PHYSICAL REVIEW B VOLUME 40, NUMBER 9 15 SEPTEMBER 1989-II

Electronic properties of Na overlayers on the GaAs(110) surface

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(Received 23 January 1989; revised manuscript received 8 May 1989)

A seven-layer slab was used to model the ideal GaAs(110) surface. Two coverages, $\Theta_t=\frac{1}{2}$ and 1 monolayer (ML) of Na atoms on the surface were studied. The total-energy calculations with the self-consistent pseudopotential method was used to determine the positions of Na atoms on the ideal GaAs(110) surface. We find that the charge transfer is from the Na to the Ga atoms. The shift of the Fermi level with respect to the valence-band maximum from coverage of $\frac{1}{2}$ to 1 ML is 0.33 eV downward. This result agrees reasonably with the measured value of 0.2 eV for the n-type GaAs(110) surface.

Alkali-metal–semiconductor interfaces have recently been one of the subjects under intensive study,[1,2] because many properties, such as the formation of the Schottky barrier, are still not fully understood.[3] Experimentally, the core-level photoemission spectroscopy (CLPS) has been used to study the effects of band bending and the shift of the Fermi level E_F in several alkali-metal–GaAs(110) surfaces.[2] In particular, for sodium (Na) adsorbed on a GaAs(110) surface, Prietsch *et al.*[2] concluded the following.

(1) The alkali-metal atoms behave as electron donors on the p-type GaAs(110) surface at low coverage [$\Theta\leq 0.01$ monolayer (ML)].

(2) The shift of E_F with respect to the valence-band maximum (VBM) is downward as the coverage increases from 0.1 to 1 ML for both n- and p-type GaAs(110) surfaces.

(3) Ga atoms play a more active role in interacting with the adsorbed Na atoms at very low coverage, $\Theta<0.01$ ML.

Furthermore, there is other experimental evidence that, even at low alkali-metal coverages, the reconstruction and relaxation of the GaAs(110) surfaces are lifted.[4]

In this paper we present theoretical results of a Na overlayer on the ideal GaAs(110) surface: (a) determining the positions of Na atoms on GaAs(110) surfaces from an energetics point of view; (b) the detailed bonding pictures between Na and surface atoms at two coverages—$\Theta_t=\frac{1}{2}$ ML (4.45×10^{14} atoms/cm^2) and $\Theta_t=1$ ML (8.9×10^{14} atoms/cm^2); and (c) the shift of E_F with respect to the VBM for these two coverages.

Our calculations were carried out by applying the self-consistent pseudopotential method within the local-density approximation. The norm-conserving pseudopotential,[5] with the momentum-space formalism for the total energy[6] and the Wigner exchange-correlation potential,[7] were used. The Hamiltonian was expressed in terms of the plane-wave basis with kinetic energy up to 5.3 Ry, corresponding to about 700 plane waves. There were 15 k points sampled in the Brillouin zone for constructing the self-consistent potential.

A supercell was used to model the ideal GaAs(110) surface. Each supercell contained seven layers of Ga and As atoms plus a vacuum region equivalent to a total of five layers in thickness. The top view and side view of the upper half of the slab for the ideal surface structures are shown in Figs. 1(a) and 1(b), respectively. The Na atom is placed above the surface layer. Four possible locations investigated by us are indicated by the Roman numerals.

We shall discuss the results in three parts: (a) the positions of Na atoms at $\Theta_t=\frac{1}{2}$ and 1 ML; (b) the total charge-density contours between the Na atom and the surface Ga and As atoms; and (c) the shift of E_F with respect to the VBM for $\Theta_t=\frac{1}{2}$ and 1 ML.

(a) The positions of Na atoms. Total-energy calculations were used to find the optimum positions for Na adatoms. With the coverage of $\Theta_t=\frac{1}{2}$ ML, a single Na atom was placed at several different locations within the ideal

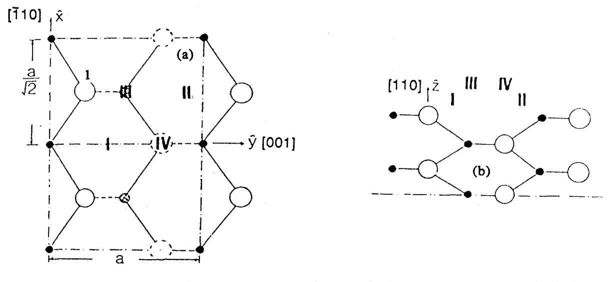

FIG. 1. Geometric configuration of the ideal GaAs(110) surface. (a) The top view (two unit cells perpendicular to the $\hat{z}$ direction). The second-layer Ga and As atoms are indicated by cross-hatched and dashed circles, respectively. (b) Side view of the slab; only four GaAs layers are shown here. Positions of the Na atom studied in this work are indicated by Roman numerals, I–IV. Ga atoms are denoted by small dots; As atoms by large open circles. a is 5.64 Å.

surface unit cell. There were two Na atoms in the supercell—one on each end of the slab. However, among these cases, we only give the results of four sites with the lowest energies. These positions are also shown in Figs. 1(a) and 1(b). For each case the total energy as a function of the vertical height z from the surface plane was calculated and then a parabola was fitted to find z_m corresponding to the minimum energy. The binding energy of the Na atom on the GaAs(110) ideal surface was calculated by subtracting the total energies of the GaAs slab and the unsupported Na atoms in the unit cell from the one of the Na/GaAs(110) system. Results for the four cases are summarized in Table I along with the corresponding optimum heights z_m.

In Table I, sites I and II have energies lower than those of the other two sites. The quasihexagonal symmetry and high coordination of the environments at sites I and II are probably the reasons for the lower energies. Between these two sites, the origin of the energy difference can be understood as follows: We shall see later from the charge-density plots that the Na atom at site I after transferring its charge to the Ga atom can easily polarize the dangling-bond charge of its nearest-neighbor surface As atom [labeled 1 in Fig. 1(a)]. For site II, the charge transfer between the neighboring Na and the surface Ga atoms has an equal chance of happening. However, the surface As atom is now located at the right-hand side of the Na atom along the $\hat{\mathbf{y}}$ direction. The dangling bond of the As atom points away from the adatom. Therefore, in this case, it is difficult to polarize the charge of the surface As atom. Furthermore, the lack of the polarization at site II pushes the Na atom away from the surface atoms (Table I). Consequently, it reduces the strength of the bonding between the Na and Ga atoms at site II. In the following discussions, site I will be used for the Na/GaAs(110) interface structure with $\Theta_t=\frac{1}{2}$ ML.

For $\Theta_t=1$ ML, both sites I and II were occupied. However, in the present studies we have kept these two Na atoms in the same plane. Hellmann-Feynman forces[8] were calculated on the Na atoms on sites I (-0.05×10^{-8} N) and II ($+0.02\times10^{-8}$ N). These results indicate that a puckering of these atoms would indeed be somewhat beneficial as far as the total energy is concerned. Such an optimization was not carried out here because forces of similar magnitudes also exist on the substrate atoms, and the electronic structure of interest is not expected to be altered by such slight changes in the atomic structure. The calculated value of the binding energy is 3.4 eV per surface unit cell. This energy is smaller than twice the value of $\Theta_t=\frac{1}{2}$ ML because of the ion-ion repulsion. The corresponding position of Na atoms above the surface plane is 1.42 Å, which is larger than the value of 1.31 Å for $\Theta_t=\frac{1}{2}$ ML. These findings indicate that the bonding between the adatoms and the surface atoms is weakened by adding another Na into the unit cell, and suggest the onset of the metallization.[9]

TABLE I. The binding energies and the corresponding vertical heights (z_m) above the ideal surface plane for four sites shown in Fig. 1 with $\Theta_t=\frac{1}{2}$ ML.

Site	Binding energy (eV) per Na atom	Vertical height (Å) above the surface
I	−2.4	1.31
II	−2.0	1.50
III	−1.3	1.95
IV	−1.8	1.77

(b) Total charge-density contours. In Figs. 2(a)–2(c) we plot the total charge-density contours of the clean, ideal $\Theta_t=\frac{1}{2}$ 1 ML surfaces in the plane containing both the

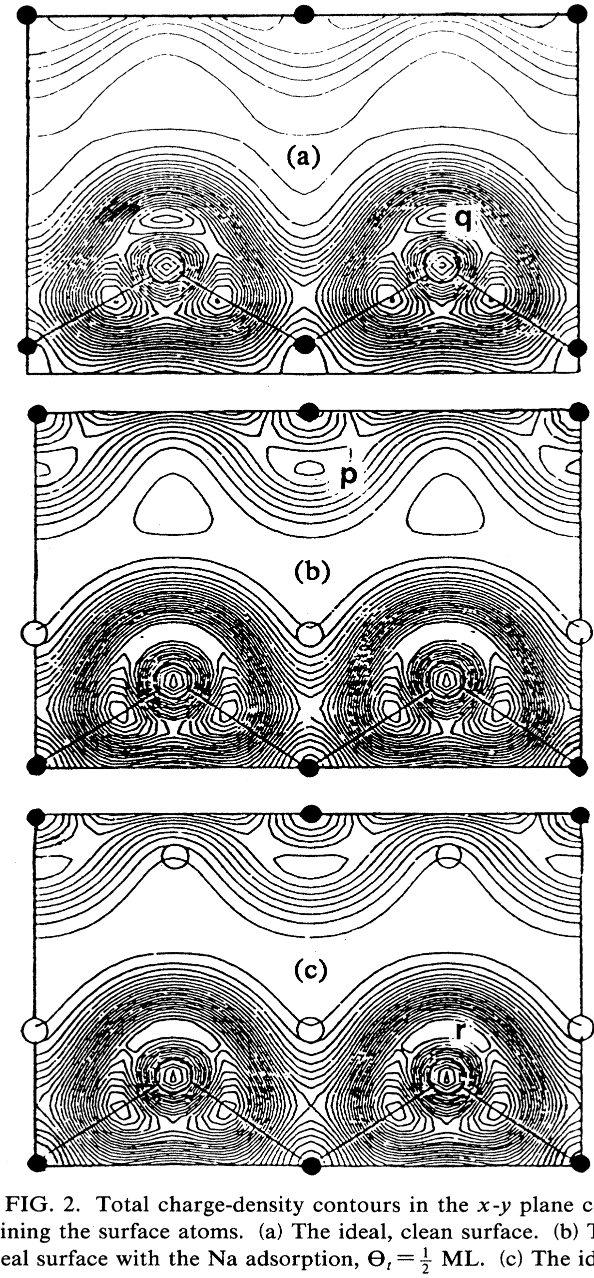

FIG. 2. Total charge-density contours in the x-y plane containing the surface atoms. (a) The ideal, clean surface. (b) The ideal surface with the Na adsorption, $\Theta_t=\frac{1}{2}$ ML. (c) The ideal surface with $\Theta_t=1$ ML. The solid circle indicates the position of the Ga atom, and the large open circle (which coincides with the charge-density contour) denotes the position of the As atom. The position of the Na atom above this plane is indicated by a small open circle.

surface Ga (solid circle) and the surface As (large open circle) atoms. The projection of the Na atom on this plane is also shown by a small open circle in Figs. 2(b) and 2(c). By comparing the results in Figs. 2(a) and 2(b), the dangling bond at Ga is more prominent [lobe p in Fig. 2(b)], which shows that the charge of the Na atom is transferred to the Ga atom. There are also some changes of contours around As atoms as compared to those in Fig. 2(a)—the lobe "q" which appeared in Fig. 2(a) is missing in Fig. 2(b). This is a consequence of the redistribution of the charge around the As atom under the influence of the Na ion. As the coverage increases to 1 ML [Fig. 2(c)], the most obvious change is the reappearance of the contour (labeled r) around the As atom due to the presence of another Na atom as compared to Fig. 2(b).

To see more clearly the charge transfer from the Na atom to the Ga atom and the charge redistribution around the As atom, we plot the charge-density difference between the cases of $\Theta_t=\frac{1}{2}$ ML and the ideal, clean surface (Fig. 3). There are three sections shown in Fig. 3: Figure 3(a) shows the charge-density difference in the (110) plane but above the surface at $z=1$ a.u. The Ga and As atoms are located below this plane and the Na atom is sitting at 1.5 a.u. above this plane. Figures 3(b) and 3(c) show contours of difference in those x-z (001) planes cutting through Ga and As atoms, respectively. The dashed contours indicate the depletion parts and the solid lines the accumulation parts of charge densities. By examining Figs. 3(a) and 3(c), the polarization effect is clearly manifested by the increase of charge density between the Na ion and the As atoms. The charge transfer from the Na atom to the Ga atom is also exhibited in Figs. 3(a) and 3(b) by the accumulation of charge at the Ga atom. Although it is difficult to determine exactly how much charge is transferred from the Na atom to the surface Ga atom, we have estimated that there is about 0.2 electronic charge of the Na atom missing in the region for z larger than z_m. This estimation is performed by calculating the total charge difference of the Na atom in the region without and with the GaAs slab. This charge-transfer result is consistent with the experimental facts that the Na atom behaves like an electron donor and the Ga atom plays a more important role for charge transfer from the alkali-metal atom than the role played by the As atom, even though our range of coverage is much higher than the experimental limit, $\Theta \leq 0.01$ ML.

(c) The shift of Fermi level from $\Theta_t=\frac{1}{2}$ to $\Theta_t=1$ ML. Prietsch *et al.*[2] deduced the E_F with respect to the VBM as a function of coverages from the CLPS. They found that the shift of E_F is downward for $\Theta > 0.1$ ML and is stabilized for $\Theta > 2$ ML. In order to compare with experimental results at $\Theta=\frac{1}{2}$ and 1 ML, it is necessary to determine the VBM in the theory. To find the VBM, we plot the charge densities for several states near the top of the occupied bands to search for the bulk-related state at $\mathbf{k}=0$. A state with the highest energy having charge density centered around the middle of the slab is found for each coverage and is associated with the VBM. In Figs. 4(a) and 4(b), the charge densities for these two states are shown. The dominant charge density is in the bulk region. Furthermore, these states are As p-like, which is consistent with the states in crystalline GaAs.

After we determined the VBM's for these two coverages, the shift of the corresponding Fermi levels with respect to their VBM's can then be calculated by choos-

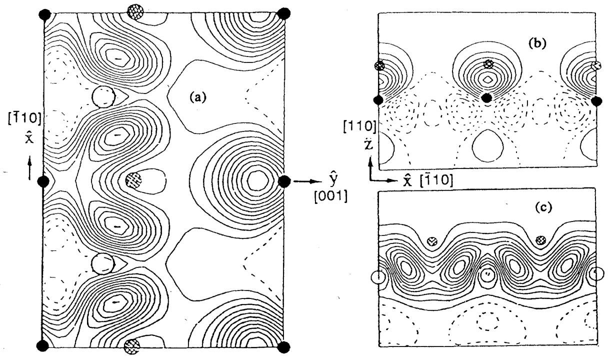

FIG. 3. The difference of charge-density contours between the $\Theta_t=\frac{1}{2}$ ML and the clean, ideal surface. (a) The x-y plane located above the ideal surface by 1 a.u. (b) The x-z plane passing through Ga atoms. (c) The x-z plane passing through As atoms. The symbols are the same as Fig. 2 for both Ga and As atoms, except the projection of the Na atom on the plane is indicated by a cross-hatched circle.

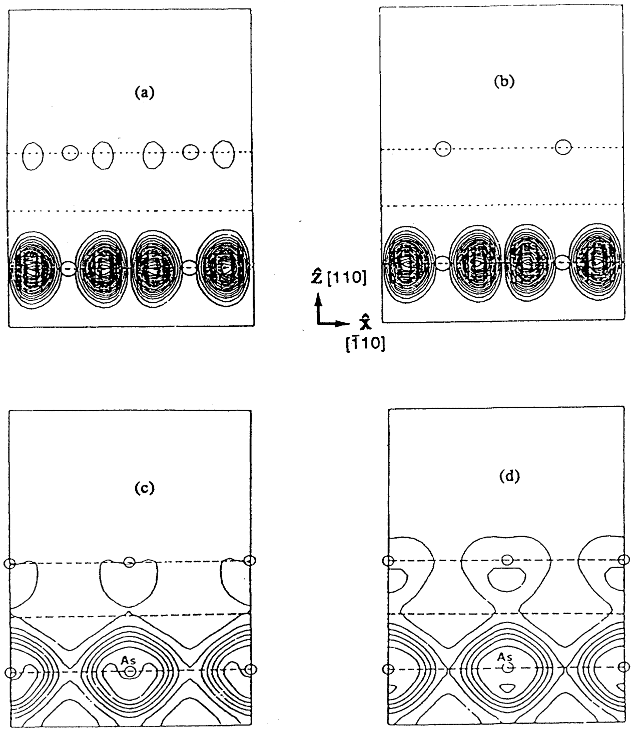

FIG. 4. The charge-density contours of the valence-band-maximum state, for (a) $\Theta_t=\frac{1}{2}$ ML and (b) $\Theta_t=1$ ML, and the charge-density contours of the bottom of the valence-band state, for (c) $\Theta_t=\frac{1}{2}$ ML and (d) $\Theta_t=1$ ML.

TABLE II. Comparison of the shift of E_F with respect to the valence-band maximum.

	Experiment E_F with respect to VBM		Shift of E_F		Theory E_F with respect to VBM		Shift of E_F
n-type surface	$\Theta=\frac{1}{2}$ ML	0.92 eV	-0.20 eV	Undoped surface	$\Theta_t=\frac{1}{2}$ ML	0.96 eV	-0.33 eV
	$\Theta=1$ ML	0.72 eV					
p-type surface	$\Theta=\frac{1}{2}$ ML	0.55 eV	-0.03 eV		$\Theta_t=1$ ML	0.63 eV	
	$\Theta=1$ ML	0.52 eV					

ing the energies of the highest occupied states as the E_F. The E_F with respect to the VBM for $\Theta_t=\frac{1}{2}$ ML is 0.96 eV, while the value for $\Theta_t=1$ ML is 0.63 eV. The resulting shift of E_F from $\Theta_t=\frac{1}{2}$ ML to $\Theta_t=1$ ML is downward and is 0.33 eV. The experimental value is a downshift of 0.2 eV for the n-type semiconductor surface. These results are summarized in Table II. Our theoretical result is too large as compared with the shifted value (<0.1 eV) for the p-type surface. For the p-type surface, the existence of the hole states in the bulk can cause significant charge transfer from the surface region to the bulk region. In the undoped and the n-doped surfaces, such charge transfer is not expected to happen. This may be the reason why the undoped results agree better with the measured values of the n-type surface. However, more importantly, the *downshift* behavior of E_F from $\Theta_t=\frac{1}{2}$ to 1 ML is qualitatively in good agreement with the experiment.

The downshift of the E_F in the range of the coverage discussed in this paper can be understood as follows: The dangling-bond state of the Ga atom forms a bonding state with the ($3s$) state of the Na atom. As the coverage from $\frac{1}{2}$ ML increases to 1 ML, more charge from the additional Na atom can be transferred to the Ga atom. The formation of the bonding state is more complete and the energy of the bonding state is thus lowered. Accordingly, the E_F is shifted down as the coverage changes from $\frac{1}{2}$ to 1 ML.

In summary, we have studied the Na atoms adsorbed on the ideal as GaAs(110) surfaces. Two coverages of $\Theta_t=\frac{1}{2}$ ML and $\Theta_t=1$ ML have been considered. The positions of the adatoms are determined by the total-energy calculations. From the total, difference charge-density contour plots, and a simple estimation of the charge of the Na atom in the vacuum regions, the charge is transferred from the Na atom to the Ga atom. The dangling-bond charge of the As atom is polarized under the influence of the Na ion. We conclude that the Ga atom plays a more active role in interacting with the adatom than the As atom. By choosing the energy of the VBM as a reference, the E_F is downshifted by 0.33 eV for the two coverages. This result agrees with the measured downshift of 0.2 eV for the n-type GaAs(110) surface.

ACKNOWLEDGMENTS

We would like to thank Dr. M. Prietsch and Dr. C. Laubschat for many helpful discussions. One of us (L.H.Y.) would like to thank the supporters from the IBM Almaden Research Center. Two of us (C.Y.F. and L.H.Y.) would like to express their gratitude for support from the Committee on Research of the University of California at Davis.

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