

Structural Energies of Al Deposited on the GaAs(110) Surface

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Major controversies over the structure of Al atoms deposited on the GaAs(110) surface have been resolved by using a first-principles energy-minimization method. The most stable configuration is that of Al atoms replacing the second layer Ga atoms beneath the surface. At temperatures where this reaction cannot be activated, two important processes are found to exist. In the low-coverage limit, Al atoms favor twofold sites to form strong bonds with the substrate atoms. At higher coverages, Al atoms tend to cluster and make new bonds among themselves.

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The Al-GaAs interface is a prototype Schottky barrier system which constitutes an essential element in many electronic devices. There exists a vast literature on the structure and the behavior of the Al atoms deposited on the GaAs(110) surface.¹⁻¹¹ With use of a simple heat-of-formation argument, it can be immediately concluded that the Al atoms eventually replace the substrate Ga atoms in the second or deeper layers to minimize the total energy. This reaction has been indeed observed for annealed Al-GaAs systems.¹ However, the interpretation of the room-temperature experimental data is still ambiguous and no consensus has been reached on the exact microscopic nature of the system.¹⁻⁵

Several theories have addressed themselves to the calculation of the microscopic structure of this system. To simplify the problem, they have usually assumed an ordered half monolayer of Al (one Al atom per surface unit cell) bonded to particular substrate atoms.⁶⁻¹⁰ An exchange reaction has also been suggested with various substrate relaxations.¹¹ In other cases, disordered Al overlayers or Al cluster formations were proposed to explain experimental observations.^{2,10} In any case, most of these attempts were directed towards optimizing the geometry to best fit a certain set of known experimental data.

The approach adopted here is quite different and more fundamental in nature; our intention is to predict the lowest energy-stable configurations by minimizing the total energy of the system with respect to its structural degrees of freedom, using, as the only inputs, the atomic numbers and the crystal structure of the substrate (zinc blende). Self-consistent pseudopotential total-energy calculations¹² were carried out for over thirty different geometries. Each geometry consisted of a completely independent self-consistent calculation. The present work represents the first *ab initio* study of a chemisorption process using a pseudo-

potential energy-minimization scheme.

In these calculations, a Hamann-Schlüter-Chiang pseudopotential¹³ was constructed with the Wigner exchange-correlation function.¹⁴ This potential has been tested for bulk GaAs and AlAs¹⁵ and proved sensitive enough to reproduce the minute binding-energy difference between them (0.20 eV difference compared to the experimental value of 0.25 eV per bond). The supercell method is used with six layers of substrate, an Al overlayer, and a four-layer thickness of vacuum. The computational effort is dramatically reduced by incorporating two additional features: an improved Löwdin perturbation scheme for reducing the basis set¹⁶ and a dielectric matrix screening method for achieving very fast self-consistency.¹⁷ The geometries we investigated are grouped into four classes and will be discussed separately below.

The first class consists of free GaAs(110) surfaces with different relaxations. The relaxation energy is found to be 0.7 eV per surface unit cell, as compared to 1.0 eV with the tight-binding method¹⁸ and 1.2 eV with the quantum chemical cluster method.⁸ Our relaxed geometry is very close to Chadi's¹⁸ and gives slightly lower energy (~0.04 eV) than that determined by dynamic low-energy electron diffraction (LEED).¹⁹ But this small difference is about the numerical uncertainty of the present calculation. From various tests, we expect that the error bar of the relative energy between different geometries in the same class is 0.1 eV.

The second class comprises exchanged geometries, i.e., the Al atoms replacing the Ga atoms in the first, second, or third layer of the substrate with ideal or relaxed configurations. Experimentally, the magnitude of the heat of formation for AlAs is 0.5 eV larger than that of GaAs. The dynamic LEED analysis suggests that a replacement reaction in the second layer always occurs for annealed systems. The first and the

second layer exchange reactions lower the total energy by 0.48 and 0.64 eV, respectively. Note that the difference in these energies is close to the energy difference between an AlAs and GaAs bond as mentioned previously. The shift from the second to the third layer replacement does not give rise to an additional energy lowering. This is expected since no additional AlAs bonds are formed. Again, Chadi's relaxation¹⁸ gives a slightly lower energy than that determined by LEED¹ when the replaced Ga atoms are allowed to leave the surface.

The first layer exchange with the replaced Ga atoms bonded to the substrate has drawn much attention.^{2-5,9,10,11} We find that the Ga atoms prefer to bond to the surface As site¹¹ rather than the surface Al site (by 0.4 eV), in contrast to the results obtained by the cluster calculations.⁸ When the Ga bonds to the substrate As atoms, it tends to unrelax the substrate atoms. This is quite a general phenomenon and will be discussed in detail later. The counterrelaxation¹¹ proposed to explain the experimental bond bending is found to be unfavorable energetically.

In the third class of geometries, an ordered half monolayer of Al is assumed to be bonded to the substrate at different sites with variable bond lengths, substrate relaxations, and in certain cases, bond angles. We have done extensive calculations on this class of geometries and have essentially mapped out the energy surface of the

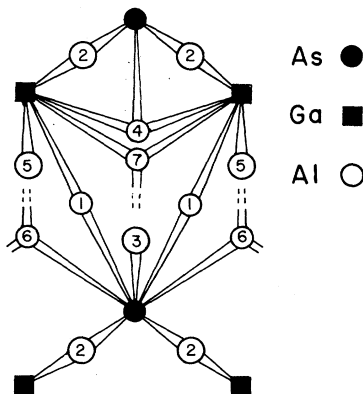


FIG. 1. Al bonding sites on the GaAs(110) surface studied in the present paper. The substrate surface lies in the plane of figure. The adsorbed Al atoms lie above the surface. The Al bonding sites are labeled in order of increasing total energy. Only one Al atom is considered per surface unit cell. The relative energy at each site in the order of site number is 0, 1.0, 1.2, 1.4, 1.5, 1.9, and 2.4 eV.

substrate. Figure 1 schematically shows the Al bonding sites labeled in order of increasing total energies. The actual geometry is more complicated; it is three dimensional and the bonding length and the substrate relaxation vary. The local minimum energy obtained at each site is given in the figure caption. The most salient features are summarized below. (a) The equilibrium Al-substrate bonding length is always close to the bulk AlAs bonding length 2.45 Å, far shorter than previous estimates in other calculations (~ 3.0 Å).⁸⁻¹⁰ (b) The Al chemisorption disturbs the relaxed GaAs surface, tending to make the surface unrelaxed. (An exception is the case of the weak Al-Ga bonding at site 5.) (c) The twofold site (site 1) gives the lowest energy in this class of geometries. The binding energy is determined to be 3.0 eV with respect to the *relaxed* free surface plus an unbound Al atom.

These results all indicate that adsorbed Al atoms are inclined to form strong bonds with the substrate atoms and saturate broken bonds. (This picture is modified somewhat when strong Al-Al

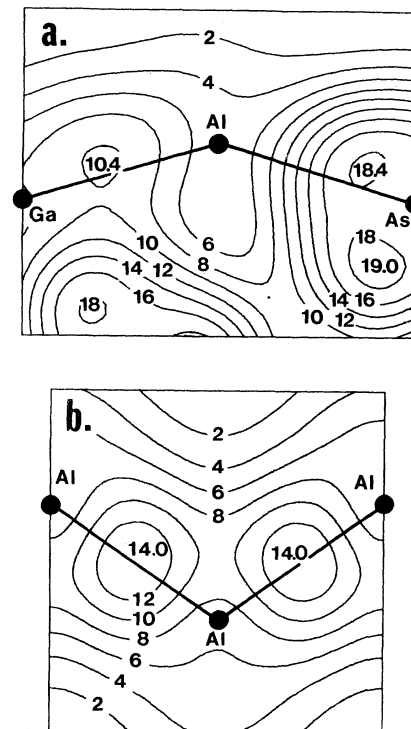


FIG. 2. Valence-charge contour plots for important bonding regions; (a) the Ga-Al-As bonding chain of site 1, and (b) the Al-Al bonding chain of geometry 8 explained in the text. The charge density is normalized to the number of electrons per unit cell of bulk GaAs.

bonds exist, as in the geometries of class four.) Twofold sites (sites 1 and 2) are energetically favorable over single sites (sites 3 and 5) because they can saturate more broken bonds. In Fig. 2(a) we illustrate the Al-substrate bonds for site 1. Note that the Al-As bond is stronger than the Al-Ga bond. This is also true for the single sites. In particular, the stronger Al bond at site 3 causes the substrate to unrelax, while the weaker Al bond at site 5 leaves the substrate relaxed. This is in sharp contrast to the cluster calculations.⁸ In addition, the charge density in Fig. 2(a) is rather spread out indicating some metallic character. This arises because of the rather close packing of the atoms.

The site 4 has a smaller binding energy although it allows for three bonds. This is understandable because the surface Ga atom has five nearest neighbors and the bonding directions are far from optimized. Three bonds from the Al atom are also weak since they are poorly oriented. The same argument applies for sites 6 and 7 where Al can have two nearest-neighbor bonds and a weaker bond. If we have an isolated Al atom adsorbed on the substrate without repetition, this argument is only partly valid and the binding-energy difference between site 1 and other multibonding sites would be smaller than listed in Fig. 1.

An important quantitative result that emerges from these calculations is that the maximum chemisorption energy of Al is quite large (3.0 eV). This, however, is not large enough to dominate the binding energy for the formation of Al bulk (3.4 eV). In the chemisorption process, the substrate relaxation plays an important role. The Al binding energy in chemisorption would be 3.7 eV if the free GaAs surface were taken to be unrelaxed. Then the chemisorption would be absolutely preferable to any kind of Al-Al bonding. In reality, the GaAs free surface lowers the energy through relaxation and the energy gained in the Al chemisorption reduces to 3.0 eV. Therefore, the twofold bonding site is not stable with respect to the Al bulk or large-cluster formation (unless there is an energy barrier to this process or one is at very low coverages.) This does not mean that deposited Al cannot bond to the substrate. Even if the Al cluster is formed, Al atoms on the surface of the cluster have less binding energy than those inside and additional bonds to the substrate can occur to lower the energy. This will lead to a strong adsorption of the cluster to the substrate and the balance will be determined by the details of the surface geometry and energetics.

In the fourth class of geometries, we put two Al atoms in the unit cell, thereby allowing the formation of strong Al-Al bonds. We have tested what we believe are the two lowest-energy geometries with different bonding lengths and substrate relaxations. In the first case, Al atoms occupy both sites 3 and 5 (which we will call geometry 8). In the second case, half the Al atoms reside at site 1 (one per unit cell) saturating all the surface bonds, and the other half are added to make bridges between them (geometry 9). Geometry 8 with an unrelaxed substrate and with all bond lengths close to 2.45 Å minimizes the energy in this class. The Al-Al bonding chain for this geometry is shown in Fig. 2(b). We note that the bonding is moderately covalent and comparable to that of Al-Ga bonding. At this point, it is intriguing to estimate the energy difference between a surface with an ordered *half* monolayer of adsorbed Al atoms and a surface with an ordered monolayer of Al atoms adsorbed only on half of it. The results of our calculations show that the former system is lower in energy by ~0.6 eV. We recall, however, that the formation of bulk Al is favorable. Thus, this energy difference is small enough that Al-Al bonding could occur by breaking the symmetry of the surface and forming clusters.

At $T \neq 0$ and about half monolayer Al coverage, the entropy term lowers the free energy of the clustered system (as compared to the ordered chemisorption) on the order of kT . (This is only a minor effect and the equilibrium is essentially determined by the total energy.) At an extremely low coverage, on the other hand, the entropy term stabilizes the chemisorption with respect to Al-Al bonding by $\sim kT \ln N$, where N is the number of surface atoms, reflecting the vanishingly small probability of having two Al atoms nearby.

Migration of the Al atoms can be induced by the heat released in Al bonding (up to 3 eV). We note that Fig. 1 identifies two favorable channels for migration, both with energy barriers of ~1 eV. These involve hopping along sites 5, 1, 3, 1, 5, etc., and 2, 4, 2, etc. Presumably the latter channel requires smaller activation energies for hopping even though the total energies are higher. Any kind of defects can be important for the Al clustering and the large latent heat given out in the Al bonding may help create one, but this subject is beyond the scope of the present work.

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¹C. B. Duke, A. Paton, R. J. Meyer, L. J. Brillson, A. Kahn, D. Kanani, J. Carelli, J. L. Yeh, C. Margaritondo, and A. D. Katnani, *Phys. Rev. Lett.* **46**, 440 (1981).

²P. Skeath, I. Lindau, C. Y. Su, W. Chye, and W. E. Spicer, *J. Vac. Sci. Technol.* **17**, 511 (1980).

³L. J. Brillson, R. Z. Bachrach, R. S. Bauer, and J. McMennan, *Phys. Rev. Lett.* **42**, 397 (1979).

⁴A. Huijser, J. Van Laar, and T. L. van Rooy, *Surf. Sci.* **102**, 264 (1981).

⁵R. Z. Bachrach and R. S. Bauer, *J. Vac. Sci. Technol.* **16**, 1149 (1979).

⁶J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, *Solid State Commun.* **20**, 641 (1976).

⁷D. J. Chadi and R. Z. Bachrach, *J. Vac. Sci. Technol.* **16**, 1159 (1979).

⁸J. J. Barton, C. A. Swarts, W. A. Goddard, III, and T. C. McGill, *J. Vac. Sci. Technol.* **17**, 164, 869 (1980).

⁹J. R. Chelikowsky, D. J. Chadi, and M. L. Cohen, *Phys. Rev. B* **23**, 4013 (1981).

¹⁰A. Zunger, to be published.

¹¹E. J. Mele and J. D. Joannopoulos, *Phys. Rev. Lett.* **42**, 1094 (1979), and *J. Vac. Sci. Technol.* **16**, 1154 (1979).

¹²J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979), and **13**, 3095 (1980).

¹³D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).

¹⁴E. Wigner, *Phys. Rev.* **46**, 1002 (1934).

¹⁵J. Ihm and J. D. Joannopoulos, to be published.

¹⁶D. Vanderbilt, Ph.D thesis, 1981 (unpublished).

¹⁷K. M. Ho, J. Ihm, and J. D. Joannopoulos, unpublished.

¹⁸D. J. Chadi, *Phys. Rev. Lett.* **41**, 1062 (1978).

¹⁹R. J. Meyer, C. B. Duke, A. Paton, A. Kahn, E. So, J. L. Yeh, and P. Mark, *Phys. Rev. B* **19**, 5194 (1979).

Theory of the Open-Orbit Magnetoresistance of Potassium

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The discovery of open-orbit magnetoresistance peaks in potassium shows that its Fermi surface is multiply connected. A charge-density-wave structure (which would have 24 domain orientations and five open-orbit directions per domain) explains the main features. The magnetic field at which open-orbit peaks appear depends on domain size, which we find to be ~ 0.1 mm.

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Recently Coulter and Datars¹ discovered open-orbit magnetoresistance peaks in potassium. Their data on two crystals, obtained with the induced-torque method, are reproduced in Fig. 1. In this paper we show that a charge-density-wave (CDW) structure^{2,3} explains the large number of open-orbit peaks, their field dependence, their width, and variations in the data from run to run.

More than twenty anomalous properties reported during the last eighteen years, which are inconsistent with the prevalent view that potassium has a spherical Fermi surface, have been explained quantitatively or qualitatively by the CDW model. (See Ref. 3 for highlights.) Therefore the authors make no apology for describing as factual the properties of a CDW derived from extensive theoretical and experimental research. Nevertheless, any reader who feels that the data shown in Fig. 1 (which are but two examples of approximately 100 runs on twelve specimens¹) can be reconciled with a horizontal line (demanded by a spherical Fermi surface) is free to substitute the subjunctive mood in what follows.

The CDW wave vector \vec{Q} in potassium has a magnitude⁴ $Q \approx 1.33(2\pi/a)$, 8% larger than the Fermi-surface diameter. Its direction is near a [110] axis⁵ but, because of elastic anisotropy, \vec{Q} is tilted 4.1° away and lies in a plane oriented 65.4° from the cubic (001) plane.⁶ Accordingly there are 24 symmetry-related, preferred axes for \vec{Q} ; so any single crystal will likely be divided into \vec{Q} domains, each having its \vec{Q} along one of these 24 axes. The resulting domain structure, which depends on metallurgical history, is responsible for the nonreproducibility of conductivity data from one run to the next, if the temperature has suffered a large excursion.³

The open orbits are created by three pairs of energy gaps, shown in relation to the Fermi surface in Fig. 2. The main gaps, associated with the CDW periodic potential, cause the 0.6-eV Mayer-El Naby optical anomaly⁴ and distort the Fermi surface nearby to form small necks or points of critical contact. The heterodyne gaps,⁷ shown in Fig. 2, arise from a sinusoidal displacement of the positive ions. The wave vector