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Quasi-one-dimensional structures and metallization for the deposition of K on GaAs(100) As-rich surfaces

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A local-density linear combination of atomic orbitals method has been applied to study the deposition of a K overlayer on the As-rich GaAs(100)-2 × 4 reconstruction. Our results show that the K atoms form quasi-one-dimensional structures along the missing rows of the semiconductor surface. The conduction band associated with the K orbitals is analyzed by means of an extended Hubbard Hamiltonian. We show that a Mott transition appears for a deposition of 6–7 K atoms per unit cell, and argue that for this coverage the metal-semiconductor barrier is almost completely formed.

The geometry displayed by different metal atoms in early stages of deposition on semiconductor surfaces, as well as the metallization of the corresponding metal overlayers, have been of great interest in the field of the metal-semiconductor interface formation.[1,2] The most complete information in this area has been obtained for alkali atoms deposited on low ionic semiconductors.[3,4] The general picture taken from the studies of alkali metals deposited on GaAs(110) is the following: (i) for coverages smaller than 1 ML the metal forms one-dimensional 1D and 2D structures exhibiting an insulating behavior;[3] (ii) for larger depositions, around 1 ML, a Mott metal-insulating transition appears;[5] then, the Fermi level is pinned by the metallic density of states induced around the semiconductor charge neutrality level.[6]

Metal-GaAs(100) interfaces have not been analyzed so thoroughly as the previously mentioned cases,[7] the main reason being the complication introduced by the geometry of the GaAs(100) surface that is far from the ideal one and displays a large reconstruction. The aim of this paper is to present a theoretical calculation for the deposition of an alkali layer (K) on GaAs(100). In our approach, we shall concentrate our discussion on the As-rich GaAs(100)-2 × 4 reconstruction with three As dimers.[8] Different authors[9] have shown, using conventional density functional calculations, that this reconstruction should be the most stable for intermediate chemical potentials of the Ga and As gas phases. This suggests that this surface could be formed when growing As-rich GaAs(100) using appropriate conditions. Our interest is addressed to finding out, first of all, the interface geometry for different metal coverages, and to determining the interface electronic properties in order to elucidate the overlayer metallization. Because of its similarity with the GaAs(110) case, we can expect a metal insulator transition[5] to appear as a function of the metal coverage. Our analysis will show that in the GaAs(100) surface, K deposition creates quasi-1D structures, the electronic properties of which can be described by means of an extended Hubbard model. An approximate solution to this problem yields the conditions for the Mott transition and the appearance of metallicity in the overlayer.

The geometrical and electronic properties of the K-GaAs(100) interface have been analyzed using a self-consistent local-density linear combination of atomic orbitals (LD LCAO) method.[10,11] This approach has been successfully applied to the analysis of the deposition of alkali atoms on GaAs(110), and other chemisorption cases.[12] The starting point of this method is the first-principles LCAO Hamiltonian $\hat{H} = \hat{H}^{\text{o.e.}} + \hat{H}^{\text{m.b.}}$, where $\hat{H}^{\text{o.e.}}$ defines a conventional one-electron part, and $\hat{H}^{\text{m.b.}}$ the many-body terms

$$\hat{H}^{\text{m.b.}} = \sum_i U_i^{(0)} \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} + \frac{1}{2}\sum_{i\neq j,\sigma\sigma'} J^{(0)}_{ij,\sigma\sigma'}\hat{n}_{i\sigma}\hat{n}_{j\sigma'}, \quad (1)$$

where $U_i^{(0)}$ and $J^{(0)}_{ij,\sigma\sigma'}$ define the intrasite and intersite Coulomb interactions, respectively. Notice that $J^{(0)}_{ij,\sigma\sigma'}$ includes all the long-range Coulomb interactions between electron charges; these interactions play a crucial role in the formation of the metal-semiconductor interface.[6] This long-range electrostatic potential shifts the electron energy levels and is responsible for the dipole induced by the charge transfer between the metal and the semiconductor; as discussed elsewhere,[6] the balance between the charge transfer and the induced interface dipole brings the metal Fermi energy close to the semiconductor charge neutrality level. Our treatment includes in a self-consistent way (see below) the potential created by the induced charges.

All the terms appearing in $\hat{H}$ are obtained by using the atomic wave functions $\phi_{i\sigma}$ and the energy levels of the independent atoms forming the system (see Refs. 10 and 11 for details). The LD solution of this many-body Hamiltonian is obtained by means of a complementary one-electron Hamiltonian,[11] in similarity with the usual Kohn-Sham approach in standard local-density approximation calculations. In the LD LCAO method the occupation numbers $n_{i\sigma}$ ($n_{i\sigma} = \langle \hat{n}_{i\sigma} \rangle$), associated with the different atomic orbitals $\phi_{i\sigma}$, take the role that the electron density $\rho(\vec{r})$ plays in the traditional Kohn-Sham method. This means that for each atomic orbital $\phi_{i\sigma}$, a local one-electron potential $V_{i\sigma}^{\text{m.b.}}$ is defined from the many-body terms of Hamiltonian (1). This potential has

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both Hartree, $V^H_{i,\sigma} = U^{(0)}_i n_{i\bar{\sigma}} + \sum_{j\neq i,\sigma'} J^{(0)}_{ij,\sigma\sigma'} n_{j\sigma'}$, and exchange-correlation, $V^{\mathrm{XC}}_{i\sigma} = \partial E^{\mathrm{XC}}/\partial n_{i\sigma}$, contributions, where E^{XC}, the exchange-correlation energy, is a function of the occupation numbers $n_{i\sigma}$. A full discussion of E^{XC} and V^{XC} has been presented in Ref. 11. We have applied this LD LCAO method to describe the interaction between the atoms forming the last three layers of the system (a Ga layer, an As layer, and the K adatoms), as well as their interaction with a semi-infinite GaAs(100) material. The electronic structure of the "frozen" GaAs(100) crystal is modeled using semiempirical parameters,[13] which provide a good electronic band structure, and the LD LCAO method is used to modify the substrate Hamiltonian parameters (up to the sixth GaAs layer) in order to include the changes induced by the new layers on the substrate. This appears through the electrostatic potential that the overlayer creates on the substrate once we include the long-range interaction associated with the charge transfer $(\sum_{j\neq i,\sigma'} J^{(0)}_{ij,\sigma\sigma'} n_{j\sigma'})$. As the last two layers of the semiconductor are fully treated with the LD LCAO method, our results are practically independent of the parametrization used for the "frozen" crystal, provided its electron band structure is well described.

The results obtained for the clean GaAs(100)-2 × 4 reconstructed surface show the consistency of this procedure. Allowing the last two layers of the semiconductor to relax, we have found the most stable configuration for the geometry shown in Fig. 1, with the surface As layer forming three dimers per unit cell. We have also found some relaxation of the Ga atoms of the second layer, similar to the results of Ohno.[9] The total adsorption energy calculated for the deposition of the last two layers of the semiconductor (eight Ga atoms and six As atoms per unit cell) on the "frozen" GaAs(100) surface yields a mean bond energy (28 Ga-As and three As-As bonds included) of 1.47 eV/bond. This is in good agreement with the GaAs bond energy of 1.63 eV and the As-As bond energy of 1.52 eV.

Deposition of K on the GaAs(100)-2 × 4 reconstructed surface has been analyzed by considering one, three, five, and seven K atoms adsorbed on the semiconductor unit cell. For each case, we have looked for the most stable geometry; thus for the first K atom we have considered the whole unit cell and have determined the most stable adsorption site. For increasing number of atoms, we have started with the previous most stable configuration and looked for the new geometry by allowing the new atoms to explore the whole unit cell, with the former atoms relaxing around their previous equilibrium positions.

The first K adatom has two equally favorable sites of adsorption, *a* and *b* in Figs. 1 and 2, respectively. In both cases the adsorption energy is found to be 1.0 eV. Although the bonds that the K atoms form with the semiconductor surface are stronger in the *b* site, the lattice loses its relaxation in this case, making its similar to the one found for the *a* site.

When three K atoms are adsorbed on the semiconductor unit cell, we find that the most stable geometry corresponds to the K atoms located on sites *b*, *c*, and *d* of Fig. 2, and the Ga atoms of the semiconductor second layer located in their unrelaxed positions. The total chemisorption energy is 3.9 eV (1.3 eV per atom), suggesting an important indirect K-K attraction through the substrate. We find an important charge transfer from atom *d* to atoms *b* and *c* and the Ga dangling bonds, reflecting a strong hybridization between these dangling bonds and the K atoms *b* and *c* of Fig. 2.

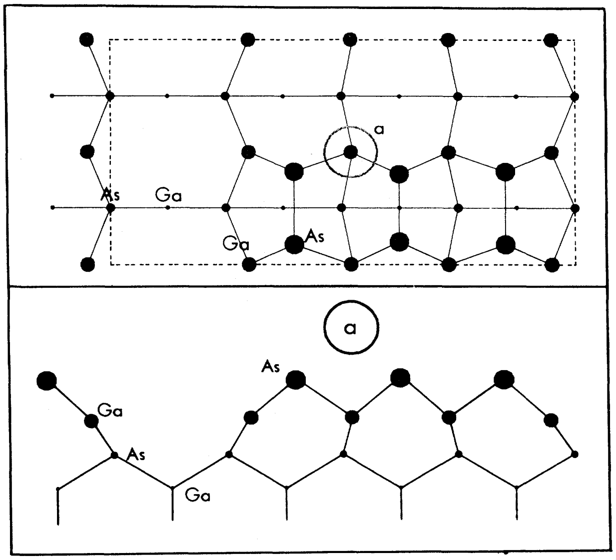

FIG. 1. Surface geometry (top and side view) for a relaxed As-rich GaAs(100)-2 × 4 reconstruction. Position *a* is one of the two most favorable adsorption sites for a K atom. The surface unit cell is indicated by the dashed lines.

For five K atoms, we find that the two new adatoms are adsorbed on the sites *e* and *f* (Fig. 2). The total chemisorption energy is 6.25 eV (1.25 eV per atom), with an energy of 1.17 eV for the adsorption of a new adatom. In this case we find that the K atoms located on the *b* and *c* sites form strong bonds with the Ga dangling bonds, *giving rise to two new occupied bands* filled by four electrons. Then, we find a "conduction" band (around 0.5 eV wide) associated with the atoms *e* and *f* having, in agreement with simple electron counting arguments, one electron per unit cell.

Finally, for seven K atoms our results are similar to the previous case. We have six K atoms in the missing row of the reconstructed surface; two of them are strongly bonded to the Ga dangling bonds, creating two occupied bands filled by four electrons, while the other four atoms in the missing row form an almost symmetric chain. Atom *d* remains isolated and the "conduction" band created by the other atoms, *e*, *f*, *g*, and *h*, is filled by three electrons. For this case, we have a chemisorption energy of 1.16 eV per atom, with an energy of 0.92 eV for the adsorption of the new adatoms.

Figures 3(a) and 3(b) show the density of states associated with the "conduction" bands formed along the K chains. For five atoms, our LD LCAO calculations show a conduction band having a $\frac{1}{4}$ occupancy, while for seven atoms we find a broader band with a $\frac{3}{8}$ occupancy (both

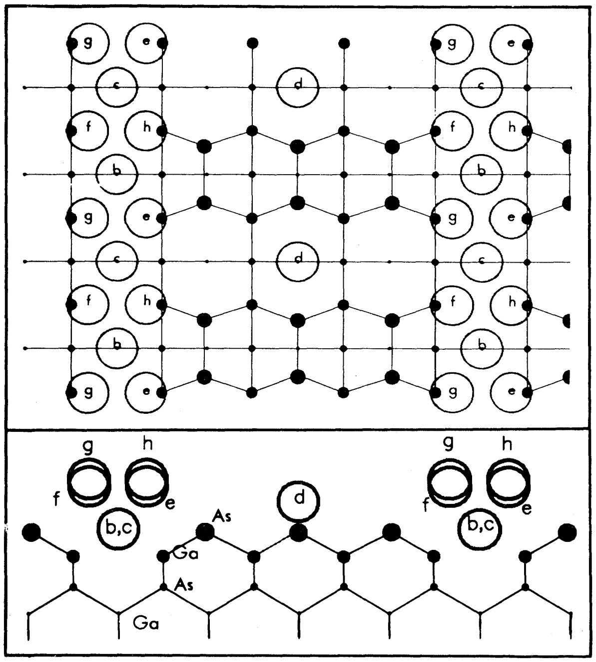

FIG. 2. Surface geometry (top and side view) for an unrelaxed As-rich GaAs(100)-2 × 4 reconstruction. Different sites of adsorption for succesive deposition of K atoms are shown by labels *b*, *c*, *d*, *e*, *f*, and *g*.

cases correspond to one and three electrons per unit cell, respectively, and two and four atoms forming the "conduction" band).

The conclusions we can reach from these calculations are the following: the K-K interaction is very strong and tends to create specific structures, with the K atoms forming quasi-1D chains along the missing rows of the (100)-2 × 4 reconstructed surface. These linear chains are strongly linked by the isolated atoms that are placed at the *d* sites of Fig. 2. Allowing this atom to desorb from the surface, we have calculated that its adsorption energy is around 1.6 eV. This shows the large stability of the isolated atom, with an adsorption energy substantially larger than the one obtained for sites *e* and *f* (~ 1.17 eV) or sites *g* and *k* (~ 0.92 eV).

The interface metallization is related to the formation of the quasilinear chains shown in Fig. 2. We can analyze the metal-insulator transition associated with the bands formed by these chains (see Fig. 3) by introducing the following Hamiltonian:

$$\hat{H} = \sum_{\alpha} E_\alpha \hat{n}_\alpha + \sum_{\alpha\sigma} t(\hat{c}^\dagger_{\alpha\sigma}\hat{c}_{\alpha+1,\sigma} + \hat{c}^\dagger_{\alpha+1,\sigma}\hat{c}_{\alpha\sigma}) \qquad (2)$$
$$+ \sum_{\alpha} U\hat{n}_{\alpha\uparrow}\hat{n}_{\alpha\downarrow} + \frac{1}{2}\sum_{\alpha\neq\beta,\sigma\sigma'} J_{\alpha\beta}\hat{n}_{\alpha\sigma}\hat{n}_{\beta\sigma'},$$

where α and β refer to the Wannier functions at each K site. In the specific case of five K atoms, we have a "conduction" band created by adatoms *e* and *f*. E_α is the energy level of each Wannier function associated with sites *e* and *f* (in our calculation both sites are almost equivalent), *t* is the effective hopping between nearest neighbors that gives rise to a bandwidth of 0.5 eV, and U and $J_{\alpha\beta}$ are the intrasite and intersite Coulomb interactions. It is important to notice that in our model Hamiltonian (2) we have introduced the off-diagonal Coulomb interactions $J_{\alpha\beta}$; this is essential to describing the insulating phase: the simplest 1D Hubbard model does not exhibit a Mott transition at one-quarter band filling.[14] For this filling, we expect the insulating phase to present an electron localized every two K sites. This localization suggests replacing the electron-electron interaction in Eq. (2) by an effective short-range interaction, $\sum_\alpha U^{\text{eff}}\hat{n}_{\alpha\uparrow}\hat{n}_{\alpha\downarrow} + \sum_{\alpha,\sigma,\sigma'} J^{\text{eff}}\hat{n}_{\alpha\sigma}\hat{n}_{\alpha+1\sigma'}$. This defines an extended Hubbard Hamiltonian that has already been analyzed by other authors,[15] allowing us to find the conditions for the Mott transition we are interested in.

We have established the equivalence between (U^{eff}, J^{eff}) and (U, $J_{\alpha\beta}$) by imposing that both interactions yield the same solution within the LD LCAO method discussed above. In this regard, we consider fluctuations of local charge with the condition $\sum_\sigma n_{i\sigma} + n_{i+1,\sigma} = 1$ as is appropriate to our one-quarter band-filling. Then, the equivalence of the Hartree (Madelung terms included) and the exchange-correlation potentials

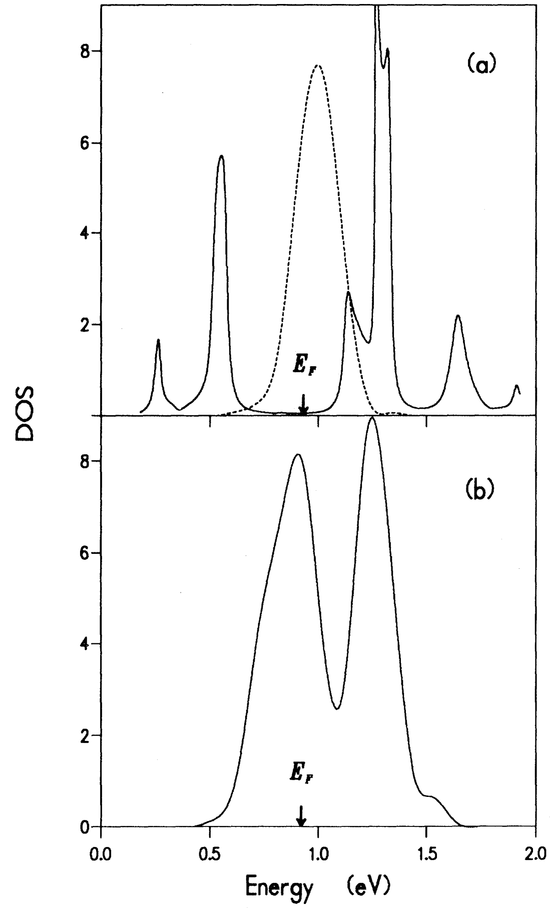

FIG. 3. Local density of states associated with the conduction band created by the deposition of (a) five K atoms (dashed line), and (b) seven K atoms. Electron correlation effects induce the spectral density of states shown in (a) by a full line. $E = 0$ is the semiconductor valence band top.

in both cases yield $U - J_{\alpha,\alpha+1} = U^{\text{eff}} - J^{\text{eff}}$ and $J^{\text{eff}} = \gamma J_{\alpha,\alpha+1}$, where $(1+\gamma)J_{\alpha,\alpha+1}$ defines the Madelung potential created on the α site [Hamiltonian (2)] by an electron charge fluctuation between nearest neighbors. Notice that the exchange-correlation potential associated with extra-atomic charge fluctuations appears as[11] $V^{\text{XC}}_{\alpha\sigma} = -J(\frac{1}{2} - n_{\alpha\sigma})$, where J (either J^{eff} or $J_{\alpha,\alpha+1}$) is the nearest-neighbor Coulomb interaction. Thus, $U - J_{\alpha,\alpha+1} = U^{\text{eff}} - J^{\text{eff}}$ takes into account that the local intra-atomic interaction between two electrons, U or U^{eff}, is screened by an extra-atomic exchange-correlation hole that is practically localized in the nearest-neighbor atoms. On the other hand, $J^{\text{eff}} = \gamma J_{\alpha,\alpha+1}$ establishes the equivalence between the Madelung potentials that other atoms create on the α site, corrected by the extra-atomic exchange-correlation effects.

Our calculations for the Wannier functions of Hamiltonian (2) yield $U = 3.4$ eV, $J_{\alpha,\alpha+1} = 2.6$ eV, $\gamma = 0.15$, and $U^{\text{eff}} \simeq 1.19$ eV, $J^{\text{eff}} \simeq 0.39$ eV. The phase diagram for the quarter-filling extended 1D Hubbard model has been analyzed by means of small cluster calculations.[15] For $U^{\text{eff}} > J^{\text{eff}}$, and $U^{\text{eff}} > 8t$, these calculations predict a metal-insulator transition when $J^{\text{eff}} \geq 2t$. We find a similar condition using a method based on Green-function techniques. In our approximation the effect of J^{eff} is first treated in a mean-field approximation, assuming a possible charge transfer between nearest neighbors. Then, intra-atomic correlation effects are incorporated through a second-order self-energy,[16] which has the important property of yielding an appropriate interpolation between both the small and large U^{eff} limits.

The calculated local spectral density for the effective interactions U^{eff} and J^{eff} given above is shown in Fig. 3(a), where the appearance of a charge-transfer gap characteristic of the insulating phase can be observed. The size of this gap is of the order of J^{eff}.

These results show that the chain created by the deposition of five K atoms is insulating; our calculations also suggest that the metal-insulator transition should appear for a metal deposition between five and seven atoms per unit cell: for seven atoms, the increase of both the bandwidth and the band filling drives the system to a metallic phase. For this deposition the Fermi level is pinned by the local density of states induced in the semiconductor gap (see Fig. 3). In this case we find $E_F \simeq 0.95$ eV, a value close to the intrinsic charge neutrality level of the semiconductor, suggesting that for this deposition the Schottky barrier is practically formed and controlled by the induced density of interface states.

In conclusion, our results for the deposition of K on the As-rich GaAs(100)-2 × 4 reconstruction show that the alkali metal forms quasi-1D chains along the missing rows of the semiconductor surface. First of all, two K atoms per unit cell are bonded to the Ga dangling bonds of the clean surface, and further alkali metal deposition completes the formation of the 1D structure. For the specific reconstruction we have analyzed, we also find an isolated K atom linking the 1D chains: the electron bands associated with these chains are described by a quarter-filled band extended Hubbard model. Our analysis shows that a Mott transition appears in the quasi-1D chains for a deposition of six to seven atoms per unit cell.

Although our discussion has concentrated on the GaAs(100)-2 × 4 surface, with three As dimers, most of the results presented here can be expected to be valid for other geometries, in particular for the one[17] having two dimers instead of three. Our results suggest a similar bonding of the alkali atoms to the Ga dangling bonds, and the formation of quasi-1D structures, that can also be expected to present a Mott transition for coverages similar to the one found in this paper.

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