

Thick sodium overlayers on GaAs (110)

Martina Heinemann

Science and Engineering Research Council, Daresbury Laboratory, Warrington WA4 4AD, United Kingdom

Matthias Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin (Dahlem), Germany

(Received 7 June 1993)

We report density-functional theory calculations of the electronic structure, total energy, and forces for the Na adsorption on GaAs (110) using the local-density approximation of the exchange-correlation functional and *ab initio* pseudopotentials. Results are presented for coverages ranging from one adatom per substrate surface cell up to the thick overlayer limit. The atomic and electronic structure of the substrate is locally changed by the sodium adsorption on GaAs (110), depending on the coverage. In particular, we analyze the wave-function character of the states at the Fermi level, how it changes with sodium coverage, and we identify the formation of metal induced gap states (MIGS) at the interface. These MIGS are found to have mostly Ga dangling-bond character for all coverages. The calculated values of the *p*-type Schottky barrier and of the variation of photothreshold as a function of coverage are in good agreement with experimental data.

I. INTRODUCTION

Metal-semiconductor interfaces have been studied for decades^{1,2} in order to explore the mechanism and properties of the formation of Schottky barriers. Of particular interest is the interdependence of the interface atomic geometry and electronic structure. Despite enormous research activities several fundamental aspects of Schottky barriers are still poorly understood and a matter of active controversies. Among the basic questions which are still under debate are those about the mechanism of the Fermi level pinning at very low coverages, the mechanism of the shift of the Fermi level as a function of coverage, and the character of the states responsible for the Fermi level pinning. Several concepts have been suggested to explain the Fermi level pinning. They can be classified into two main groups. First, there is the concept of *metal induced gap states* (MIGS) proposed by Heine.³ Its basic idea is that the metal states which have an energy within the semiconductor energy gap tail into the semiconductor side and induce interface states which control the position of the Fermi level with respect to the band edges at the interface. Based on the MIGS idea Tejedor *et al.*⁴ developed the *induced density of interface state* model and introduced the concept of the *charge neutrality level*. The *branch point* of Tersoff⁵ and *average hybrid energy* of Harrison and Tersoff⁶ describe the same physical mechanism. Second, there is the *unified defect model* proposed by Spicer *et al.*^{7,8} that explains the Fermi level pinning due to gap states related to structural semiconductor defects. Mönch⁹ recently combined interface defect states and MIGS to describe the Fermi level pinning at different coverages, but overall there seems to develop an agreement that the MIGS based description of the Schottky barrier formation is the most appropriate for nonreactive interfaces.

The aim of the present study is to apply self-consistent

total energy calculations to determine the character of the states which pin the Fermi level in the range from submonolayer to high coverages. In order to predict the Fermi level pinning and thus the Schottky barrier height from a theoretical point of view it is necessary to know the electronic structure of the metal covered semiconductor surface. As the electronic structure is closely related to the atomic geometry it is crucial to determine the atomic positions of the semiconductor substrate and of the adsorbate atoms. Our theoretical approach therefore optimizes both the atomic and the electronic degrees of freedom of the Na/GaAs (110) system.

Among the metal-semiconductor interfaces studied in the past decades those based on III-V compounds as substrate are most intensively investigated. In our work we explore a sodium covered GaAs (110) surface. The rather simple electronic structure of alkali atoms makes such a system an attractive candidate for the theoretical description of metal-semiconductor interfaces. Furthermore, alkali-metal-semiconductor interfaces are known to be nonreactive at low temperatures.²⁵

Throughout this paper we define the coverage such that $\Theta = 1$ corresponds to an adatom density of 9.34×10^{14} atom/cm², i.e., it corresponds to two adsorbate atoms per pair of Ga and As atoms on the surface. *One monolayer*, on the other hand, means a close packed layer of adatoms and therefore depends on the size of the particular adatom. In the case of sodium one monolayer corresponds to $\Theta = 1$.

The remainder of the paper is organized as follows. Section II contains an outline of the method. In Sec. III we present the results for the sodium covered GaAs (110) surface for coverages ranging from $\Theta = 0.5$ to thick overlayers. We discuss the metallization process, the Schottky barrier, and the photothreshold as a function of coverage. Finally, the paper is concluded with a summary in Sec. IV.

II. METHOD

We perform self-consistent density-functional theory^{10,11} calculations using the local-density approximation for the exchange-correlation functional.^{12,13} The atomic potentials are represented by Kleinman-Bylander-type *ab initio* pseudopotentials,¹⁴ taking the nonlinearity of exchange correlation for Na properly into account.^{15–17} The integration in \mathbf{k} space is replaced by a summation over four special \mathbf{k} points in the irreducible part of the surface Brillouin zone.¹⁸ We use a plane wave basis set with a kinetic energy up to 8 Ry. The atomic and electronic ground state of the system is reached using a Car-Parrinello-like scheme.^{19,20} The GaAs substrate is represented by a seven layer slab and the Na atoms are adsorbed on both (110) surfaces. All atoms with the exception of the central GaAs layer are allowed to relax. The Kohn-Sham states are occupied according to the Fermi-Dirac statistic with $k_B T = 0.01$ eV. The accuracy for the structural parameters of the system was carefully checked^{16,17} and uncertainty is less than 0.05 Å. The uncertainties of the one-particle energies in this setup due to the incompleteness of the basis set can be estimated to be not larger than 0.1–0.2 eV.²² All further effects need to be dealt with in a self-interaction corrected picture. The accuracy of our calculation, however, is entirely sufficient to obtain the kind of information we are interested in, namely, wave-function character and trends in the energetic positions.

III. THE SODIUM COVERED SURFACE

A. Atomic geometry

The only noticeable relaxations even for higher coverages can be seen in the first substrate layer. Figure 1 shows the relaxation of the first layer substrate atoms as function of the sodium coverage. Nearly the entire relaxation of the Ga atom of the clean (110) surface is already undone at $\Theta = 0.5$. There is only a small effect on the position of the interface As atom at this coverage, but after the completion of the first monolayer ($\Theta = 1$) also the arsenic is practically back at the perfect crystal position. The relaxation of the other atoms are small (< 0.1 Å).

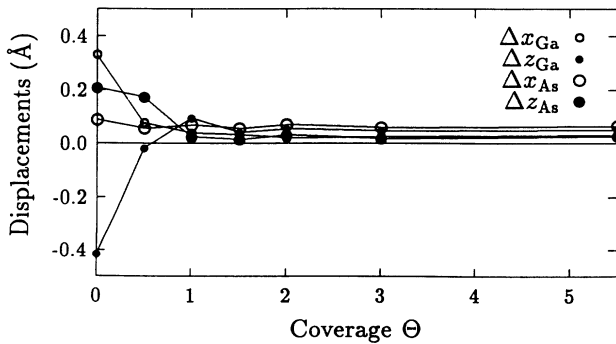


FIG. 1. Relaxation of the substrate surface atoms as a function of the sodium coverage. There is no relaxation in the y direction due to the symmetry of the surface cell.

When sodium grows epitaxially on GaAs (110) the dimensions of its structure in a plane parallel to the interface are determined by the substrate. If the epitaxial Na layers were planar they could be compared to (110) planes of bcc Na. The (theoretical) equilibrium bcc lattice constant would then be contracted by 3% each along the $[1\bar{1}0]$ and the $[001]$ direction. In order to study the adsorption of Na on GaAs(110) we started from different guessed initial positions of the Na atom(s) and then allowed all atoms to move according to the forces.

For the half monolayer coverage ($\Theta = 0.5$) there are two stable configurations. As described in Refs. 16 and 17, in one of the structures the Na atoms sit on a line parallel $[001]$ through the surface Ga atoms (see Fig. 2, bottom picture) and in the other structure the line goes through the surface As atoms.

In the stable geometry for the full monolayer coverage ($\Theta = 1$) one Na atom is found at the site next to the Ga atom and the other one slightly higher, bridging the two Ga atoms as reported in Ref. 17. Fig. 2 shows the positions of the adsorbate atoms and the top layer substrate

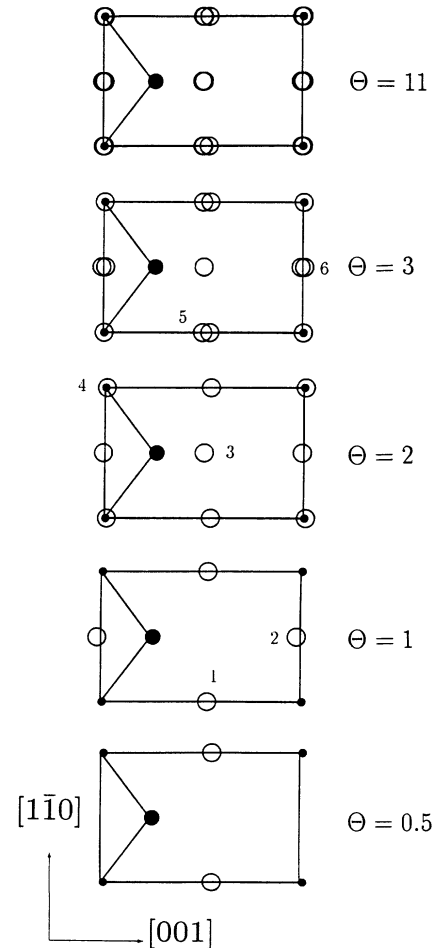


FIG. 2. Positions of the sodium adatoms projected on the interface plane. Small full circles represent Ga interface atoms, large full circles As interface atoms, and open circles the Na adatoms. Only the first adlayer Na atoms are noticeably in-plane distorted.

atoms projected onto the interface plane. In addition to the $\Theta = 1$ structure shown in Fig. 2 we find a metastable geometry²¹ where one Na atom sits on the [100] As line and the other one bridges the two As atoms. The first structure is energetically favorable compared to the second by 0.3 eV.

Increasing the coverage from $\Theta = 1$ to $\Theta = 1.5$ we find the third adatom in a position directly above the second substrate layer Ga atom. The next Na atom ($\Theta = 1.5 \rightarrow \Theta = 2$) adsorbs above the top substrate layer Ga atom (Fig. 2). The buckling of this second Na layer (i.e., the surface layer) is 0.67 Å and the interface Na layer buckling is reduced from 1.11 Å to 1.01 Å. The GaAs surface layer buckling, which was 0.62 Å for the clean GaAs (110) surface, is nearly removed at this stage.

As expected the Na atoms of the third adlayer ($\Theta = 3$) sit approximately above the first adlayer atoms. A top view (Fig. 2) shows a highly regular rhombic pattern for all but the interface Na layers. Solely the sodium atoms bound to the Ga atoms are pulled away from these regular sites. The value for the interface Na layer buckling lies slightly above 1 Å and for the other two layers slightly below 1 Å. The small increase in the top Na layer rumpling from $\Theta = 2$ to $\Theta = 3$ can be explained in simple geometric terms: For $\Theta = 2$ the surface Na atoms sit on hollow sites above the interface Na layer. They can therefore accomplish the flattest possible structure in accordance with sufficient volume per atom. The surface atoms for $\Theta = 3$, on the other hand, sit above the interface Na atoms, as mentioned above. The latter form a substantially rumpled layer. In a perfect bcc lattice atoms of interface as well as the subsurface layer would be nearest neighbors of the surface atoms. For the slightly distorted adsorbate structure this means that the surface atoms now sit directly above (nearly) nearest neighbors which form a strongly rumpled layer. Therefore the atoms of the third adlayer assume a position which is more sensitive to the interface layer buckling than it was for the second adlayer atoms.

Finally we performed calculations for the limit of a very thick sodium overlayer. Such a system was modeled in a supercell with seven layers GaAs as before and the rest of the cell filled with eleven layers of sodium. Thus we are dealing with a heterostructure $(\text{GaAs})_7(\text{Na}_{22})_{11}$. The total energy was optimized with respect to the cell length and all atoms with the exception of those in the central GaAs layer were allowed to relax. In the equilibrium arrangement the volume per atom in the sodium region is identical to that of bcc Na. The intralayer buckling decreases from 0.98 Å in the interface Na layer to zero in the central Na layer. The zero buckling in the central sodium layer is forced upon the system by the periodicity of the supercell. The adlayers (Fig. 2) show a perfect rhombic overlayer pattern for all but the interface Na layer.

Figure 3 shows the distances between the interface substrate and adsorbate atoms as a function of the coverage. If the character of the bonding were changed or noticeably weakened with increasing coverage this would likely be reflected in a change in bond length, but nothing like this is found.

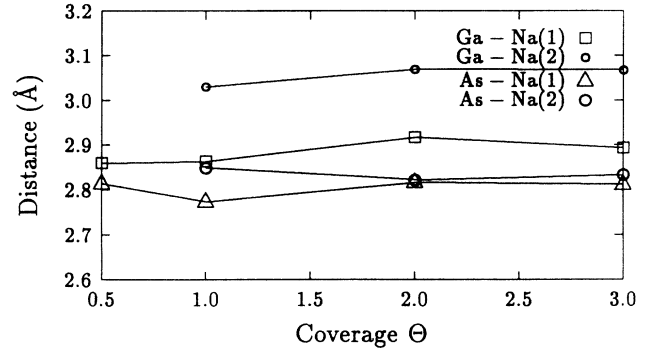


FIG. 3. Distance between the interface atoms as a function of coverage.

B. Density of states and wave-function character

In Fig. 4 we show the evolution of the density of states with increasing Na coverage. For $\Theta = 0.5$ one can identify a state in the middle of the gap. This state is filled with one electron per surface unit cell. The wave-function character of this state is that of the clean substrate Ga dangling orbital which was previously identified as a highly correlated state.^{16,17,23} For $\Theta = 1.0$ this state has moved away from the Fermi energy towards the va-

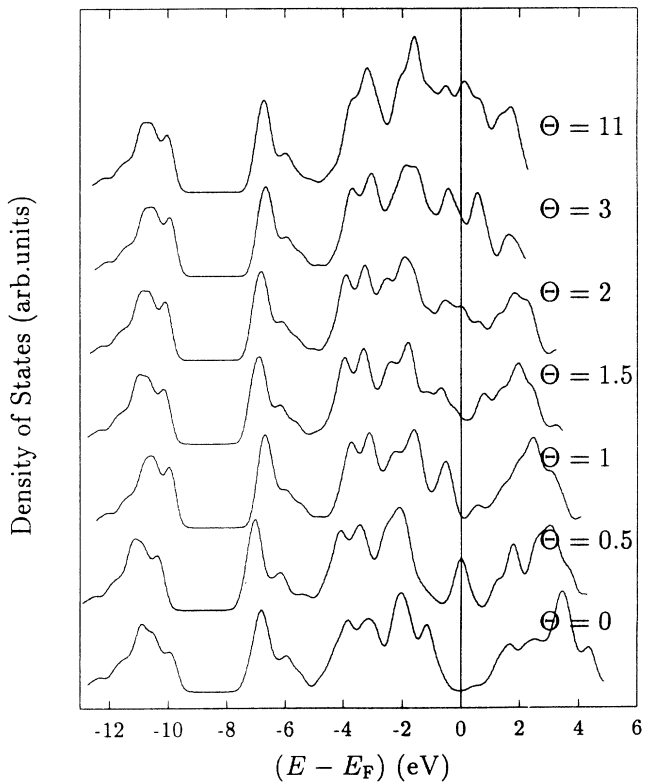


FIG. 4. Density of states for the seven layer GaAs plus Na slab for different sodium coverages. The discrete calculated energies have been broadened with a Gaussian function of width $\sigma = 0.2$ eV for a clearer picture.

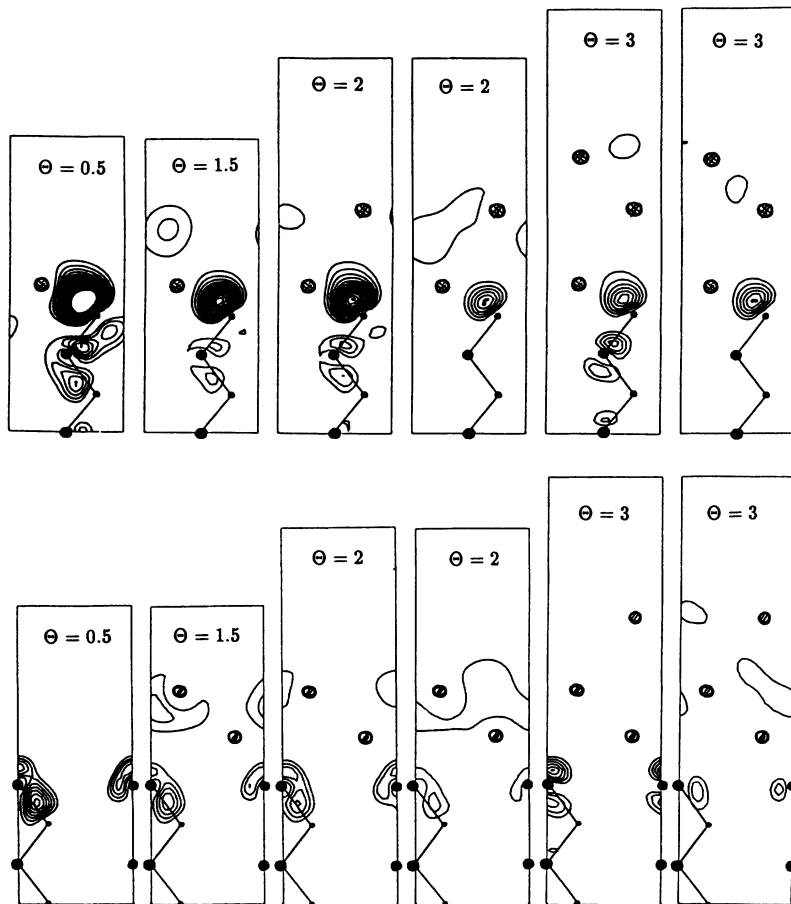


FIG. 5. $|\psi_i|^2$ for the states at the Fermi level. Depicted are $(1\bar{1}0)$ planes perpendicular to the interface. The upper panel shows a cut through the topmost Ga atoms and the lower through the As interface atoms. The minimal charge density corresponds to $1 \times 10^{-3} e^-/\text{bohr}^3$ and the difference between contours is $5 \times 10^{-4} e^-/\text{bohr}^3$. For the higher coverages several states occur at the Fermi energy.

lence band so that the Fermi energy is in a gap of the (Kohn-Sham) density of states. At coverage $\Theta = 1.5$ the density of states in the gap region becomes noticeable and after completion of the second adsorbate monolayer the system is metallic. The wave-function character of the states at the Fermi level can be seen in Fig. 5. The upper panel shows the $(1\bar{1}0)$ plane through the interface Ga and the lower panel the $(1\bar{1}0)$ plane through the interface As atom. For all coverages one can clearly identify the Ga sp^3 -like orbital at the interface, but the increasing delocalization of these states with coverage is also obvious. For $\Theta = 0.5$ the state is practically a pure Ga dangling orbital into which the adsorbed Na atom has donated its valence electron, although, as shown in the lower panel, there is also a contribution at the surface As atoms. For $\Theta = 1.0$ the Fermi level lies in the gap. The highest occupied states still look very similar to those of half a monolayer coverage, just slightly more delocalized. At $\Theta = 1.5$ a metallic electron distribution starts to form in the Na overlayer. For this and all higher coverages there is still a remarkable electron density between the uppermost Ga and its nearest neighbor Na atom. This result clarifies that the coupling of the metal and semiconductor states happens via these dangling-bond orbitals and stresses the importance of semiconductor surface states for the build up of metal induced gap states.

C. Energies

The atomic geometry as well as the direct inspection of the electron density already showed the coverage dependence in the development of the metal-semiconductor interface. A further important quantity is the adsorption

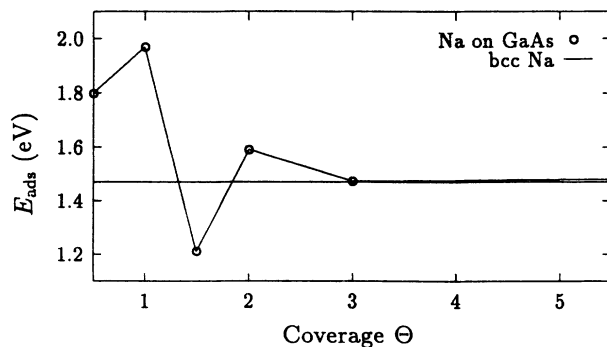


FIG. 6. Adsorption energy per Na atom as function of coverage. The calculated cohesive energy for bcc sodium is shown for comparison. Spin polarization effects are not included but would solely result in a rigid shift of the energy scale to 0.2 eV lower values. From $\Theta = 3$ on the adsorption energy of Na on GaAs (110) is equal to the cohesive energy of bcc Na.

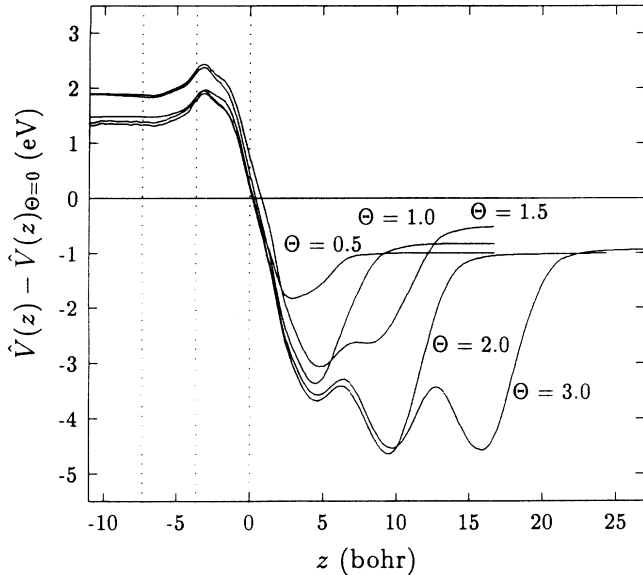


FIG. 7. Difference in the macroscopic electrostatic potential between the sodium covered and the clean relaxed GaAs (110) surface. The dotted lines indicate the GaAs layer positions.

energy of the deposited Na atoms as a function of the coverage. This is shown in Fig. 6. The calculated cohesive energy for bcc Na is shown for comparison. Spin polarization effects are not included, but would merely lead to a rigid shift of the energy scale of 0.2 eV to lower values. The first two adatoms are comparatively strongly bound, but already the third monolayer atom adsorption energy is equal to the cohesive energy of bulk bcc sodium.

D. Photocurrent and Schottky barrier

The photocurrent is defined as the difference between the vacuum level and the top of valence band at the interface/surface. The change in photocurrent with respect to the clean GaAs (110) surface can be calculated from the difference in the macroscopic electrostatic potential^{24,16,17} between the sodium covered and the clean surface. First the electrostatic potential of the slab is averaged parallel to the (110) surface, and then this averaged potential is convoluted with a window function $f(z)$ with the width of the window equal to the GaAs bulk layer distance. The difference between this quantity for the clean and the sodium covered surface contains the shift in the valence band maximum and the vacuum level as shown in Fig. 7 and therefore directly gives the photocurrent shown in Fig. 8. These results are in fair agreement with experimental data of Prietsch *et al.*²⁵

The p -type Schottky barrier is given by the difference between Fermi energy and the valence band maximum at the interface. The latter has to be calculated in two steps. From a calculation for GaAs bulk we obtain the valence band maximum with respect to the bulk potential. The difference between the valence band maximum at the interface and in the bulk is called the band bending. This can be evaluated from the difference between the macroscopic bulk—in the slab calculations the central

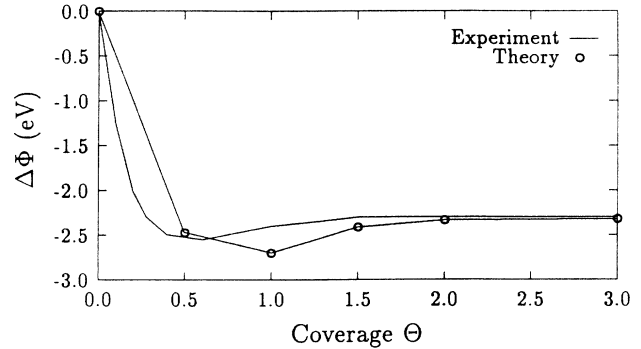


FIG. 8. Variation of the photocurrent $\Delta\Phi$ as a function of alkali coverage. Circles represent the results obtained from the variation of the macroscopic electrostatic potential and the solid line shows the experimental data for the nonreactive interface taken at 85 K from Ref. 25.

layer potential—and surface potential. The Fermi energy is obtained in the self-consistent calculation by using the Fermi-Dirac statistic. The theoretical value of 0.4 eV for the p -type Schottky barrier is smaller but in reasonable agreement with the experimental result of 0.53 ± 0.05 eV.²⁶ McLean *et al.* had reported a larger experimental value of about 0.7 eV, but inferred from the substrate core level shifts that the interface had reacted.²⁷

IV. SUMMARY

We calculated the electronic and atomic structure of the Na/GaAs (110) system in the sodium coverage range from $\Theta = 0.5$ up to several monolayers. Up to coverages of $\Theta = 1.5$ we find that the positions of the substrate atoms change with coverage, but for $\Theta > 1.5$ no further changes occur. The sodium structure is well described as a distorted bcc lattice—the bcc (110) layers parallel to the interface—with the lattice parameter parallel to the interface reduced by $\sim 3\%$ and increased perpendicular to the interface by $\sim 7\%$. With this distortion the volume per atom is practically the same as in Na bcc. The interface Na layers are buckled by about 1 Å and a view of the adlayers (Fig. 2) shows a nearly perfect rhombic overlayer pattern for all but the interface Na layer. The states at the Fermi energy evolve from very localized Ga sp^3 -like orbitals at $\Theta = 0.5$ into metal induced gap states. The surface electron density is metallic for $\Theta \geq 1.5$. The tails of the metallic Na states which enter the GaAs substrate have a significant sp^3 -like character. They are MIGS in the sense that they would not be in a position in the gap if the metal were not adsorbed on the surface. These states are basically empty surface states of the clean unrelaxed GaAs (110) surface which have been moved back into the gap and filled by the metal adsorbate. Therefore the dependence of the Schottky barrier height on the metal and on the coverage will be weak. The results for the change in photocurrent and the p -type Schottky barrier are in fair agreement with experimental values.^{25,26}

- ¹L. J. Brillson, *Surf. Sci. Rep.* **2**, 123 (1982).
- ²E. H. Rhoderick and R. H. Williams, *Metal-Semiconductor Contacts* (Clarendon Press, Oxford, 1988).
- ³V. Heine, *Phys. Rev.* **138**, A1689 (1965).
- ⁴C. Tejedor, F. Flores, and E. Louis, *J. Phys. C* **10**, 2163 (1977).
- ⁵J. Tersoff, *Phys. Rev. Lett.* **52**, 465 (1984).
- ⁶W. A. Harrison and J. Tersoff, *J. Vac. Sci. Technol. B* **4**, 1068 (1986).
- ⁷W. E. Spicer, I. Lindau, P. Skeath, and C. Y. Su, *Phys. Rev. Lett.* **44**, 420 (1980).
- ⁸W. E. Spicer, T. Kendelewicz, N. Newman, R. Cao, C. McCants, K. Miyano, I. Lindau, and E. R. Weber, *Appl. Surf. Sci.* **33/34**, 1009 (1988); M. Yamada, C. J. Spindt, K. E. Miyano, P. L. Meissner, A. Herrara-Gomez, T. Kendelewicz, and W. E. Spicer, *J. Appl. Phys.* **71**, 314 (1992).
- ⁹W. Mönch, *Rep. Prog. Phys.* **53**, 221 (1990).
- ¹⁰P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ¹¹W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ¹²D. M. Ceperley and B. A. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ¹³J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ¹⁴X. Gonze, P. Käckell, and M. Scheffler, *Phys. Rev. B* **41**, 12 264 (1990); X. Gonze, R. Stumpf, and M. Scheffler, *ibid.* **44**, 8503 (1991).
- ¹⁵S. G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26**, 1738 (1982).
- ¹⁶J. Hebenstreit, M. Heinemann, and M. Scheffler, *Phys. Rev. Lett.* **67**, 1031 (1991).
- ¹⁷J. Hebenstreit and M. Scheffler, *Phys. Rev. B* **46**, 10 134 (1992).
- ¹⁸H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ¹⁹R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- ²⁰R. Stumpf and M. Scheffler, *Comput. Phys. Commun.* (to be published).
- ²¹This geometry is stable under the constraint of the periodicity of the GaAs(110) surface unit cell. It is not clear whether the local energy minimum exists if the constraint is lifted.
- ²²J. L. Alves, J. Hebenstreit, and M. Scheffler, *Phys. Rev. B* **44**, 6188 (1991), and references therein.
- ²³O. Pankratov and M. Scheffler, *Phys. Rev. Lett.* **70**, 351 (1993).
- ²⁴A. Baldereschi, S. Baroni, and R. Resta, *Phys. Rev. Lett.* **61**, 734 (1988).
- ²⁵M. Prietsch, M. Domke, C. Laubschat, T. Mandel, C. Xue, and G. Kaindl, *Z. Phys. B* **74**, 21 (1989).
- ²⁶M. Prietsch, C. Laubschat, M. Domke, and G. Kaindl, *Europhys. Lett.* **6**, 451 (1988).
- ²⁷A. B. McLean, D. A. Evans, and R. H. Williams, *Semicond. Sci. Technol.* **2**, 547 (1987).