Fermi level for 0.5 ML near $\bar{X}'$ (a) drawn along a horizontal plane 0.8 Å below the Al atoms and (b) drawn along a folded plane containing both the Al–As and Al–Ga bonding. The contours are spaced by 0.00025 $e\times$ Bohr^{-3}.

Table 1. Adsorption energies (E_{ad} in eV per adatom) and bond lengths (d in Å) for the 8 structures examined for the 1 ML coverage of Al on GaAs 9110).

	IRC	dimer (As)	ECLS	dimer (Ga)	EOCS	Ortega's model	EOTS	p^3 model
E_{ad}	3.45	3.44	3.42	3.38	3.26	3.25	3.21	2.91
Band gap[a]	m	s	s	s	m	s	m	m
d(Al–Al)	2.77	2.73	2.73	2.73	2.98	3.35	2.84	2.57
d(Al–As)	2.60	2.46	2.43	2.78	2.76	2.45	2.50	2.47
d(Al–Ga)	2.60	2.77	2.48	2.44	2.75	2.57	2.52	2.57

[a] m, metallic; s, semiconducting with a very small band gap.

The maximum pseudocharge density both between the Al atoms and between Al and Ga is 0.03 $e\times$ Bohr^{-3}, whereas we find this value to be 0.07 $e\times$ Bohr^{-3} between Al and As. These values resemble the charge density for the half-monolayer case discussed above. The

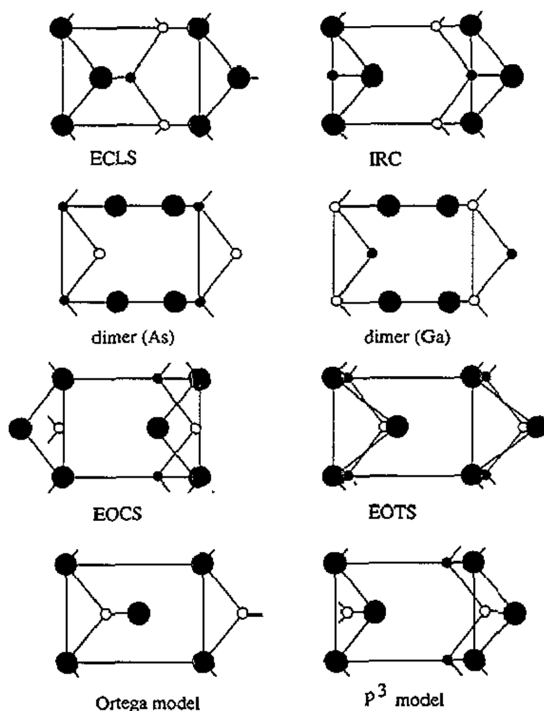

Figure 4. Top view of different structures for 1 ML coverage of Al on GaAs(110).

weak bonding in the overlayer chain and between Al and Ga allows Al to occupy different adsorption sites corresponding to different adsorption geometries without much change in energy. The cohesive energy of bulk Al in the FCC structure (as an upper limit for the energy gain upon clustering) obtained by the same method is 4.3 eV.

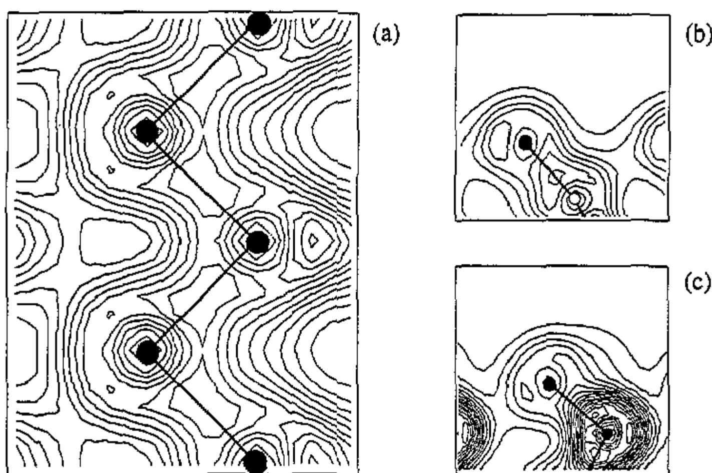

Figure 5. Contour plots of the total valence pseudocharge density for IRC, drawn (a) along a horizontal plane containing the Al atoms with contours spaced 0.0025 $e\times$ Bohr^{-3}, and (b) and (c) along vertical planes containing the Al–Ga and Al–As bonding, respectively, with contours spaced by 0.005 $e\times$ Bohr^{-3}.

We also made calculations with Al exchanged with the substrate Ga in the most favoured

IRC model. The adsorption energy was found to increase by 0.17 eV, due to the greater heat of formation for AlAs compared with GaAs. Therefore it is clear that clustering of Al atoms on the surface and penetration of Al atoms into the substrate, as observed experimentally (Daniels *et al* 1982, Suzuki and Fukuda 1991, Nishikawa *et al* 1984), are more favourable than any of the ordered one-monolayer structures considered in this work. Especially interesting with respect to the experimental works are the dimer structures. The Al atoms in the dimer configuration bound to either As or Ga relax to positions which are nearly equidistant (within 2%) in the [001] direction, thus forming a linear chain rather than a dimer. This chain can be understood as the first layer of epitaxially growing Al in the FCC structure, but rotated by 90° with respect to the substrate, as observed experimentally (Prinz *et al*, 1982). The energy difference between the favourable IRC model and the dimer at As (0.01 eV), or the dimer at Ga (0.07 eV), can be readily provided by the heat of formation of Al in the FCC structure. However, this epitaxial growth requires low temperatures, since the high mobility of Al on GaAs(110) at room temperature (Prinz *et al*, 1982), together with the flexibility of Al in occupying different adsorption sites according to different models, results in formation of clusters which are not correlated to the crystallographic direction of the substrate (Suzuki and Fukuda, 1991). A similar effect may be responsible for the lack of formation of a fully ordered monolayer of Al on InP(110) at room temperature (McKinley *et al*, 1982).

It is also interesting to note that while the adsorption energies for the one and half-monolayer coverages of Al on GaAs(110) lie in the same range, the half-monolayer case is preferred slightly by 0.04 eV. This contradicts both Ihm and Joannopolous, and Ortega *et al*. The results obtained by Yi and Bernholc, on the other hand, are not directly comparable to our work, due to the reasons mentioned above.

To ensure convergence of results with respect to the number of plane waves and $\boldsymbol{k}$-points, we made calculations for the most favourable structure for the half-monolayer as well as for the one-monolayer IRC model with an energy cutoff of 15 Ryd and a Brillouin zone integration with uniformly distributed 20 $\boldsymbol{k}$-points. We obtained adsorption energies of 3.49 eV for the half-monolayer case and 3.44 eV for the IRC model, results which are almost identical to those obtained with 8 Ryd cutoff and 4 special $\boldsymbol{k}$-points. This comparison clearly suggests that the conclusions drawn from this work with the 8 Ryd cutoff are on a firm footing.

It is interesting to compare the interface structural parameters for Al/GaAs with those for Sb/GaAs. We find that upon chemisorption an ordered monolayer of Al in the ECLS removes the relaxation of the substrate GaAs, and there is only a small vertical buckling between the two inequivalent Al atoms. The GaAs substrate layer shows a vertical shear of 0.06 Å and a tilt angle of 2.5°. The Al overlayer is characterized by a vertical shear of 0.15 Å and a tilt angle of 4.5°. A similar behaviour was also found for Sb on GaAs and InP (Srivastava 1992). However, in the IRC model the (buckling, tilt angle) results are (0.25 Å, 8.5°) and (0.51 Å, 15°) for the GaAs substrate and Al overlayer, respectively. It is striking that the bond lengths within the overlayer and from the adatoms towards the substrate differ appreciably if one compares the different models of Al adsorption. It is clear from table 1 that the concept of conservation of covalent radii fails for the Al overlayer, in contrast to the case of Sb overlayer where it was observed that different structures tend to preserve the covalent radii of Sb, As and Ga (Srivastava 1992, 1993, Schmidt *et al* 1993). This is not surprising because there are no strong covalent Al–Al and Al–Ga bond formations, as seen in figure 5.

As pointed out earlier, Al atoms have a tendency to cluster and penetrate into the substrate. It is nevertheless interesting to investigate the electronic structure of the ordered

overlayer system. In figure 6 we show the DOS for the most favourable IRC model. The Schottky barrier established at the half-monolayer coverage has now been completed, but the barrier height of approximately 0.6 eV has not changed. Once again our calculated Schottky barrier height is in apparent agreement with the photoemission measurement of Daniels *et al* (1982), in spite of the obvious differences in the ordered geometry considered in this work and the experimentally observed Al–Ga replacements. However, our work clearly shows that while the DOS at the Fermi level can be described as merely finite for the half-monolayer coverage, it is significantly large for the one-monolayer coverage in the IRC model. There are two additional features in the DOS for the one-monolayer coverage, one in the range of the stomach gap at about E_F - 5 eV and one just below the Fermi level. The appearance of the feature about 5 eV below the valence-band maximum after deposition of approximately one monolayer was also found in photoemission experiments (Bachrach *et al*, 1978). We also note that the Al coverage leaves the ionic gap of GaAs free of states, in contrast to the Sb coverage (Schmidt *et al*, 1993) for which s-like states of the overlayer atoms are found.

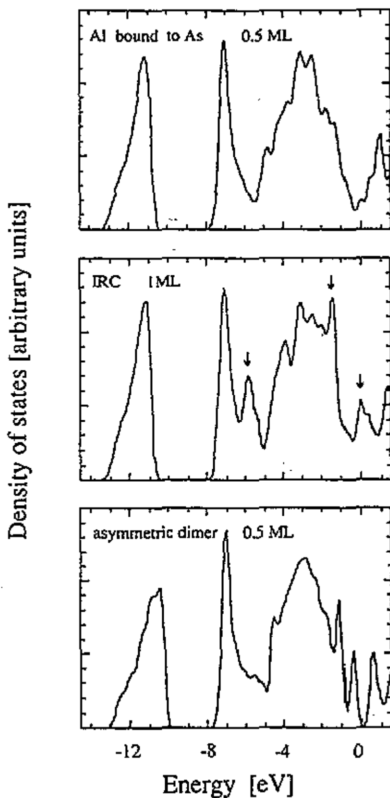

Figure 6. Smoothed DOS as calculated for 0.5 ML coverage with Al bonded to As, the 1 ML case in the IRC model, and 0.5 ML coverage in the asymmetric dimer model. The energy cutoff is 15 Ryd for the top two structures and 8 Ryd for the third structure. The energies are referred to the Fermi level in each case.

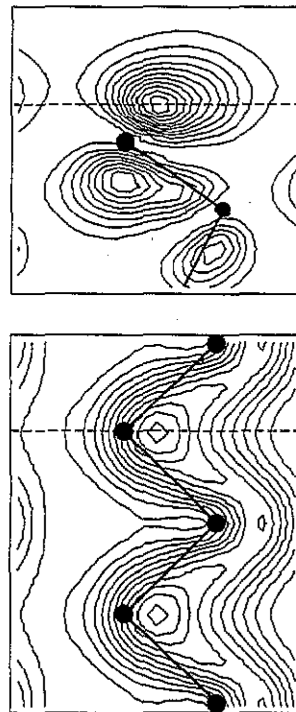

Figure 7. Orbital character near $\bar{X}'$ of the half-occupied state pinning the Fermi level in the IRC model. The contours are drawn along a vertical and a horizontal plane which cross each other at the dashed lines. The contours are spaced by 0.0005 $e\times$ Bohr^{-3}.

The orbital character of the half-occupied state is shown in figure 7. This state shows only a weak coupling between Al and the substrate As atoms, and its metallic character is mainly due to the interaction between the Al atoms. Thus our work clearly shows that the Schottky barrier formation at the GaAs(110)–Al interface for both half- and one-monolayer coverages of Al is contributed to by Al–Al interaction, which increases with increasing coverage (cf. figures 3 and 7). Our interpretation of Schottky barrier formation at this interface is not dissimilar to the predictions of the weakly-interacting-cluster model of Zunger (1981), which is also favoured by the work of Daniels *et al* (1982).

The metallicity of the Al covered GaAs surface as calculated by us both for half- and one-monolayer coverages is in serious disagreement to the recent LCAO results of Ortega *et al* (1992) who report a gap of 1.2 eV. Their claim that their results are consistent with the STM measurements of Suzuki and Fukuda (1991) is, to our mind, unreasonable. This is because in their work Suzuki and Fukuda have clearly shown the semiconducting nature of only a large cluster containing 200 atoms of Al on the GaAs(110) surface. As far as the present work is concerned, since we have only considered ordered structures which have not been clearly observed in the STM pictures of Suzuki and Fukuda, we can assume that there is no contradiction between our result and the experimental result.

It is interesting to compare the nature of the electronic structure of this system with those obtained for sodium (group I) and antimony (group V) adsorptions. For Na/GaAs(110)(1 ML) a band gap of about 0.7 eV was reported (Hebenstreit and Scheffler, 1992). The sodium valence electron was found to be transferred into the Ga-like surface state, resulting in a partial ionization of the adatom. The interaction between the Na adatoms could be described as a screened ion–ion repulsion. For Sb/GaAs(110)(1ML) also a band gap of approximately 0.7 eV has been found (Schmidt *et al* 1993, Srivastava 1993). Here, however, it is due to the strong covalent bonds within the overlayer and with the substrate.

3.3. *The asymmetric dimer model*

In order to understand the semiconducting nature of the Al/GaAs(110) overlayer system seen in the STM images (Suzuki and Fukuda, 1991) we examined further structures. We chose a 2×1 surface unit cell, with doubled periodicity along $[\bar{1}10]$, and with one Al occupying the long-bridge-bond position and another Al occupying a site along the neighbouring As dangling bond. A top view of the relaxed positions of Al atoms for this geometrical model can be seen in the last diagram of figure 1. The Al atom originally placed in a long-bridge-bond position has relaxed towards the other Al atom decreasing the Al–Al bond length to 2.55 Å. In equilibrium atomic geometry we get an adsorption energy of 3.43 eV per adatom. This energy is only slightly smaller than the energy calculated in the 1×1 structure with the Al atom bonded to As. Nevertheless, we find its electronic properties interesting. The asymmetric dimer structure yields an indirect band gap of 0.7 eV. The DOS shows two occupied peaks at the top of the bulk valence band edge and an unoccupied peak in the upper half of the bulk band gap. If one takes the well known effect of gap-narrowing due to the local density approximation into account (see, e.g. Godby *et al* 1987, Jenkins *et al* 1993), the band gap would become comparable to the experimentally observed value of 1 eV in the STM measurement of Suzuki and Fukuda. It is, however, important to point out that we are not claiming a proper agreement between the band gap obtained for this structure and that observed in the experiment for a large cluster of Al atoms. The main conclusion to be drawn from here is that although the asymmetric dimer structure considered may not represent the lowest global energy configuration, our study nevertheless provides an indication that a cluster of Al atoms rather than a well ordered overlayer may result in a

finite band gap, thus somewhat supporting the work of Suzuki and Fukuda. Unfortunately computer time limitations prevented us from pursuing this issue further, including larger unit cells with adsorbed clusters.

4. Conclusion

From a first-principles pseudopotential study we have found several stable structures for Al chemisorption on GaAs(110) for the half- and one-monolayer coverages. Most of these structures lie in the same energy range, but in equilibrium the half-monolayer coverage has a slightly lower energy than the full-monolayer coverage. The reason why a variety of different structures lie in the same energy range is that there is only a weak interaction between the Al atoms and between Al and Ga atoms. This feature might explain both the difficulty in the growth of an ordered overlayer structure and the missing correlation between the overlayer clusters and crystallographic directions of the substrate. The chemisorption energies for all the structures considered in this work are found to be lower than the cohesive energy of bulk Al (in the FCC structure) and the energy gain due to an exchange reaction, indicating that at higher temperatures both processes are very likely to take place. The Schottky barrier formation for the ordered Al/GaAs(110) interface is established at the half-monolayer coverage and completed at the full-monolayer coverage, and is contributed to by the Al–Al interaction. The large band gap observed in a recent STM experiment may only be interpreted as a result of clustering of a number of Al atoms. However, the electronic character of such clusters and their influence on the Fermi-level pinning need further investigation, both experimentally and theoretically.

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