

Bound Bipolaron at the Surface: The Negative- U Behavior of GaAs(110) with Adsorbed Alkali Metals

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Using density-functional theory we investigate the electron-lattice coupling of Ga dangling bonds at GaAs(110)/Na and GaAs(110)/K. We find that the electron capture at the bond causes a significant local surface unrelaxation. The lattice distortion even overcompensates the electron-electron repulsion, leading to the formation of a two-electron bound state (surface bipolaron), which manifests the negative- U behavior of the Ga orbital. The electron pairing favors the clustering of adatoms. The influence of the pairing on scanning tunneling microscope images and surface core-level spectra is discussed.

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Alkali-metal adsorbates on semiconductors are important model systems for studying the metal-semiconductor interfaces and fundamental mechanisms of adsorption [1–5]. However, the most basic aspects of these “classical” systems, namely, the atomic geometry and electronic properties, are not yet identified unambiguously and certainly are not understood.

Scanning tunneling microscopy (STM) shows that Cs adatoms on GaAs(110) form one-dimensional (1D) zigzag chains, which at higher coverage arrange in a 2D “closely packed zigzag” structure (Fig. 1) [2,3]. This structure corresponds to the coverage $\Theta = 1/4$ if we define $\Theta = 1$ as the coverage of one adatom per each substrate surface atom. Surprisingly, much smaller Na atoms appear in STM as linear chains arranged in a twice sparser 2D structure [4]. A low energy electron diffraction study of GaAs(110)/K [5] suggests that alkali-metal adsorption removes the relaxation of a clean GaAs(110) surface already at about one-half of the saturation cover-

age. The formation of chains and the substrate unrelaxation have not been explained so far—*ab initio* density-functional theory (DFT) calculations predicted a weak repulsion of adatoms and only a slight change of the relaxation for $\Theta = 1/4$ and $\Theta = 1/2$ [6,7].

The electronic properties of the surface are largely determined by the Ga-derived surface states which are partially occupied by the alkali-metal valence electrons [6–10]. The Bloch description of these states would automatically imply a metallic character of the surface at all coverages $\Theta < 1$ as the Ga band gets completely filled only for $\Theta = 1$. However, direct and inverse photoemission [1], electron energy loss spectroscopy [11,12], and STM [3,4] identify that the surface is insulating. This means that once the surface state accepts an electron it becomes localized and the Bloch picture breaks down. *The electron localization can be caused by the Hubbard-type correlations or by a very strong electron-lattice interaction.* In Ref. [6] we calculated the Hubbard repulsion at the Ga orbital as $U \approx 0.56$ eV, which is comparable but somewhat smaller than the hopping integral. Although this result shows the importance of the on-site correlations, it is not sufficient to conclude if they alone can trigger the metal-insulator transition in the partially occupied (e.g., to one-quarter at $\Theta = 1/4$) surface band. In the present paper we show that it is the electron-lattice interaction which is the major cause for the insulating behavior of alkali-metal adlayers on GaAs(110).

A strong coupling of the dangling bond states to atomic displacements at clean GaAs(110) is evident already from the fact that the surface relaxation is able to sweep the empty Ga- and occupied As-surface states out of the bulk band gap (see, e.g., [13]). Our calculations show that the capture of an electron at Ga dangling orbital causes a local surface unrelaxation which lowers the energy level of this orbital. As a result the localized state becomes energetically favorable. This mechanism of electron localization—the surface polaron effect—is favored by the small surface-state bandwidth and the two-dimensional character of electron motion [14]. We in-

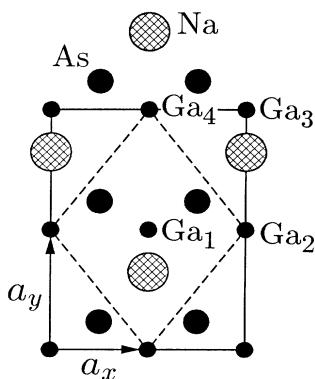


FIG. 1. The “closely packed zigzag” structure of an alkali-metal adlayer on the GaAs(110) surface. a_x and a_y are the clean surface unit-cell vectors. The overlayer elementary cell is indicated by the dashed lines. The larger 2×2 surface cell (solid lines) is used to vary the electron occupation on sites $Ga_1, Ga_2, Ga_3,$ and Ga_4 .

investigate this effect by using parameter-free DFT total-energy calculations. We displace the valence electron from one surface Ga atom to the other and then let the lattice adjust to the new charge distribution. We find a significant energy gain $U_p \approx 1$ eV due to the lattice distortion. This value even exceeds the on-site Coulomb repulsion U , which enables the formation of a two-electron bound state, i.e., a surface bipolaron. The calculation shows that the electron pair is localized at the closest to the adatom Ga orbital (Ga_1 or Ga_3 in Fig. 1), which thus behaves as a negative- U center [15]. A completely filled one-electron energy level of this orbital shifts deeply into the bulk energy gap. Hence the bipolaron state corresponds to an insulator, giving an alternative to the Mott-Hubbard mechanism of a metal-insulator transition. The calculated “effective U ” is $U^* = U - U_p \approx -0.61$ eV for GaAs(110)/Na and ≈ -0.35 eV for GaAs(110)/K. These results seem to support the idea by Allan and Lannoo [16] that the adatom-substrate bond can exhibit a negative- U behavior. However, in contrast to these authors we consider the negative U^* as a property of the Ga dangling orbital rather than of the Ga-alkali-metal bond, because the Ga surface states remain practically unchanged upon adsorption.

Our DFT calculations are performed with the local-density approximation (LDA) for the exchange-correlation functional [17]. We use fully separable norm-conserving ionic pseudopotentials [18], taking into account (for Na and K) the nonlinearity of the exchange-correlation interaction [8,19]. For the plane-wave basis set an energy cutoff of 8 Ry was chosen (compare, e.g., Ref. [13]). The surface is modeled by a periodic slab of seven GaAs(110) layers and a vacuum region with a thickness of five such layers. We consider the adlayer structure shown in Fig. 1. The surface elementary cell, indicated by the dashed line, contains two Ga and one alkali-metal atom ($\Theta = 1/4$). In a Bloch picture this implies that the Ga-derived band is one-quarter filled, and the surface should be metallic. To account for the possible electron localization we use an extended 2×2 cell as shown in Fig. 1 by the solid line. This enables us to control the electron occupation of orbitals centered at four sites, Ga_1 , Ga_2 , Ga_3 , and Ga_4 .

Using the Kohn-Sham formulation of DFT, we represent the total electron density as a sum over “effective” one-particle wave functions

$$\rho(\mathbf{r}) = \sum_{j,\mathbf{k}} |\psi_{j,\mathbf{k}}(\mathbf{r})|^2 + \sum_{i=1}^4 n_i |\Phi_i(\mathbf{r})|^2. \quad (1)$$

The first term on the right-hand side of Eq. (1) is the contribution of states which lie deeper than the Ga dangling bond state. It contains a summation over the surface Brillouin zone (SBZ), which we perform using four two-dimensional Monkhorst-Pack \mathbf{k} points [20] (see, e.g., [13]). The second term describes the contribution of the four localized Ga orbitals Ga_1 – Ga_4 with occupation num-

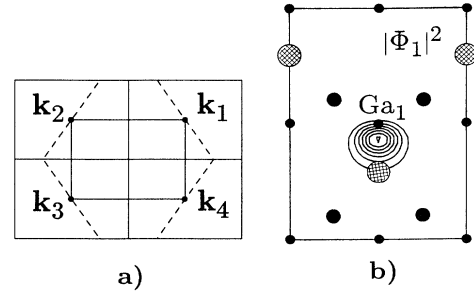


FIG. 2. (a) Brillouin zones for three surface elementary cells shown in Fig. 1. The dashed lines refer to the alkali-metal overlayer cell and the outer and inner rectangles to 1×1 and 2×2 surface unit cells. (b) The contour plot of a surface-band eigenstate $|\Phi_1(\mathbf{r})|^2$ at $\mathbf{k} = \mathbf{k}_1$. The plot is in the x - y plane passing through the maximum of a Ga dangling orbital between Ga and alkali adatom.

bers n_1 – n_4 .

The functions $\Phi_i(\mathbf{r})$ we use to represent the localized charge density are the four Ga-surface-band eigenfunctions at point $\mathbf{k}_1 = \pi(1/2a_x, 1/2a_y)$ in the SBZ of a 2×2 cell [Fig. 2(a)]. A simple tight-binding analysis (analogous to that in Ref. [6]) shows that at this particular \mathbf{k} point the four Bloch states are standing waves, each with a maximum at one of the four considered Ga sites and nodes at the other three sites. Our self-consistent DFT-LDA calculation confirms this analysis. One of the surface states, $|\Phi_1(\mathbf{r})|^2$, calculated for GaAs(110)/Na, is shown in Fig. 2(b). The other three states look identical, but are centered at sites Ga_2 , Ga_3 , and Ga_4 .

It is important to realize that functions Φ_i in Eq. (1) are *eigenfunctions* of the Kohn-Sham equation. Therefore the constraint on the occupation numbers of these orbitals does not violate the variational principle on which the DFT is based [21]. After the variation with respect to the Kohn-Sham orbitals, the total energy is a function of n_i , which reaches its minimum for the true ground state occupations. In the following we use the localized character of $\Phi_i(\mathbf{r})$ to simulate the electron transfer between different Ga sites by changing the corresponding occupation numbers.

Figure 3 shows the total energy as a function of electron transfer in the case of a Na adlayer. The initial configuration at $\delta n = 0$ was obtained for $n_1 = n_3 = 1$, $n_2 = n_4 = 0$ by the relaxation of all coordinates of the adatoms and the substrate atoms in three upper layers. The dashed curves were calculated keeping this geometry frozen; the solid curves were obtained relaxing the atomic coordinates for each value of δn . The upper two curves refer to the transfer between nonequivalent Ga atoms $\text{Ga}_{1,3} \rightarrow \text{Ga}_{2,4}$ (see Fig. 1), with $\delta n = n_2 = n_4$ and $n_1 = n_3 = 1 - \delta n$. In this case the energy minimum occurs at $\delta n = 0$, i.e., for $n_1 = n_3 = 1$ and $n_2 = n_4 = 0$, when the valence electrons occupy the closest to adatoms Ga_1 and Ga_3 orbitals. Because of

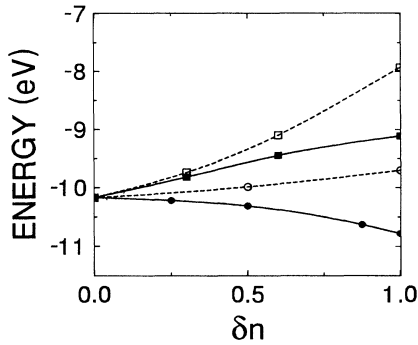


FIG. 3. The total energy for GaAs(110)/Na (per adsorbate overlayer unit cell; the origin of the energy axis is arbitrary) as a function of an electron transfer: $\text{Ga}_{1,3} \rightarrow \text{Ga}_{2,4}$ (the upper two curves); $\text{Ga}_3 \rightarrow \text{Ga}_1$ (the lower two curves). The dashed curves are calculated with the frozen atomic configuration (the equilibrium geometry at $\delta n = 0$). To calculate the solid curves we relax the atomic coordinates at each δn .

the adatom-induced potential the one-electron levels of these orbitals are lower than the levels of the Ga_2 and Ga_4 orbitals. We determine the value of this splitting as $2\Delta \approx 0.76$ eV and the on-site Hubbard repulsion as $U \approx 0.50$ eV from the dependence of the one-electron eigenvalues on δn (by comparison with the mean-field solutions of the 2D Hubbard Hamiltonian, see Ref. [6]). Almost the same U value, $U \approx 0.56$ eV, was found in Ref. [6] for a K overlayer. This confirms that U characterizes the Ga orbital and does not depend on the adsorbate. In contrast, the 2Δ splitting for K is significantly smaller, $2\Delta \approx 0.42$ eV [6], which means that K adatom polarizes the Ga bond weaker than Na.

The upper solid curve in Fig. 3 reflects a large polaron shift, but the energy still increases under the electron transfer. The result is qualitatively different for the $\text{Ga}_3 \rightarrow \text{Ga}_1$ transfer, which is displayed by the lower two curves. In this case we define $\delta n = n_1 - 1$ and vary the occupation n_1 from 1 to 2, keeping $n_1 + n_3 = 2$ and $n_2 = n_4 = 0$. This charge transfer breaks the equivalence of Ga_1 and Ga_3 and changes the translational periodicity. The lower dashed curve reflects solely the Hubbard repulsion, since the two sites are geometrically equivalent and the crystal-field splitting 2Δ does not enter. The solid curve, calculated with the simultaneous atomic relaxation, shows the decrease of the energy, which in a Bloch picture would mean the charge-density-wave instability. However, in view of a very small hopping integral (see below), we interpret the $n_1 = 2, n_2 = n_3 = n_4 = 0$ state as a bound bipolaron. The formation of this state can be, in other words, attributed to negative- U behavior of the Ga_1 orbital.

Figure 4 displays the Kohn-Sham eigenvalues of the states Φ_1 and Φ_3 . Only the $\text{Ga}_3 \rightarrow \text{Ga}_1$ electron transfer is shown; the dashed and solid lines refer to the nonrelaxed and relaxed calculations, respectively. The split-

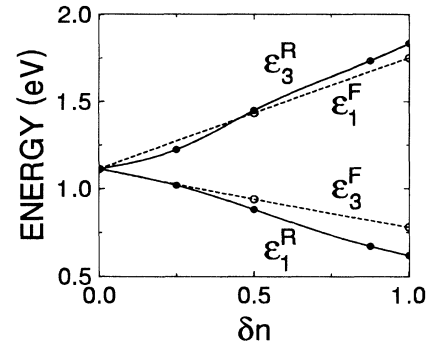


FIG. 4. Kohn-Sham eigenvalues [for GaAs(110)/Na] of the surface eigenstates Φ_1 and Φ_3 as a function of an electron transfer $\text{Ga}_3 \rightarrow \text{Ga}_1$, calculated at a frozen (ϵ_1^F and ϵ_3^F) and relaxed (ϵ_1^R and ϵ_3^R) geometry.

ting of the two dashed lines manifests a positive- U (the electron is transferred from the lower level to the upper), whereas the solid curves show the negative- U behavior (in this case the electron is transferred from the upper state to the lower). The splitting of the solid curves at $\delta n = 1$ gives $2U^* \approx -1.2$ eV, which is in a fair agreement with the energy gap of ≈ 1.1 eV, observed for GaAs(110)/Na in the STM measurements [4].

The atomic geometry in the region of the surface Ga site is shown in Fig. 5. The pronounced unrelaxation due to the electron localization (polaron state) is clearly seen. Upon capture of a second electron the Ga atom shifts even higher than the truncated bulk position. The displacements of the neighboring As atoms are an order of magnitude smaller. Since the Ga-Ga hopping integral in a truncated bulk geometry is much smaller than for a relaxed surface [6–8], the unrelaxation should lead to the electron localization. The calculation shows indeed a very small “bandwidth” (≤ 0.03 eV) of the bipolaron level.

The bipolaron state is certainly not spin polarized, which justifies the use of the DFT [not the spin-density-functional (SDF)] approach. The SDF corrections for a single-electron polaron state are expected to be small.

To evaluate the adatom-adatom interaction, we com-

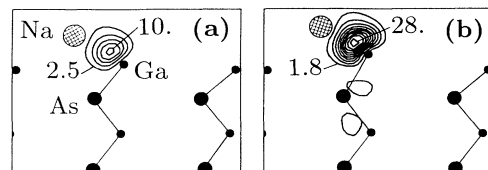


FIG. 5. The atomic geometry of Ga-Na negative- U center (side view) and the highest occupied state $|\Phi_1(\mathbf{r})|^2$ (in units 10^{-3} bohr $^{-3}$). (a) One electron is captured—the partial unrelaxation of the surface Ga atom is seen. (b) Two electrons are trapped—the surface Ga atom shifts higher than the truncated bulk position.

pare adsorption energies at different coverages. For $\Theta = 1/8$ (a single Na atom in a 2×2 surface cell) we obtain the value 1.86 eV. In a structure of Fig. 1 ($\Theta = 1/4$) with equally charged Ga_1 and Ga_3 orbitals it becomes 1.82 eV, but due to the electron pairing it increases to 2.11 eV. This result identifies an effective Na-Na attraction and explains the tendency of adatoms to form clusters.

For the K overlayer our results are qualitatively similar. We find $U^* \approx -0.35$ eV, which is approximately half of the value for Na. From this trend we expect $U^* > 0$ for Cs. This assumption could not be checked so far by direct calculation, because we doubt the validity of a frozen-core approximation in case of Cs. However, it is consistent with the STM data. Because of the electron transfer to the Ga surface state, protrusions, which are interpreted as the alkali adatoms [3,4], are actually the occupied Ga dangling orbitals. For $U^* > 0$ they reflect the positions of Cs adatoms rather closely and the 2D "zigzag" structure of Fig. 1 is imaged. In accordance with the calculated adsorption energies we suggest that Na adatoms build the same zigzag structure as Cs. However, in this case the Ga orbitals, which supply electrons to form pairs on the other sites, become invisible in the occupied-state image. This results in an STM image where half of the adatoms are missing. We speculate that this could be the reason for the observation of Na "linear chains" [4]. In the empty-state image only "missing" Na atoms should be seen.

The positive U^* implies another scenario of localization in case of Cs. First the polaron effect [see Fig. 5(a)] strongly narrows the surface band, which splits into a half-filled and an empty subband due to the adsorbate-induced potential. Then already a modest Hubbard repulsion can lead to the insulating state.

The negative U implies that there are two non-equivalent alkali-metal atoms on the surface. This may be the reason for the doublet structure of Na core-level photoemission spectrum, which has been recently observed for GaAs (110)/Na and GaP (110)/Na [22].

From our DFT calculations we conclude that GaAs (110)/alkali-metal structures can be viewed as 2D Hubbard-Peierls systems. The dominant role is played by the electron-lattice interaction which promotes the insulating state. In the case of Na or K it leads to the formation of bipolarons, whereas for Cs, acting in combination with the Hubbard repulsion, it gives rise to the localized polarons.

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