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Geometric and electronic structure of a magnesium overlayer on the GaAs(110) surface

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Abstract. The electronic structure of a magnesium overlayer on the GaAs(110) surface is calculated in the self-consistent tight-binding approximation. It is found that the surface relaxation structure is important for low-coverage adsorption, and for determining the bonding energy state in particular. The Fermi level is pinned close to the top of the valence band by the covalent hybridization of the highly localized adatom Mg s orbitals and the surface Ga sp^3 dangling bonds. Our results show a higher density of unoccupied states than occupied states on Mg atoms, which is in good agreement with scanning tunnelling microscopy (STM) images. A comparison is made with theoretical and experimental results of free and other adsorbate GaAs(110) surfaces.

1. Introduction

It is widely recognized that the GaAs(110) surface relaxes via approximately bond-length-conserving rotations with the anion moving outward and the cation inward [1–4]. However, what happens for an adsorbate overlayer on the top of the relaxed surface has drawn considerable attention recently. One idea generally held is that the adsorption of atoms on the surface removes the free surface relaxation. However, this has been questioned by some authors. Recently, calculations on Na/GaAs(110) [5] and Sm/GaAs(110) [6] systems have shown that only the substrate surface atoms nearest to the adatoms are approximately unrelaxed. Is it a general relaxation effect for other group elements at low coverage? And what is the role of the surface relaxation in revealing the electronic property of the metal–semiconductor interface? To answer these questions is our main purpose in the present work.

Of equal importance as the surface relaxations themselves are the calculations of the electronic structure of the Mg/GaAs(110) surface, because to our knowledge there are few results available for adsorption of group IIA atoms on the cleavage face of binary compound semiconductors with zincblende structure. At the time of the alkali-metal chemisorption, a jellium/slab model [7] was adopted to describe the electronic structures calculated by the linearized augmented plane-wave (LAPW) method. The authors discovered the metal-induced gap state (MIGS) for Fermi level pinning and explained the experiments which found that the caesiated GaAs(110) is still not metallic up to one monolayer coverage. Thus the hypothesis had given valid insights of alkali-metal chemisorption, but it subsequently fell on hard times, when the study of other group elements with a high ionization energy on

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the GaAs(110) surface demonstrated the importance of atomic properties and adsorption structures which are beyond the reach of the jellium approximation.

Very recently, in a self-consistent tight-binding scheme, Allan and Delerue [6] have calculated the electronic structures of a Sm rare-earth atom overlayer on a GaAs(110) slab taking the adsorption properties into account. They found that the Fermi level is pinned close to the semiconductor conduction band minimum, which is mainly contributed by the interaction of one d state on an Sm rare-earth adatom with a Ga dangling bond. Their potential values are also in good agreement with the experimental observation of the surface-atom core-level shifts.

Encouraged by the success in studying the rare-earth atom on GaAs(110), we have extended this study to a magnesium overlayer, trying to elucidate the difference between their adsorption behaviours at low coverage, which cannot be understood by other methods that neglect the adsorption structure. Furthermore, we hope to show the importance of the surface relaxation and its dominant role in determining Fermi level pinning, which will lead to a good knowledge of Schottky barrier formation at an early stage of the metal-semiconductor connection.

2. Description of method and adsorption structure

Our calculations are based on the self-consistent total energy method within the tight-binding approximation using the sp^3s^* Vogl model [8]. The values of the parameters used are a slightly modified version of those in the model of Vogl *et al* [8] as applied to the Sm/GaAs(110) structure in our earlier work [6]. The first-nearest-neighbour Slater-Koster parameters are scaled according to the interatomic distance d [6]

$$V_{\beta}(d) = V_{\beta}(d_0) \exp(-q(d - d_0)) \quad (1)$$

where d_0 is the bulk equilibrium distance, and $\beta = ss\sigma, sp\sigma, pp\sigma$ and $pp\pi$, respectively. The exponent formula used here is close to Chadi's one [9].

The total energy is calculated self-consistently by assuming a simple intra-atomic relationship between the electrostatic potential V_i and the local atomic charge q_i :

$$V_i = Uq_i \quad (2)$$

where U is the intra-atomic Coulomb parameter. On the adatoms it is selected to be equal to the substrate one ($U = 8.0$ eV). Such a value gives quite good results near bulk impurities [10]. Delerue *et al* [10] have proved that as long as the Coulomb parameter is much larger than the coupling energy, the exact value of this parameter is found to be unimportant for the accuracy of the results. For the relaxed surface, the calculated self-consistent potential on the surface Ga (-0.31 eV) and As (0.32 eV) atoms are in good agreement with the experimental surface core-level shifts -0.37 eV and 0.28 eV, respectively [11].

To ensure bulk crystal stability, a repulsive potential V_{rep} between first-nearest neighbours is added to the electronic energy calculated from the band structure:

$$V_{\text{rep}}(d) = V_0 \exp(-\alpha_0(d - d_0)). \quad (3)$$

By fitting the bulk cohesive energy and modulus, we take $V_0 = 5.10$ eV and $\alpha_0 = 5.58/d_0$, respectively. Such a procedure has been used by Yeh *et al* [12] with slightly different expressions(1) and (3) to calculate the alloy interatomic distances. Allan and Delerue [6]

have tested the validity of the model by calculating the relaxation of a free GaAs(110) surface and then comparing with experiments.

To obtain the optimum configuration before adsorption, we have evaluated the free surface relaxation of GaAs(110) by minimizing the total energy of four-, eight- and twelve-layer slabs with respect to the location of its outermost atomic layers, while holding the perfect bulk position of its central two, six and ten layers, respectively. By inspecting the degeneracy of the surface-localized states, it is possible to avoid interaction between the two surfaces by using a twelve-layer slab model. This has been also confirmed by first-principle linearized augmented plane-wave calculations for the GaAs(110) surface [7]. For the surface geometry the total energy is minimized by calculating the Hellman-Feynman forces [13], and the energy minimum is obtained by the Verlet method [14]. Eight special points [15] are taken into account in summation over the surface Brillouin zone. As shown in table 1, the theoretical results are in good agreement with experiments using low-energy electron diffraction (LEED) [16].

Table 1. Surface atomic relaxation after adsorption of a 0.25 magnesium monolayer. All quantities are in Å.

| | $d_{\perp}(110)$ | $d_{\parallel}(110)$ |
|--------------------------|------------------|----------------------|
| <i>Adsorbate surface</i> | | |
| Ga (close to adatom) | -0.40 (-0.04*) | 0.40 (0.22*) |
| Ga | -0.50 (-0.47*) | 0.45 (0.49*) |
| As | 0.06 (0.09*) | 0.24 (0.27*) |
| <i>Free surface</i> | | |
| Ga | -0.50 (-0.51**) | 0.45 (0.49**) |
| As | 0.07 (0.14**) | 0.21 (0.33**) |

* Corresponding theoretical results for the Sm/GaAs(110) surface [6].

** Corresponding experimental results for the free GaAs(110) surface [14].

An adsorption structure proposed to describe a magnesium overlayer on the GaAs(110) surface at low coverage ($\theta = 0.25$ monolayer) is shown in figure 1. The adatoms are located on the dangling bond of a surface Ga atom and form ordered zigzag chains. The two-dimensional arrays of the Mg atoms with a 2×1 structure with respect to the GaAs(110) substrates have been confirmed by analysis of STM images [17]. A value of 2.67 Å for the Mg-Ga bond length is taken to be equal to the sum of their covalent radii. In the calculations, the tight-binding interaction parameters between the adatom and the substrate are determined by Harrison rules [18].

3. Self-consistent calculation

3.1. Surface relaxation

Using the model described above, a self-consistent total-energy minimization computation was performed for the Mg/GaAs(110) surface with a free relaxed surface as the starting geometry. The displacements of Ga and As atoms in a surface unit cell are listed in table 1, where the theoretical and experimental results of free and Sm adsorbate GaAs(110) surface atomic relaxation are also given.

From table 1, it is found that the surface atoms relax obversely, even for a Ga which is close to the adatom. The displacements of the Ga atom close to the covalent adatom are

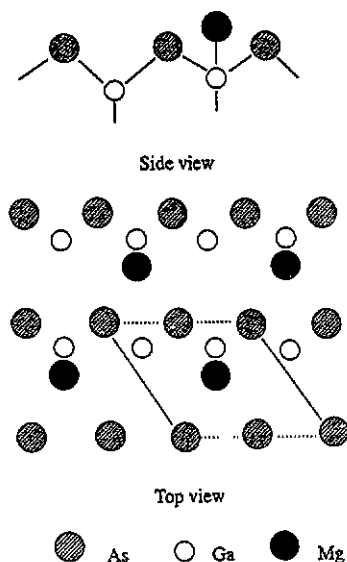


Figure 1. Schematic diagrams of the atomic structure of the Mg/GaAs(110) surface used in the calculations, where the adatoms are adsorbed on the dangling bonds of the surface Ga atoms with a coverage $\theta = 0.25$ monolayer and form ordered zigzag chains. The interactions between the adatoms are small.

reduced by 20% (normal to the surface) and 11% (in the surface), respectively, and those of the others in the (110) surface unit cell are almost the same as those of the free surface atoms. The surface atom relaxation under the adsorption of a Mg overlayer is much stronger than the case of a rare-earth overlayer, which shifts the bonding states and affects the Fermi level pinning significantly. The main reason is that the attraction between overlayer and substrate is much stronger in a rare-earth adsorption than in a covalent one, which gains more energy to ease the free surface relaxation.

When the covalent atoms are adsorbed on the surface Ga atoms, the bond length (2.407 Å) between the Ga atom, which is close to the adatom, and its As neighbour in the surface plane does not change much from the value (2.402 Å) of a free surface. However, the adsorption increases the interatomic distance (2.421 Å) between the Ga atom and its As neighbour in the second layer. So an approximate validity of a bond length conservation has been confirmed by independent LEED intensity analyses for the (110) surface relaxations of binary compound semiconductors with zincblende structure [19, 20], the situation becoming even more complicated at low coverage adsorption.

Based on the above calculations, we believe that the surface relaxation structure at low coverage could be a common characteristic, independent of various adatoms. The origin of this resides in the subsequent rehybridization of the orbitals between the adatom and the substrate atom to lower the surface energies. An important test of the lowering energy mechanism by adsorption surface relaxation at low coverage is to measure the core-level shifts of the surface atom. The photoemission spectroscopy of Mg/GaAs(110) [17] has shown the relative binding energy shifts. The agreement between the experiments and our self-consistent tight-binding calculations confirms that a modification of the ideal surface geometry is an important aspect of the minimum energy structure.

3.2. Surface state and Fermi level pinning

For a rare-earth adatom, the wider s state is repelled to high energy due to orbital orthogonalization. Therefore, the most important coupling occurs between the rare-earth d state and the Ga dangling bond, which forms a strong ionic bond. On the other hand, the s states of the magnesium are more localized and play a dominant role in the interactions with the substrate. The hybridization of the Mg s orbitals with the substrate sp^3 dangling bonds leads to covalent bonds between the overlayer and the substrate. Thus, the qualitative differences between the predicted adsorption systems could, in principle, be used to differentiate between their electronic structures.

The surface states calculated for covalent and rare-earth adatom reflect the significant differences in the electronic structure corresponding to the two adsorbates. In the rare-earth adsorption, the adatom s levels are repelled to the top of the conduction band (see figure 3(a) [6]); they do not mix significantly with the substrate dangling-bond orbitals. The bonding d state with the Ga dangling bond is localized in the semiconductor band gap, and the non-bonding d state shifts into the conduction band (see figures 3(a) and (b) [6]). The electronic structure of the covalent adsorption is completely different. The highly localized magnesium s states are just at the top of the valence band (see figure 2(a)). The covalent bonding states formed by the rehybridization between the adatom s and p orbitals and the Ga dangling bonds lead to Fermi level pinning at an energy (~ 0.6 eV) above the top of the valence band in the band gap (figures 2(a) and (b)).

It is known that a charge transfer from a surface As atom to a surface Ga atom will happen on a clear GaAs(110) surface. As a result, an electrostatic potential is set up to screen the transfer, which is repulsive for the As atoms and attractive for the Ga atoms. When a rare-earth atom is adsorbed, the surface Ga atoms also have 1.7 eV repulsive potential due to the formed adatom–Ga anionic bonds. In order to keep the excess electron transfer, the corresponding As potential rises to 1.0 eV [6]. Therefore, it can explain the experimental results [21] showing that the As core-level shift is strongly modified, even if the rare-earth atom is adsorbed on a Ga surface atom. This, however, does not happen for magnesium adsorption. Compared with an Sm adatom, the Mg one has strong attractive potential (-2.3 eV). No more excess electrons appear on Ga in the covalent adsorption, which rises to a repulsive potential on Ga close to 0.66 eV. At the same time, it is found that the change of the repulsive potential on an As atom is only from 0.31 eV (free surface) to 0.52 eV (adsorption surface). Therefore, we expect that the shift of the surface As core level is not as significant as is the case in a rare-earth adsorption. These results are in good agreement with the measured As core-level shift [17]. Furthermore, the modification of the other Ga atom, which is not close to the adatom in the surface unit cell, is also small. The value is -0.20 eV for the adsorbate case and -0.31 eV for the free one. This is quite different from the rare-earth adsorption, where it also has a repulsive potential. Because of the change of these potentials, the non-bonding states of the adatom move into the lower part of the conduction band at an energy close to 3.0 eV, and its antibonding p states are localized at 7.2 eV in the top of the conduction band (figure 2(a)). In figures 2(d) and (b), one can also see that the As dangling bonds are shifted somewhat towards the high-energy region in the semiconductor gap. The Fermi level pinning could be mainly due to the shift of the bonding states from the top of the valence band to the lower part of the energy gap.

Furthermore, we can see in figure 2(a) that the density of the unoccupied non-bonding p states is much higher on a Mg atom compared with the occupied bonding states. Since the brightness of the adatom features in an STM topography relates to their height, the brightness reflects the difference between the occupied and unoccupied state images of an adatom. From the different brightness shown in STM images [17], one can easily indicate

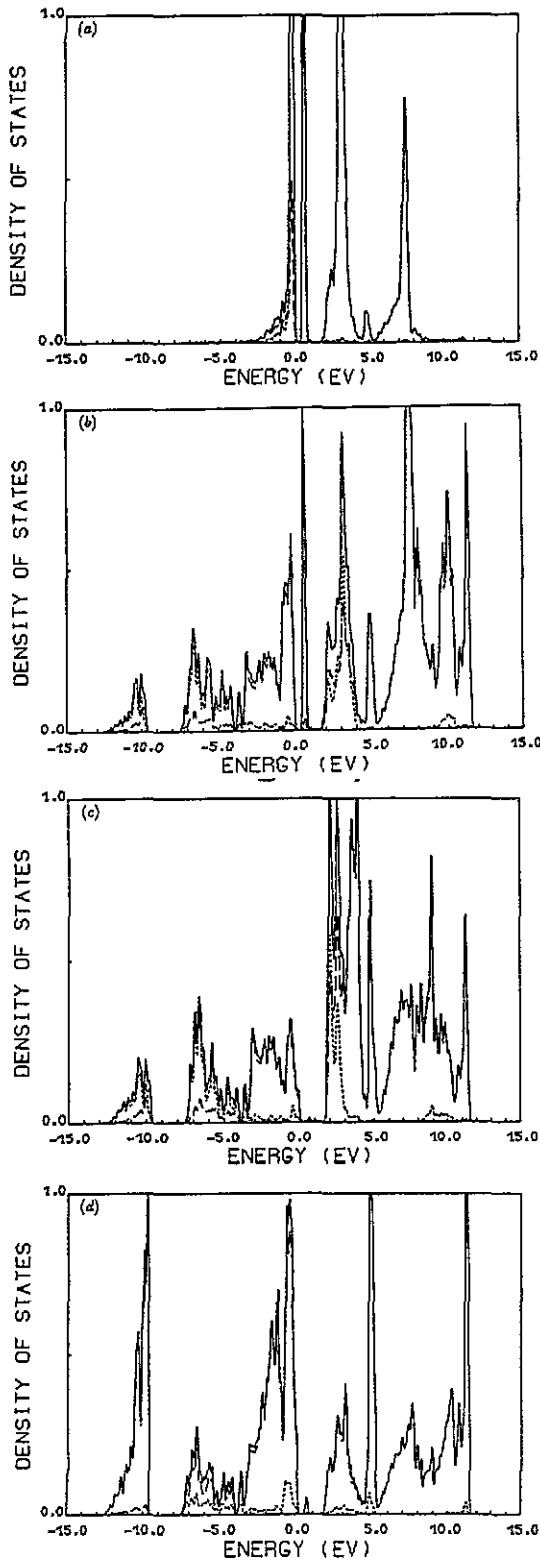


Figure 2. Local density of states (DOS) on the Mg atom (a), on the surface Ga atom close to Mg (b), on the other Ga atom in the surface unit cell (c), and on a surface As atom (d). The full curves are the total DOS, the short broken curves the s DOS and the long broken curves the p DOS. Notice the significant difference of DOS around the band gap between (b) and (c), which is induced by the changing of the relaxation after Mg adsorption.

a higher density for unoccupied states than occupied states, when Mg atoms are deposited on GaAs(110) at low coverage. This is in agreement with our theoretical calculations here, which suggest that a charge transfer occurs from the Mg adatom to the substrate. However, based on our calculations, it is found that only 20% of the adsorbate electrons in the Mg overlayer penetrate into the substrate, while a large number of electrons are strongly localized around the Mg–Ga atom bonds. The covalent features are also shown.

4. Conclusions

We have presented the results obtained in a self-consistent tight-binding approximation, which clearly show that the bonding state is fixed by the covalent hybridization between the highly localized adatom Mg *s* orbitals and the surface Ga sp^3 dangling bonds. Our calculations have directly confirmed the STM images [17] where the density of unoccupied states is higher than that of occupied states on an Mg adatom. The displacements of surface Ga and As atoms determined by self-consistent total-energy minimization for the Mg/GaAs (110) system reveal that the surface relaxation structure is an important characteristic for low coverage adsorption. For covalent adsorption in particular, the overlayer makes it more difficult to ease the free surface relaxation due to the smaller gain in energy. This relaxation is important to accurately determine Fermi level pinning close to the top of the valence band. The obtained repulsive potentials on the Ga close to a magnesium adatom and on its surface neighbour As are 0.66 and 0.52 eV, respectively, proving that their core-level shifts are not significant as is the case in rare-earth adsorption. This result is in good agreement with measurement by photoemission experiments.

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