

Atomic and Electronic Structures of GaAs(110) and Their Alkali-Adsorption-Induced Changes

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We performed density-functional-theory total-energy and force calculations of clean and Na-covered GaAs(110) for two coverages: $\Theta = \frac{1}{2}$ (one Na atom per pair of Ga and As) and $\Theta = \frac{1}{4}$. The atomic positions of the adsorbate and of the top three substrate layers are fully relaxed. We discuss the nature of the adsorbate-substrate interaction, the adsorbate-adsorbate interaction, how the adsorbate modifies the clean-surface geometry, and how the atomic and electronic structures are correlated. It is found that the adsorption is partially ionic. The highest occupied adsorbate-induced "band" reflects the properties of a Mott-insulator state, whereas the lowest unoccupied state is a one-dimensional Bloch state.

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The electronic, optical, magnetic, and chemical properties of polyatomic systems are sensitively affected by the atomic geometry. In this respect semiconductor surfaces have attracted particular attention in recent years, the most studied system being GaAs(110). It is now well established that the GaAs(110) surface atoms relax by a significant amount such that the As anions move outwards and the Ga cations move inwards (e.g., Ref. [1] and references therein) (see Fig. 1).

There is an ongoing debate as to how alkali atoms adsorb on this surface, and how they modify the surface geometry. The plausible idea of an ionic adsorption is often questioned [2], because the Coulombic repulsion should hinder the experimentally observed close packing at low coverage. With respect to the surface geometry it is usually assumed that even a low adsorbate coverage will unrelax the surface completely [2-5], but a proof of this assumption is lacking. These aspects are crucial for a better understanding of Schottky-barrier formation and the nature of the electronic states responsible for the Fermi-level pinning (see, for example, Ref. [6] and references therein).

In this paper we present parameter-free calculations addressing the above-mentioned questions. We will show that the alkali adsorbate is partially ionized, and that it can move rather freely with low migration barriers over the surface. However, the diffusion should be practically one dimensional. In contrast to the generally applied assumption we find that at low coverage the clean-surface relaxation is significantly modified, but it is not removed. Furthermore, the standard argument that the (partial) ionization of the alkali adsorbate should induce a strong adsorbate-adsorbate repulsion is shown to be incorrect. We find a very localized polarization of the surface electron density. This implies an efficient screening, by which, together with the coverage dependence of the lattice relaxation, the direct ion-ion repulsion term is more than compensated. Of particular interest are the highest occupied and the lowest unoccupied adsorbate-induced states, as they have qualitatively different character. Whereas the highest occupied Na-induced state is best

understood in a localized picture as a Mott-insulator state, the lowest unoccupied state has a one-dimensionally delocalized density.

Our conclusions are drawn from density-functional-theory calculations, applying the local-density approximation for the exchange-correlation functional [7]. We

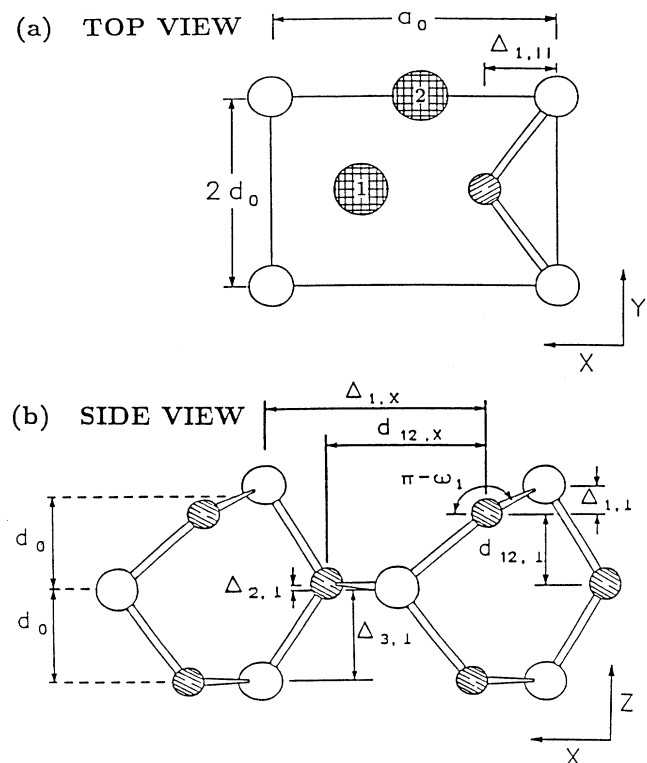


FIG. 1. Atomic geometry for GaAs(110). Open circles are As atoms and hatched circles are Ga atoms. Cross-hatched circles indicate possible Na adsorption sites. (a) Top view of the surface unit cell together with two important adsorption sites. (b) Side view of the first three layers of the GaAs(110) surface. $a_0 = 5.5 \text{ \AA}$ is the theoretical bulk lattice constant, $d_0 = \frac{1}{2} \sqrt{2} a_0$, $\Delta_{1,\perp} = 0.63 \text{ \AA}$, $d_{12,\perp} = 1.46 \text{ \AA}$, $\Delta_{2,\perp} = -0.086 \text{ \AA}$, $\Delta_{3,\perp} = 2.03 \text{ \AA}$, $\Delta_{1,x} = 4.355 \text{ \AA}$, $d_{12,x} = 3.145 \text{ \AA}$, $\Delta_{1,\parallel} = 1.15 \text{ \AA}$, and $\omega_1 = 28.6^\circ$.

emphasize the importance of a proper treatment of the exchange-correlation potential. To our knowledge, all previously published self-consistent pseudopotential calculations for alkalis at surfaces (for example, Refs. [5,8-10]) linearized the core-valence exchange-correlation functional:

$$E_{XC}[n_{\text{core}} + n_{\text{val}}] \approx E_{XC}[n_{\text{core}}] + E_{XC}[n_{\text{val}}].$$

However, this approximation is not acceptable for treating alkalis [11] and induces significant errors in the calculated atomic and electronic structure (see below). The ionic (frozen core) potentials are described by fully separable, norm-conserving pseudopotentials [12,13]. We use a plane-wave basis with an energy cutoff of 8 Ry which corresponds to about 1500 (for $\Theta = \frac{1}{2}$) and 3200 (for $\Theta = \frac{1}{4}$) plane waves. The k_{\parallel} integration is replaced by a sum over four Monkhorst-Pack special points in the irreducible part of the surface Brillouin zone [14]. This basis set and the k_{\parallel} summation have been tested for bulk GaAs, where we obtain a good description of the structural and elastic properties of GaAs. The theoretical bulk lattice constant of $a_0 = 5.50 \text{ \AA}$ (experimental, 5.65 \AA) is used for the calculations described below. The surface is simulated by a periodic slab geometry along [110] with eight layers of GaAs and a vacuum region which has a thickness of six such layers.

Figure 1 shows a top view of the surface with two Na positions which will be discussed later in more detail. We also show a side view of the first three layers of the clean, relaxed surface. Our results for the clean-surface geometry are summarized in Ref. [1]. In Fig. 2 we show the surface band structures of the clean surface using the geometry of a truncated bulk [Fig. 2(a)] and using the relaxed surface geometry [Fig. 2(b)]. The highest occupied surface state is an As-derived state and the lowest unoccupied state is a Ga dangling-orbital state. The energy of the latter band shifts up upon surface relaxation by about 1 eV. The occupied As dangling-orbital band shifts down in energy (towards the valence band) by about 0.5 eV.

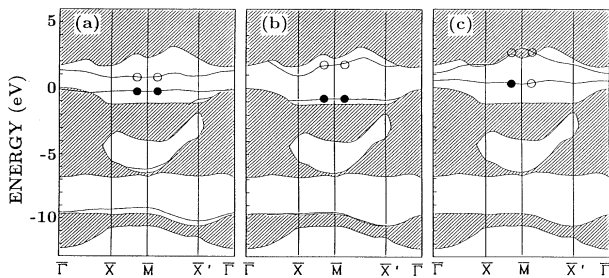


FIG. 2. Calculated surface band structures for clean and Na-covered GaAs(110): (a) clean, unrelaxed; (b) clean, relaxed; (c) relaxed, $\Theta = \frac{1}{2}$ Na-GaAs(110). The occupation of the highest occupied and the lowest unoccupied state is indicated with solid circle for electron and open circle for hole.

The stable atomic position of adsorbed Na on GaAs(110) is not known [15]. Neither is it known how the GaAs(110) surface geometry will be modified upon adsorption. Obviously, as the results for the clean surface have shown, the knowledge of the geometry is of significant importance for the understanding of the surface electronic structure. We therefore evaluated the Born-Oppenheimer total-energy surface of a surface Na atom. For thirty sodium positions within the two-dimensional surface unit cell the adsorbate-surface distance as well as the positions of the Ga and As atoms in the top three layers were fully relaxed. In Fig. 3 we show the total-energy surface for the half-monolayer case. For a clearer presentation the energy is plotted on an area of two surface unit cells, together with the surface atomic chains. We find one minimum close to the Ga surface atom [site 1 in Fig. 1(a)] and another minimum close to the As surface atom [site 2 in Fig. 1(a)]. The adsorption energies [16] are 1.6 eV (site 1) and 1.55 eV (site 2). Note that the total-energy surface has a deep channel which is quite flat parallel to the surface zigzag atomic chains. Along this channel the energy minima are separated only by small barriers. For the $1 \rightarrow 2$ path the barrier height is 0.2 eV and for the $2 \rightarrow 1$ path it is 0.15 eV.

The $\Theta = \frac{1}{2}$ sodium adsorption reduces the clean-GaAs(110)-surface relaxation. However, a buckling of about 0.2 \AA of the top GaAs layer remains. Table I summarizes the relative displacements of the surface atoms with respect to the unrelaxed geometry. The analysis of the electronic structure shows that it can be understood such that the Na valence electron is transferred into the Ga dangling-orbital "band" (the lowest unoccupied state of the clean surface). The resulting wave function is shown in the left panels of Fig. 4. The clear Ga dangling-orbital [17] character of this wave function implies that this bond may well be described as partially ionic. However, the p character of this wave function contributes to some covalent bonding as well. Because of this Ga p -orbital character we think that a quantitative

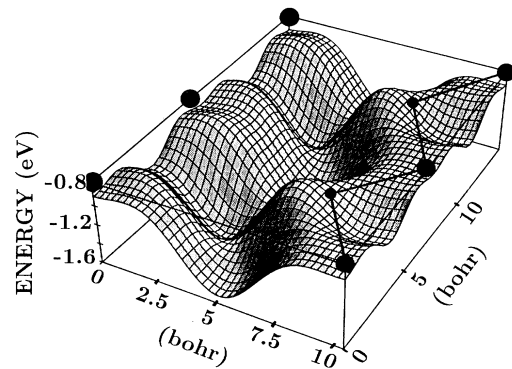


FIG. 3. Total-energy surface of the Na-GaAs(110) system for $\Theta = \frac{1}{2}$ together with the projected surface atoms. Small circles indicate Ga atoms and large circles indicate As atoms.

TABLE I. Atomic displacements with respect to the truncated bulk geometry: $\Delta R = (\Delta x, \Delta y, \Delta z)$ in Å. In the $\Theta = \frac{1}{4}$ case the \pm sign indicates that both As neighbors move towards the Na adsorbate. The Na position is given with respect to a surface Ga site of the unrelaxed geometry. The x, y, z , directions are defined in Fig. 1.

	Na	1. layer		2. layer		3. layer	
		Ga	As	Ga	As	Ga	As
clean surface	—	(0.30, 0.00, -0.40)	(0.07, 0.00, 0.23)	(-0.08, 0.00, 0.09)	(-0.08, 0.00, 0.00)	(-0.02, 0.00, 0.01)	(-0.01, 0.00, 0.00)
$\Theta = \frac{1}{2}$ (site 1)	(3.10, 0.00, 1.69)	(0.10, 0.00, 0.00)	(0.09, 0.00, 0.17)	(-0.02, 0.00, 0.06)	(0.00, 0.00, 0.03)	(0.00, 0.00, 0.00)	(0.00, 0.00, 0.02)
$\Theta = \frac{1}{2}$ (site 2)	(3.97, 1.95, 1.85)	(0.18, 0.00, -0.07)	(0.11, 0.00, 0.23)	(-0.03, 0.00, 0.08)	(-0.01, 0.00, 0.05)	(-0.01, 0.00, 0.02)	(0.01, 0.00, 0.04)
		1. layer					
	Na	Ga	Ga (close to sodium atom)	As	As (close to sodium atom)		
$\Theta = \frac{1}{4}$ (site 1)	(3.13, 0.00, 1.79)	(0.36, 0.00, -0.39)	(0.09, 0.00, -0.08)	—	(0.09, ± 0.02 , 0.19)		

evaluation of the ionic degree is not useful. As Fig. 4 shows, the highest occupied state (HOMO in molecular-orbital theory) consists of highly localized and practically non-overlapping orbitals. Therefore this state should not be described in a Bloch picture, but rather in a localized Hubbard picture. For this state, which is marked in Fig. 2(a) with two holes and in Fig. 2(c) with one electron and one hole, we therefore put the word *band* in quotes. We have estimated the Hubbard correlation energy for a localized surface Ga dangling orbital as $U = 1.5 \pm 0.3$ eV.

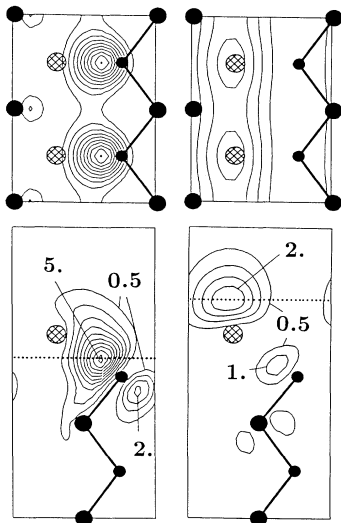


FIG. 4. Squared wave functions for Na-GaAs(110) at $\Theta = \frac{1}{2}$ at the \bar{X}' point of the surface Brillouin zone [see Fig. 2(c)]. Lower panels give a side view and upper panels give a top view along a plane indicated in the lower panels by dashed lines. As atoms are marked by large solid circles, Ga atoms by small solid circles, and hatched circles mark the Na atoms. Units are 10^{-3} bohr $^{-3}$. Left: The highest occupied state [indicated by an electron and a hole in Fig. 2(c)]. Right: The state indicated by two holes in Fig. 2(c).

This value is obtained from three self-consistent calculations for the (fixed) equilibrium geometry of the Na-GaAs(110) surface, occupying the HOMO “band” [see Fig. 2(c) and Fig. 4, left panels] with 0.5, 1, and 1.5 electrons. Thus, this value of U includes the adsorbate-substrate hybridization as well as the surface screening. The size of U implies that although the “band” [see Fig. 2(c)] is only half occupied, an electron which is added to the system would in fact go into the next higher band, indicated in Fig. 2(c) by two holes. The wave function of this band is shown in the right panels of Fig. 4. It has a qualitatively different character than the HOMO orbital. This lowest unoccupied state (LUMO) is mainly built from Na s and p valence orbitals. It is a clearly extended state, for which the Bloch picture is appropriate, and it should behave as a one-dimensional conductor. We obtain practically the same results for all Na positions in the channel.

For the $\Theta = \frac{1}{4}$ Na coverage we considered the periodic arrangement of two GaAs surface unit cells (such as in Fig. 3). We obtain a qualitatively similar total-energy surface as in the case discussed before, although we find only one minimum in the total energy, which is close to site 1 of the $\Theta = \frac{1}{2}$ coverage (see Fig. 1 and Table I). The adsorption energy [16] is 1.58 eV. Thus, the adsorption in the open $\Theta = \frac{1}{4}$ structure is slightly less favorable than in the closer-packed $\Theta = \frac{1}{2}$ adlayer. This means that there is an effective Na-Na attraction and the adparticle surface diffusion will be highly anisotropic, i.e., along the atomic zigzag chains of the substrate.

The single sodium atom influences mainly the electron density of its nearest neighbors. There is (a) an increase in the charge density at the surface Ga atom, which arises from the transfer of the Na $3s$ electron into the Ga dangling bond, and (b) a significant increase in the electron density between the surface As and the adsorbate as a result of a polarization of the surface As atom. The alkali-adsorption-induced structural changes (see Table

I) happen mainly at the adsorbate nearest neighbors, which unrelax to some extent, although a significant buckling between the inward-moved Ga and the outward-moved As atoms of about 0.5 Å remains. The neighbors further away remain close to the positions of the clean, relaxed GaAs(110) surface.

As we mentioned above, a proper description of the core-valence exchange-correlation interaction is crucial for the description of the chemical bonding of alkalis. When this interaction is linearized, the orbital energies of an ionized or *s-p* hybridized alkali become wrong. As a consequence, the calculated alkali position would be much closer to the surface than what we found in this work (the differences are about 1 Å). Furthermore, the covalent character of the bond would be less pronounced, and the alkali-induced band [see the two-hole band in Fig. 2(c) and the wave function in Fig. 4, right panels] would be outside the gap, in the conduction band.

Our theoretical results may be compared to recent electron-energy-loss [18] and scanning-tunneling-microscopy (STM) [2,19] studies. Although these studies were concerned with the adsorption of cesium on GaAs(110) the results of our study can explain several aspects of these exciting experiments. The highly anisotropic channel in the total energy (Fig. 3), together with the result that there is an effective Na-Na attraction, explains why there is a preference to form one-dimensional adsorbate chains rather than two-dimensional islands. With respect to the alkali-alkali interaction it is important that the partially ionized adparticles are effectively screened, which cancels the direct ion-ion repulsion. One question, however, remains. The STM observes zigzag adsorbate chains, which we are not yet able to calculate. The mechanism giving rise to this zigzag structure therefore requires further investigations. According to our calculations the tunnel current from the sample to the tip should show the Ga dangling bonds, rather than a *direct* picture of the adparticles. The electronic state responsible for this tunnel current was noted to be a Mott-insulator state (see Fig. 4, top left). Thus, although this state is not fully occupied, the system should not behave metallically. This result fully supports and specifies the interpretation of the electron-energy-loss results of DiNardo, Wong, and Plummer [18]. Furthermore, we predict that tunneling from the tip to the sample should give a significantly different result. Then the responsible sample state is a one-dimensional Bloch state (see Fig. 4, top right).

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- [16] For the adsorption energy we calculate the total energy of the free Na atom using the same energy cutoff and the same local-density-approximation exchange-correlation functional as for the adsorbate system. Taking spin-polarization of the atom into account would reduce our numbers by 0.2 eV.
- [17] The empty state in Fig. 2(a) or the half-filled state in Fig. 2(c) may be called a metal-induced gap state (MIGS). We feel that this nomenclature is often misunderstood, and we prefer to call this state, according to its wave-function character (see Fig. 4, left panels), a Ga dangling orbital. This is what it is, and what gives rise to the virtual gap states in the complex band structure of the perfect crystal, and to the MIGS at the surface.
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