Atomic Structure of Al-GaAs(110) Interfaces

Jae-Yel Yi and J. Bernholc
Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202

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Atomic structures of Al on GaAs(110) are studied by *ab initio* molecular dynamics for coverages of $\frac{1}{8}$ to 1 monolayer (ML). A single chemisorbed Al atom resides at the center of a triangle of one Ga and two As atoms. Al dimers have very long bond lengths and bind due to substrate-mediated interactions. Epitaxial growth of 1 ML of Al is less stable than the formation of islands. Preformed clusters bond strongly to the substrate, which shows that the absence of Fermi-level pinning in samples grown by cluster deposition is due to suppression of reactivity rather than lack of interactions.

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Most properties of metal-semiconductor interfaces are already determined at monolayer (ML) or submonolayer coverage of the metal. A key to understanding the electronic properties of the interface is the determination of the atomic structures at the various stages of growth. Although cluster formation and exchange reactions at metal-semiconductor interfaces have been confirmed [1-6], such determination has not yet been carried out for any interface. GaAs(110) is one of most widely studied semiconductor surfaces. Recently, a novel cluster deposition growth technique [4] has been developed. It produced abrupt and defect-free interfaces [4], but the reasons for their formation are not well understood. Other experimental studies showed that metal atoms on GaAs(110) bond with surface Ga atoms in small clusters at less than 0.1 ML coverage [7,8].

In this Letter we describe the results of extensive *ab initio* calculations of the atomic structures of Al atoms on GaAs(110) with coverages ranging from $\frac{1}{8}$ to 1 ML. The results show that single Al atoms interact strongly with the substrate. A similarly strong interaction is also observed for Al clusters. Two Al atoms prefer a dimer-like structure to separate adsorption, but the Al-Al distance is much larger than the Al-Al bond in bulk Al. The barrier for Al diffusion is only 0.75 eV, and the binding energy of Al islands on GaAs(110) is greater than that of an epitaxial ML of Al. The last two results explain the tendency for clustering observed in the experimental data [9]. Although Al cluster deposition does not lead to disruption of the GaAS(110) surface [4], the present results show that even preformed Al clusters interact strongly with this surface.

The calculations used the *ab initio* molecular-dynamics (Car-Parrinello) method [10], which is based on local-density theory and uses a plane-wave basis set. The modified pseudopotentials by Stumpf, Gonze, and Scheffler [11] were employed for Al, Ga, and As. Plane waves (PL) with kinetic energies up to 14 Ry were included in the calculations, which corresponds to 13000 PL at the Γ point. Most of the calculations used Γ-point sampling but several tests included other k points as well. Tests for bulk GaAs and several small Al clusters reproduced previous theoretical and experimental results. The theoretical lattice constant of 5.61 Å was used in all calculations.

The ideal surface of GaAs(110) was simulated using a periodic slab geometry with six layers of GaAs and four layers of vacuum. Each layer contained four surface unit meshes (see Fig. 1). Two top and two bottom layers were allowed to relax using Γ-point sampling. As a check, we also relaxed the top three layers using two special surface k points [12]. Both calculations produced very similar results, confirming that for a supercell of the present size Γ-point sampling and the relaxation of two layers are sufficient. The deposition of Al was studied employing six layers of GaAs, 1-2 layers of Al, and 4-5 layers of vacuum. The two top layers of GaAs and the Al layers were allowed to relax in order to find local minima. We did not consider the exchange of Al with Ga, although this structure has the lowest total-energy geometry [1,6], because we are only concerned with the initial stages of growth at low temperatures.

For clean GaAs(110), the relaxation causes a significant change in surface morphology. The heights of Ga and As atoms of the outermost layer, which are the same in the ideal geometry, differ by 0.60 Å. The As atoms move outwards by 0.15 Å from their original positions,

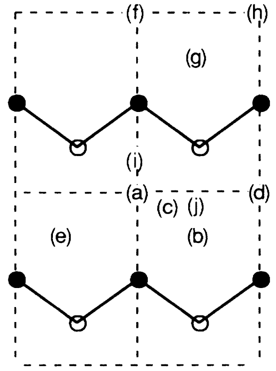

FIG. 1. The supercell used in the present calculations. The open and solid circles denote As and Ga atoms, respectively. The sites (a)-(j) indicate the position of Al atoms as discussed in the text.

while the Ga atoms move inwards by 0.45 Å. The surface relaxation energy per unit cell is 0.32 eV and the calculated photoemission threshold is 5.15 eV. Comparing these to previous calculations, our results are in very close agreement with those of Qian [13], but differ somewhat from those of the Berlin group [14] which finds a slightly larger displacement of the outer As atom and a slightly smaller displacement of the Ga atom. We attribute these minor differences to different plane-wave cutoffs, numbers of relaxed layers, pseudopotentials, k-space samplings, etc. All three sets of calculations fall within the error bars of existing measurements and agree very well with the LEED [15] and photoemission data [16], e.g., the measured photoemission threshold is 5.15–5.75 eV.

We chose three important sites for chemisorption of a single atom, which corresponds to $\frac{1}{8}$ ML coverage in our unit cell (see Fig. 1): (i) The center site between a Ga atom and two As atoms [site (a)], (ii) the center site between two Ga atoms and an As atom [site (b)], and (iii) the bridge site between Ga and As atoms [site (c)]. The binding energies were 3.4, 3.0, and 2.7 eV for sites (a), (b), and (c), respectively. In all cases the nearest neighbors of the Al atom partially recovered the unrelaxed positions of the ideal surface. The calculated Al-Ga and Al-As bond lengths for site (a) are 2.50 and 2.54 Å, respectively. For site (b) these lengths are almost the same, while the greater bonding distances at site (c) result in bond lengths which are about 0.1 Å greater. In disagreement with the previous calculation [17], our highest-binding-energy site is (a) rather than (c). Furthermore, our calculated largest binding energy of Al to GaAs is 1.1 eV greater, which shows that the thermodynamic force for clustering is much smaller than previously thought [6,17]. The disagreement with the previous results is most likely due to the size of the supercell and to the much smaller plane-wave cutoffs used in the previous calculation. A small supercell allows some surface atoms to have more than four nearest-neighbor atoms for sites (a) and (b) and it is not large enough to allow for full relaxations of the nearest neighbors of the chemisorbed atom. A recent calculation for Na on GaAs(110) [18] predicted chemisorption on site (a). However, the interactions of a Na adatom with GaAs(110) are ionic, while they are covalent for Al.

A straightforward *ab initio* molecular-dynamics (MD) simulation of Al diffusion, although possible in principle, would be prohibitively expensive. Given the present computer capacity, we thus have to consider well-defined migration paths. Two such paths have been considered in the past [17,18]: (i) through the interstitial channel, and (ii) through the centers of the bonds of surface atoms. Since only path (i) passes through the highest-binding-energy sites, we selected it for further study. The conventional methods to compute surface migration barriers are still very time consuming because many calculations are needed in order to determine the total energy along the path, unless the position of the saddle point can be inferred by symmetry. However, the *ab initio* MD methodology allows for evaluation of the total energy along a given path in a single "adiabatic trajectory" simulation [19]. We carried out such simulation along the path (a) → (c) → (b) in Fig. 1. In this simulation, the diffusing atom moves with a small fixed velocity, corresponding to thermal velocity at 50 K, along the path. Since the velocity of the Al atom is small, the Ga and As atoms can follow and are continuously relaxed using Hellman-Feynman forces. In order to maintain numerical stability in case level crossings occur along the path, finite-temperature *ab initio* MD [20] is used, with the electronic temperature of 1000 K [21]. From the variation of the total energy along the path and from additional total-energy studies in the direction perpendicular to this path we found that site (c) is indeed the saddle point and that the energy barrier is 0.75 eV. The small barrier allows for easy migration of Al on GaAs even at relatively low temperatures. The high binding energy of Al on GaAs combined with the low activation energy for diffusion may favor islands and/or chains rather than 3D cluster formation at low coverages. Such clustering was observed for Au [7] and Sm [8] on GaAs(110) and is also predicted by our calculations for Al (see below).

In the study of dimer formation, the following starting geometries were considered: (i) Al atoms occupying sites (a) and (d), (ii) sites (b) and (e), (iii) sites (a) and (b), (iv) sites (a) and (f), (v) sites (a) and (g), and (vi) sites (a) and (h) (see Fig. 1). The binding energies per Al atom after structural relaxations were 3.5, 3.4, 3.5, 3.6, 3.8, and 4.1 eV, respectively, and the distortions were similar to those occurring in the adsorption of single atoms. We also tested adsorption of two Al atoms in adjacent bridge sites and adjacent ideal lattice sites. Both turned out to be energetically unstable and the Al atoms moved to either geometry (i) or (ii). The reason for the relatively low stability of cases (i)-(iii) is overcoordination, since some of the surface atoms become fivefold coordinated. The most stable structure (vi) has an Al-Al bond length of 6.87 Å, which is much greater than that of the Al diatomic (2.51 Å) [22] or bulk Al (2.86 Å). The dimerlike geometry (vi) is very different than that of Ref. [17], again due to differences in supercell sizes. Since the Al atoms are clearly much too far apart to interact directly in (vi), the energy gain must be due to interactions through the substrate, and in particular to structural relaxations. Since the binding energies per Al atom in all cases are larger than the single-Al-atom chemisorption energy, Al dimer formation is preferred to single-atom adsorption. The dimerlike structure (vi) is similar to that observed in a scanning-tunneling-microscopy study of Sm on GaAs(110) [8], but is different from that of Au on GaAs(110) [7], since the Au atoms occupy two second-nearest Ga-bonded sites.

We compare two cases of 1-ML Al coverage with cluster deposition. For 1 ML coverage, we consider (i) an epitaxial monolayer on the original lattice sites, and (ii) Al atoms occupying sites (a) and (b) of Fig. 1. Both structures were fully relaxed. As expected, since Ga and As atoms have five nearest neighbors in the starting geometry (ii), the relaxations were substantial in this case. After structure optimization, the Al atoms occupied sites equivalent to (i) and (j) in Fig. 1, although the resulting chain was quite irregular. For the epitaxial Al overlayer, the Ga and As atoms at the interface unrelax, i.e., move outwards and inwards, respectively. This is analogous to the motion of the atoms in the second layer of a clean surface. Despite the lattice mismatch of 1.6 Å between bulk Al and GaAs, the atomic displacements at the interface are small (<0.12 Å). However, the binding energy per Al atom for the epitaxial ML is only 3.4 eV, while it is 3.6 eV for the irregular chain (ii).

Cluster deposition was simulated by placing an eight-atom Al cluster on two sites on the relaxed surface. The structure of this cluster was previously optimized in vacuum, which led to a trigonal geometry; see Fig. 2(a). Following this "deposition," we relaxed all the atoms again and found the geometries shown in Figs. 2(b) and 2(c). It is clear that this cluster interacts strongly with the substrate, since it distorts substantially from its original shape and binds by 5.1 and 4.0 eV, respectively, to the sites shown in Figs. 2(b) and 2(c). The binding energies per Al atom were 3.4 and 3.2 eV, respectively, which are smaller than that of the most stable dimerlike structure or of the irregular chain discussed above. Although computer-time limitations prevented us from pursuing this issue further, it is likely that other low-energy configurations of this cluster on GaAs(110) may be found [23]. The results of a very recent scanning tunneling microscopy study of the deposition of atomic Al on GaAs(110) [9], which were communicated to us after the completion of the present work, show that large Al clusters form even at submonolayer coverages.

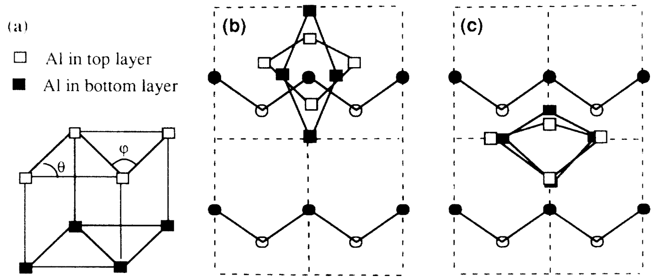

FIG. 2. (a) The structure of an eight-atom Al cluster optimized in vacuum. The average bond distance is 2.63 Å and φ and θ are 61.2° and 58.8°, respectively. (b),(c) The structures of this cluster on GaAs(110) after relaxation. The average distances between the two Al layers are 2.50 and 2.66 Å, respectively. However, the heights of Al atoms in each layer differ by up to 1.4 Å in (c).

The large chemisorption energies computed for the single Al atoms, their dimers, the Al monolayers, and the preformed clusters modify substantially the existing picture of Al adsorption and deposition [6,17]. Our predicted adsorption sites for atoms and dimers are different and these predictions should be tested experimentally. The adsorbed atoms and dimers are bound much more strongly to the surface than expected, although their mobility remains high. The thermodynamic force for the formation of Al clusters is thus reduced. The Al monolayers and clusters are also strongly bound to the surface. This includes the preformed clusters we have studied.

Pioneering low-temperature cluster deposition experiments by Weaver and co-workers [4] led to abrupt, nearly ideal interfaces with Fermi-level positions quite different from those obtained by atom deposition. Furthermore, the Fermi-level positions in cluster deposition depended only weakly on the deposited metal. Although the clusters used in these experiments were much larger than the eight-atom cluster studied above, several points can still be made on the basis of our calculations. In agreement with the suggestion by the original workers [4], we find that a partial surface "unrelaxation" does occur upon the deposition of the cluster, but a similar unrelaxation occurs also in the vicinity of a deposited atom or dimer. The strong interaction between the cluster and the substrate is very likely to occur even for large clusters. Therefore, the differences between Al atom and Al cluster deposition cannot be explained by the "weak interaction" model [6]. The remaining possibility is the decrease in reactivity in the case of cluster deposition. Such a decrease is expected on general grounds in more fully coordinated structures and should result in more abrupt interfaces. Indeed, metal-atom–substrate intermixing has been observed during atom deposition under identical conditions [4], but, with the exception of the very reactive Ti, not during cluster deposition [4]. Although one cannot examine this issue by calculations at present, we speculate that the difference in Fermi-level positions between cluster and atom deposition [4] is mainly due to reactions occurring at the interface during atom deposition, but not during cluster deposition. Indeed, the largest deviation from the "common" (average) Fermi-level position in cluster deposition occurred for the case of Ti, where some intermixing is likely to occur even at the lowest temperatures used in the deposition process.

If the main difference between atom and low-temperature cluster deposition is the suppression of reactivity, rather than the weakening of metal-substrate interactions, it should be possible to devise other, potentially easier deposition techniques. For example, one could experiment with various Al-containing precursors that are chemically saturated and attempt to devise reaction sequences or add additional precursors that would prevent the presence of highly unsaturated Al atoms on the GaAs surface. This approach would be much in the spirit of atomic layer epitaxy [24], although the lack of Al epitaxy on GaAs(110) would make the controlled growth of a well-defined number of layers unattainable.

In summary, we investigated atom and cluster deposition of Al on GaAs(110) as a paradigm of the initial stages of the formation of a metal-semiconductor interface. A single Al atom is strongly bound to the surface and prefers a threefold-coordinated site. The barrier for surface diffusion is small, allowing for the formation of dimers and islands. These are thermodynamically preferred, but the energetic gain is much smaller than previously thought. The Al-Al binding in an Al dimer is solely due to interactions through the substrate. The epitaxial growth of an Al monolayer on GaAs(110) is thermodynamically unstable. Preformed Al clusters interact strongly with the substrate, which leaves the suppression of interface reactions as the only plausible explanation of the differences between cluster and atom deposition under otherwise identical conditions.

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