Existence of localized interface states in metal/GaAs(100) junctions: Au versus Al contacts

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Using an *ab initio* pseudopotential approach, we have investigated the existence of localized interface states in epitaxial Al/GaAs and Au/GaAs(100) junctions. In spite of the fact that the Al/GaAs and Au/GaAs(100) contacts possess relatively similar Schottky barrier heights, their interface-band structures differ significantly in the region of the GaAs fundamental band gap. Our results indicate that truly localized interface states can exist near the Fermi energy in Au/GaAs(100) junctions, even at defect-free interfaces, whereas no such states are allowed in Al/GaAs(100) junctions. For the abrupt As-terminated Au/GaAs(100) junctions, in particular, we find As-bridge-bond interface states located near the Fermi energy, which derive from frustrated covalent bonds at the interface. The presence of such states could explain the recent observation, by nonlinear spectroscopy, of a sharp midgap interface-state peak in As-rich Au/GaAs(100) junctions.

I. INTRODUCTION

The existence of interface states has been extensively studied theoretically in the case of semiconductor heterojunctions.[1–5] Such studies, however, are much more scarce for metal/semiconductor interfaces[6,7] and in particular for metal contacts to III-V semiconductors such as GaAs.[8] Most of the recent theoretical work on these contacts has focused on the properties of the Schottky barrier[9–13] without actually addressing the possible existence of localized interface states near the Fermi energy. This is an important issue in general, as localized interface states can act as traps for carriers, and may degrade the transport properties of the junctions.

In an early paper, using a nearly free-electron description of metal and semiconductor valence electrons, Heine suggested the possible existence of an important difference between Al and Au contacts.[14] He argued that because of the small (large) Fermi momentum k_F of Au (Al) as compared to that of a typical semiconductor such as Si or GaAs, localized interface states might exist near the Fermi energy at Au/semiconductor junctions, but would be unlikely to be present at Al/semiconductor junctions. To our knowledge, except for an early work using a jellium model at the Al density,[6,8] no self-consistent study of Au/semiconductor and Al/semiconductor interface states has been reported, so that to this day the issue remains unresolved.

Here we address the existence of localized interface states in the prototype Al/GaAs(100) and Au/GaAs(100) epitaxial junctions. Al and Au exhibit a close lattice match to GaAs, which gives rise experimentally to quasi-epitaxial interfaces.[15–18] Furthermore, these two systems are characterized by relatively similar Schottky barriers.[19] Our choice of systems is also motivated by the fact that recent nonlinear-spectroscopy measurements have provided evidence of localized interface states in Au/GaAs(100) junctions.[20] In the present study, we use first-principles calculations to compare the Al/GaAs and Au/GaAs interface-band structures. We will show, in particular, that truly localized interface states can exist in the semiconductor fundamental gap at Au/GaAs(100) junctions, even at a defect-free interface, whereas no such states are allowed in Al/GaAs(100) junctions.

II. INTERFACE BAND-STRUCTURE CALCULATIONS

The epitaxial geometry considered in this work for the Al/GaAs and Au/GaAs(100) junctions is illustrated in Fig. 1(a). We consider abrupt defect-free junctions with an As-terminated GaAs (100) surface. Al (Au) and GaAs verify experimentally the epitaxial condition $a_{\mathrm{Al(Au)}} \simeq a_{\mathrm{GaAs}}/\sqrt{2}$ within 1% (2%). This implies that an Al or Au(100) film may be grown epitaxially on GaAs(100) with the metal fcc lattice rotated by 45° about the [100] axis with respect to the GaAs cubic substrate.[15] In a recent study, we have shown that the interface geometry represented in Fig. 1(a) corresponds to the lowest-energy Al/GaAs(100) epitaxial structure obtained by translating the Al overlayer parallel to the GaAs surface.[9] In this configuration, one half of the metal atoms (Al-I) occupy substitutional sites in the continuation of the bulk semiconductor structure, whereas the other metal atoms (Al-II) occupy interstitial (tetrahedral) sites.

In our *ab initio* calculations, we use the theoretical lattice parameters of the metals and semiconductor, namely, 3.97, 4.08, and 5.53 Å for Al, Au, and GaAs, respectively; the experimental values are 4.05, 4.08, and 5.65 Å , respectively. The compressive strain in the metal in-plane lattice constant is accommodated by a tetragonal elongation of the metal film following macroscopic elasticity theory. The corresponding Al (Au) lattice constant $a_\perp$ along the growth direction is calculated using the theoretical elastic constant ratio $C_{12}/C_{11}=0.6$ (0.9) for Al (Au), and amounts to $a_\perp^{\mathrm{Al(Au)}} = 4.05$ (4.40) Å . For the interplanar distance at the interface, we use the average between the interplanar distances in the semiconductor and in the metal, consistent with the results of total-energy calculations.[9] We will concentrate on the ideal epitaxial geometry shown in Fig. 1(a) with no atomic relaxation at the interface. The effect of atomic relaxation will be discussed later in this paper, and will be shown not to have a major influence (0.1–0.2-eV changes, at most) on the energy spectrum of the interface states.

Our first-principles calculations are performed within the local-density approximation to density functional theory, using the pseudopotential plane-wave method.[21] We used Troullier-Martins pseudopotentials[22] in the Kleinman-Bylander nonlocal form.[23] The exchange-correlation func-

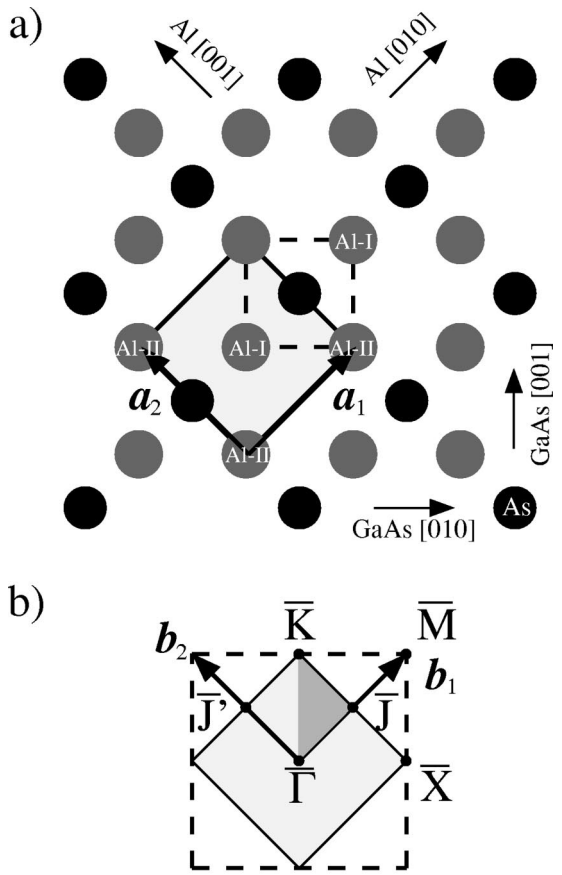

FIG. 1. (a) Top view of the metal and semiconductor atomic layers adjacent to the interface in the Al/GaAs(100) epitaxial junction. The interface unit cell is indicated by the grey square. The dashed square corresponds to the metal surface unit cell. (b) Brillouin zone (BZ) of the Al/GaAs(100) interface (grey square), which coincides with the BZ of the Al(100) $c(2\times2)$ surface and that of the GaAs(100) surface. The dark triangle is the irreducible wedge of the two-dimensional BZ of the interface in the supercell geometry (see text) which is two times smaller than that of the isolated interface (where $\overline{J}$ and $\overline{J'}$ are not equivalent). The BZ of the Al(100) surface with the high-symmetry points $\overline{X}$ and $\overline{M}$ are also shown (dashed line).

tional by Ceperley and Alder is employed.[24] To model the isolated metal/GaAs (100) interface, we use supercells consisting of 13 layers of GaAs and seven metal layers. These supercells contain two equivalent interfaces rotated by 90°, one with respect to the other. We have checked that a change in the supercell size from 13+7 to 17+9 modifies the energy of the interface states by less than 50 meV.

The calculations are carried out with a plane-wave kinetic-energy cutoff of 20 Ry (40 Ry) for the Al/GaAs (Au/GaAs) interface. In the supercell calculations, the Brillouin zone integrations are performed using a (6, 6, 2) Monkhorst-Pack grid,[25] corresponding to six special k points. We employ a Gaussian broadening scheme,[26] with a full width at half maximum of $\sim$0.1 eV to locate the Fermi-energy position.

The two-dimensional (2D) Brillouin zone (BZ) of the Al/GaAs and Au/GaAs(100) interfaces is shown in Fig. 1(b), and corresponds to the 2D BZ of the GaAs(100) (1×1) and of the Al or Au(100) $c(2\times2)$ surfaces. The point-group symmetry of the isolated interfaces is C_{2V}, and the irreducible wedge of the 2D BZ, is one-quarter of the full BZ. In the supercell geometry, however, an additional rotoinversion symmetry operation $(x\rightarrow -x, y\rightarrow z, z\rightarrow -y)$ is present, which transforms the two equivalent interfaces of the supercell into each other. As a consequence, the irreducible wedge of the 2D BZ in our calculations is only one-half of that of the isolated metal/GaAs(100) interface. Because of the rotoinversion symmetry, the bands of interface states along, e.g., the high-symmetry direction $\overline{\Gamma}$-$\overline{J'}$ ($\overline{J'}$-$\overline{K}$) in the irreducible wedge of the 2D BZ of the isolated interface will be folded onto the $\overline{\Gamma}$-$\overline{J}$ ($\overline{J}$-$\overline{K}$) direction in the irreducible wedge of the 2D BZ of the superlattice [see Fig. 1(b)].

To generate the interface-band structures from the supercell calculations, we consider only electronic states whose density is much larger at the interface than in the bulk regions. Such states can be ''true'' (localized) interface states, which decay exponentially in the two bulk materials, or resonances. Localized interface states can exist, in principle, only in the mutual gaps of the projected band structures (PBS's) of the two bulk materials, while resonances are degenerate with bulk Bloch states of one or both materials.[27] Interface-band structures are therefore generally represented together with the joint PBS of the bulk constituents to identify the possible localized interface states.

Bulk calculations for PBS's are performed using a four-atom unit cell with the same lateral dimensions as those of the supercell used to describe the interface. In order to align the PBS's of Al (Au) and GaAs, we use the calculated value of the Schottky barrier obtained following the procedure described in Ref. 9, namely, $\phi_p^{\mathrm{Al/GaAs}}=0.64$ eV ($\phi_p^{\mathrm{Au/GaAs}}=0.48$ eV); the experimental values for the p-type barrier are in the range 0.61–0.69 (0.50–0.53) eV.[19,28] To align the interface-state spectrum—measured with respect to the average electrostatic potential in the supercell—and the metal PBS, we use the computed difference between the average electrostatic potentials in the supercell and in the metal slab. This band alignment could also be performed by lining up the calculated Fermi levels of the supercell and the bulk metal. We have checked that the two procedures give the same result within 30 meV. Our overall numerical accuracy on the energy position of the interface states is estimated as 0.1–0.2 eV.

III. INTERFACE STATES

A. Al/GaAs(100) interface

In Fig. 2, we show the Al/GaAs(100) interface-band structure along the high-symmetry directions of the 2D BZ together with the bulk-band structures projected along the [100] direction. No interface state is found in the region of the GaAs fundamental gap. In fact, the joint PBS in Fig. 2 shows that no such state may exist in the GaAs gap region, irrespective of the translation state of the metal overlayer and of the local atomic structure of the interface. Modifying the interface atomic structure may change the Schottky barrier by a few tenths of an eV, and rigidly shift by this quantity the two PBS's, one with respect to the other. Such a rigid shift, however, cannot produce any common gap in the region of the GaAs fundamental gap.

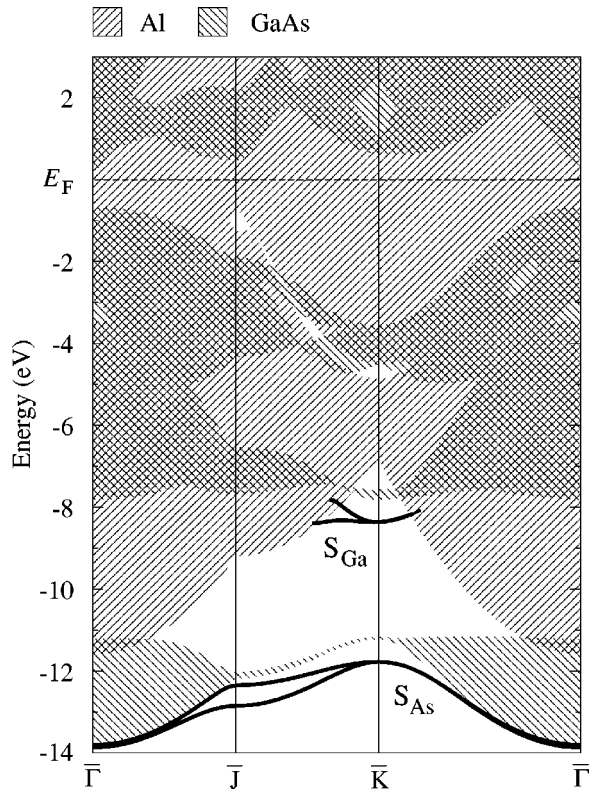

FIG. 2. Interface-band structure of the Al/GaAs(100) As-terminated junction. The localized interface states are indicated by solid lines. The projected bulk band structures are shown as hatched areas.

Bands of localized interface states are present, instead, below the As-*s* valence band and in the ionic valence gap of GaAs. These localized states have been labeled according to their dominant atomic character in Fig. 2. The probability densities of these states at the zone-edge $\bar{K}$ point are illustrated in Fig. 3. The interface states in the energy range from -14 to -12 eV (S_{As}) derive from the 4*s* orbitals of the As atoms at the interface. The variation in the GaAs crystal potential near the interface pulls these states from the GaAs As-*s* band into the gap region. This can be understood from the fact that replacing a Ga layer of the semiconductor adjacent to the metal by an Al layer essentially increases the

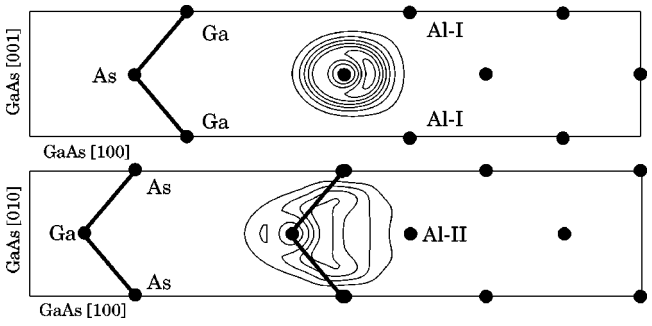

FIG. 3. Probability densities of the S_{As} (upper panel) and S_{Ga} (lower panel) interface states in the Al/GaAs(100) As-terminated junction at $\bar{K}$ (contours are separated by five electrons per a.u.$^{-3}$). The density of the S_{As} (S_{Ga}) state is displayed in a (010) [(001)] plane containing Ga, As, and Al ions (also shown).

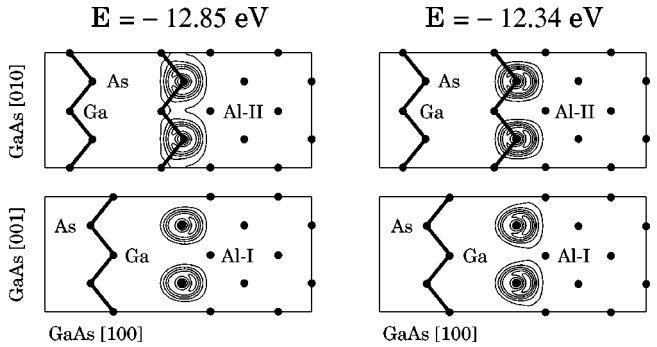

FIG. 4. Probability densities of the S_{As} interface states in the Al/GaAs(100) As-terminated junction at $\bar{J}$ (contours are separated by five electrons per a.u.$^{-3}$) displayed in a plane that contains twice the interface unit cell along the [010] (upper panels) and [001] (lower panels) directions.

average ionic charge per (1×1) surface layer from 3 to 6 (or ~5, taking into account the semiconductor $\rightarrow$ metal volume change). The resulting attractive ionic potential on the semiconductor side of the junction is fully screened by the metal electronic charge far away from the interface, but is expected to be only partially compensated at short distance,[29] i.e., a few layers away from the metal. Such a variation in the ionic potential is a driving force for localizing, in this region, orbitals deriving from semiconductor bulk bands with low dispersion and well-defined atomic character. In the case of the rather flat As-*s* band, in particular, the resulting S_{As} interface states have a fully localized character in the whole 2D BZ. Except for a noticeable polarization toward the metal, these states retain a strong atomic identity (see Fig. 3).

It should be noticed that the two S_{As} bands displayed in Fig. 2 derive from the only existing S_{As} band in the BZ of the isolated interface. The two S_{As} bands for the superlattice correspond to the S_{As} band of the isolated interface and to this band after the rotoinversion operation. In particular, the two split S_{As} bands along the $\bar{\Gamma}$-$\bar{J}$ direction correspond to the S_{As} band of the isolated interface along the nonequivalent $\bar{\Gamma}$-$\bar{J}$ and $\bar{\Gamma}$-$\bar{J}'$ directions in the BZ. The probability densities of the two split S_{As} states at $\bar{J}$ are represented in Fig. 4. These two states have different energies because the GaAs [010] and GaAs [001] directions are not equivalent at the interface. The highest-energy state here is associated with the $\bar{J}'$ point in the BZ of the isolated interface. $\bar{J}'$ corresponds to a zone-edge **k** vector that points in the direction of the Ga-As nearest-neighbor chains of the GaAs bilayer adjacent to the metal. This **k** vector leads to an unfavorable phase in the corresponding Bloch state, which reverses the sign of the *s*-atomic-like orbitals on neighboring As atoms of the chain, and renders the Bloch state antibonding. The **k** vector associated with $\bar{J}$, instead, is perpendicular to the chain and does not change the sign of the neighboring *s* orbitals in the Bloch state. This state exhibits bridge-bond features along the chains (see Fig. 4, upper left panel) and is energetically more favorable.

The interface states which occur in the region of the GaAs ionic valence gap near the $\bar{K}$ point (in the energy range from -9 to -8 eV, in Fig. 2) derive mainly from the 4*s* orbitals of the Ga atoms in the bilayer adjacent to the metal. Simi-

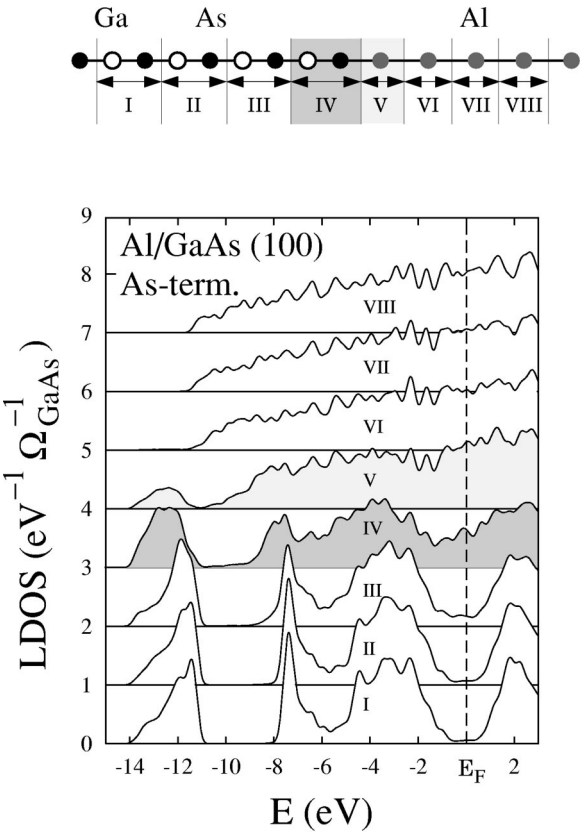

FIG. 5. Local density of states (LDOS) in the Al/GaAs(100) junction. The regions of the 13+7 supercell corresponding to the different curves are illustrated in the upper part of the figure. A Gaussian broadening with a standard deviation of 0.15 eV has been used for the LDOS.

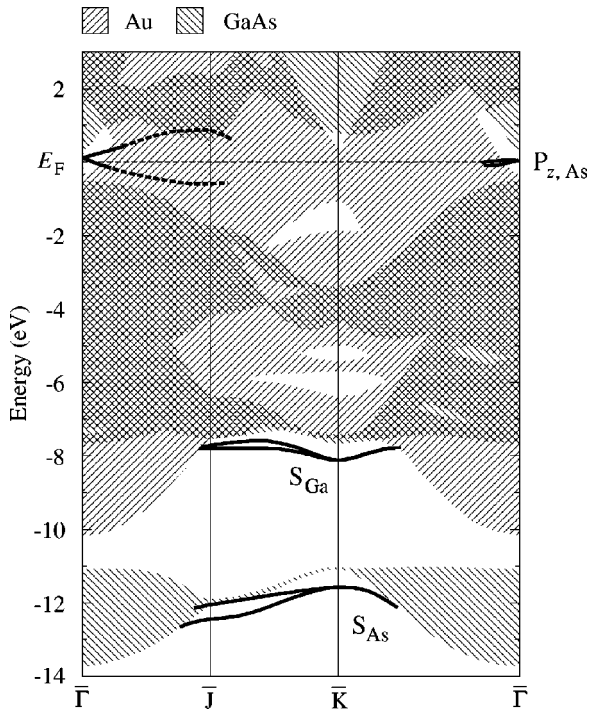

FIG. 6. Interface-band structures of the Au/GaAs(100) As-terminated junction. The localized states and resonances are indicated by solid and dashed lines, respectively. The projected bulk band structures are shown as hatched areas.

larly to the S_{As} states, these interface states (S_{Ga}) are pulled from the nearby GaAs band edge into the ionic gap by the more attractive ionic potential near the interface. As compared to the S_{As} states, these states have an increased p component, and are more strongly polarized towards the metal (see Fig. 3). The energy positions and the atomic character of the two types of interface states (S_{As}, S_{Ga}) occurring at the Al/GaAs(100) junction are consistent with those reported by Louie *et al.* in their study of the jellium/GaAs(110) interface.[8] This feature suggests that such interface states are induced by a change in the electrostatic potential near the interface rather than by the local interface chemistry, in agreement with our analysis.

The S_{As} and S_{Ga} interface states induce some noticeable changes in the GaAs and Al density of states (DOS) near the interface. This is illustrated in Fig. 5, where the Al/GaAs local density of states (LDOS) is represented in different GaAs and Al regions of the junction including one GaAs bilayer and one Al monolayer, respectively. The presence of the S_{As} interface states, in particular, modifies significantly the shape of the As feature in the GaAs spectrum, between -14 and -11 eV, in the region of the GaAs bilayer adjacent to the metal (region IV). The peak density is significantly increased on the low-energy side, at the expense of the high-energy side. The S_{As} interface states also induce some density on the metal side of the junction, in the region of the first Al layer (region V) below the Al DOS spectrum. The S_{Ga} interface states produce, instead, a feature in the GaAs spectrum between -9 and -8 eV, in the bilayer region IV. These states are also responsible for a shoulder which occurs at similar energies in the Al spectrum, in the region of the first metal layer.

B. Au/GaAs (100) interface

The Au/GaAs interface-band structure is shown in Fig. 6, together with the Au and GaAs bulk PBS's. The striking differences with respect to the Al contact are the presence of a common gap and the occurrence of interface states in the region of the GaAs fundamental gap. These interface states are close to the Fermi energy, and have a localized character near the center of the BZ. Away from $\bar{\Gamma}$, they become resonances along the $\bar{\Gamma}$-$\bar{J}$ direction, and extend over the whole GaAs fundamental energy-gap region.

The lower-energy section of the interface-band structure in Fig. 6 is similar, instead, to that of the Al/GaAs interface-band structure. The S_{As} (S_{Ga}) interface states are slightly shallower, and extend over a smaller (larger) portion of the BZ around $\bar{K}$ than the corresponding Al/GaAs interface states (see Fig. 2). The probability densities of the Au/GaAs S_{As} and S_{Ga} interface states at $\bar{K}$ are displayed in Fig. 7. Except for a weak mixing with the $5d$ orbitals of the neighboring Au atoms, these states are very similar to the Al/GaAs interface states. The localization of these states may also be understood in terms of the ionic potential induced by replacing a Ga layer adjacent to the metal by a Au layer, assuming an effective ionic charge for Au intermediate between ~ 2 and 11 electrons per atom.[30]

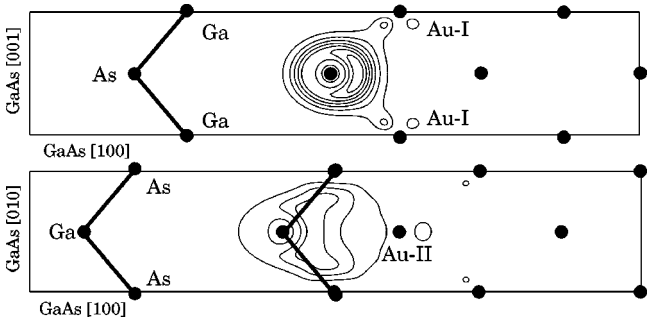

FIG. 7. Probability densities of the S_{As} (upper panel) and S_{Ga} (lower panel) interface states in the Au/GaAs(100) As-terminated junction at $\bar{K}$ (contours are separated by five electrons per a.u.$^{-3}$). The density of the S_{As} (S_{Ga}) state is displayed in a (010) [(001)] plane containing Ga, As, and Al ions (also shown).

A three-dimensional isodensity surface plot of the interface state located in the GaAs fundamental gap near the Fermi energy at $\bar{\Gamma}$ is illustrated in Fig. 8. A contour plot of the probability density of this state in a plane containing the interfacial As and Au-I atoms is also shown in Fig. 9, together with a planar average of its probability density in the junction. This state is formed essentially by the p_z orbitals of the As atoms at the interface, which form weak antibonds with the d_{xz} orbitals of the nearby Au-I atoms. Except for this interaction, the $P_{z,As}$ interface state we find here is similar to the bridge-bond surface state found at ideal (unreconstructed) Si and GaAs(100) (1×1) surfaces.[31,32] At such unreconstructed (100) surfaces, two surface states occur at $\bar{\Gamma}$ in the semiconductor fundamental gap, which derive from the linear combination of the two dangling-bond states associated with each surface atom. The first one is composed of sp dangling-bond orbitals perpendicular to the surface, while the second one is formed by purely p-type bridge-bond orbitals lying in the surface plane and perpendicular to the remaining bonds of the surface atoms with their nearest neighbors in the semiconductor.

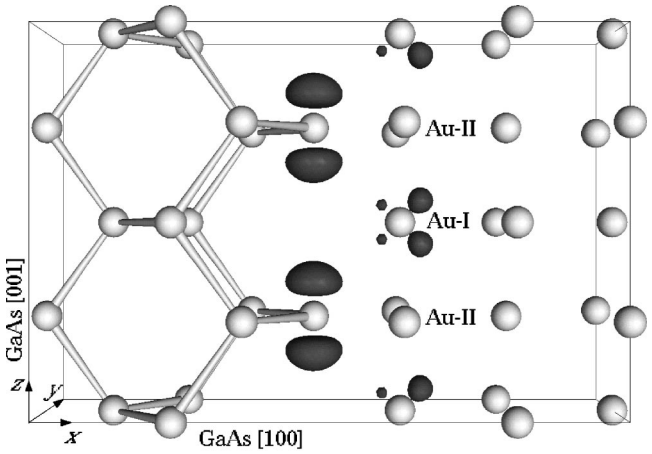

FIG. 8. Isosurface corresponding to a high probability density (1.5 electrons Ω_{GaAs}^{-1}) of the $P_{z,As}$ interface state at $\bar{\Gamma}$ in the Au/GaAs(100) As-terminated junction. The isosurface is displayed in a cell which contains twice the Au/GaAs(100) interface-unit cell along the [001] direction.

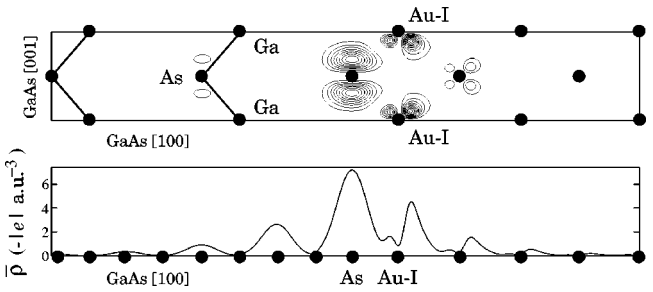

FIG. 9. Probability density of the $P_{z,As}$ interface state at $\bar{\Gamma}$ in the Au/GaAs(100) As-terminated junction (top panel) and its planar average $\bar{\rho}$ (lower panel). The contour plot is shown in a (010) plane containing Ga, As, and Au ions.

At the Au/GaAs(100) As-terminated junction, the nature of the bridge-bond $P_{z,As}$ interface states can be analyzed in a similar way. At the interface, each As atom forms two hybrid bonds, intermediate between bulk sp^3 hybrids and the planar sp^2 hybrids, with the two neighboring Ga atoms. These two bonds involve the p_x and p_y orbitals of the interface As atom. The p_z orbital, instead, would normally be involved in the other two bonds with the missing nearest-neighbor Ga atoms. At the Au/GaAs interface, the missing Ga nearest neighbors are replaced by Au atoms. Contrary to the situation in the Al/GaAs(100) junctions, directional covalentlike bonds with the metal-I atoms are highly unfavorable; the corresponding As-Au bonds would be strongly undersaturated. As a result, the p_z orbitals of the As atoms at the Au/GaAs interface go up in energy as compared to the bulk As p states of the GaAs valence-band edge, and give rise to interface states that resemble the bridge-bond states of the isolated surface.

Similarly to the other interface bands, the two $P_{z,As}$ bands along $\bar{\Gamma}$-$\bar{J}$, in Fig. 6, correspond to the dispersions along $\bar{\Gamma}$-$\bar{J}$ and $\bar{\Gamma}$-$\bar{J}'$ of the single $P_{z,As}$ band of the isolated interface. For the interface geometry shown in Fig. 8, the lowest $P_{z,As}$ state corresponds to the $\bar{J}'$ point in the BZ of the isolated interface. The corresponding **k** vector leads to a phase in the Bloch function that reverses the sign of the As p_z orbitals on neighboring sites, and produces a bonding interface state.

It should be noted that the existence of the bridge-bond interface states in the GaAs band gap is related to the As termination of the semiconductor at the junction. We have performed a preliminary study of the Ga-terminated (100) interface, and in this case no localized state is found in the fundamental-gap region. Such a disappearance of the bridge-bond interface states may be understood relatively easily in terms of the reduced number of p electrons of Ga, as compared to As.

We have investigated the effect of atomic relaxation at the interface, and checked that it does not affect the existence of the localized interface states. In particular, the $P_{z,As}$ interface states near $\bar{\Gamma}$ remain localized at the As-terminated Au/GaAs junction.[33] Atomic relaxation at this interface essentially reduces the As–Au-I bond length from 2.65 to 2.51 Å, and increases the As–Au-II bond length from 2.65 to 2.83 Å. Such a relaxation has a negligible effect on the Schottky barrier ($\sim$20 meV), and globally shifts up the energy of the interface states, in Fig. 6, by 0.1–0.2 eV with respect to the

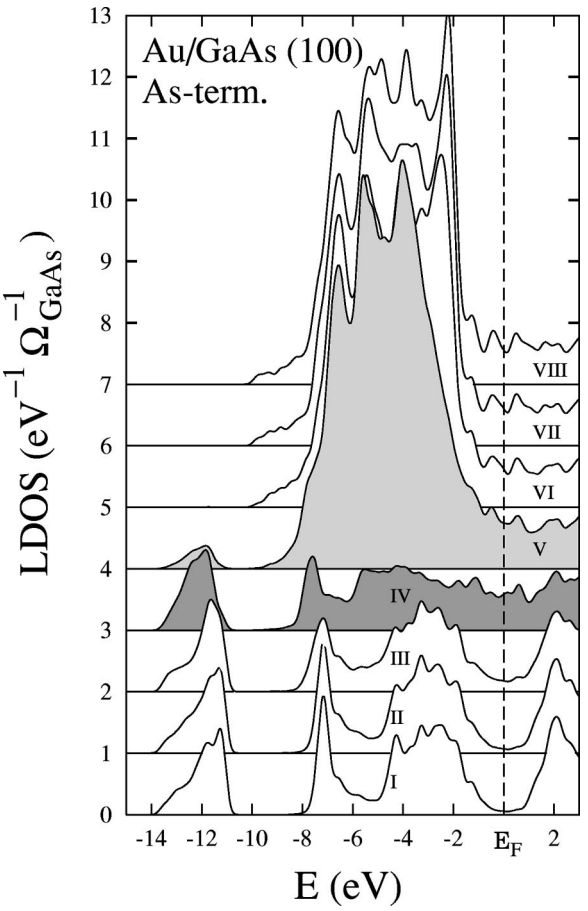

FIG. 10. Local density of states (LDOS) in the Au/GaAs(100) As-terminated junction. The regions of the 13+7 supercell corresponding to the different curves are illustrated in the upper part of Fig. 5. A Gaussian broadening with a standard deviation of 0.15 eV has been used for the LDOS.

PBS's. The $P_{z,As}$ states are shifted by about 0.1 eV, while the S_{As} and S_{Ga} states are shifted by $\sim +0.2$ eV.

In Fig. 10, we show the LDOS of the unrelaxed As-terminated Au/GaAs(100) junction. We note that the effect of relaxation would be negligible on this scale. The Au 5*d* electrons mainly contribute to the metal LDOS between -8 and -1 eV. The behavior of the LDOS near the Fermi energy, instead, is dominated by the 6*s* electrons. Due to their smaller extension in the BZ, the S_{As} localized states induce smaller—but still visible—changes in the low-energy part of the As LDOS feature than in the Al/GaAs junction. The S_{Ga} interface states, instead, give rise to a more pronounced feature (between -8.5 and ~ -7.5 eV, in region IV) than in the Al/GaAs junction. The density of states at the Fermi energy in the bulk metal is lower in Au (0.6 $eV^{-1}\Omega^{-1}_{GaAs}$) than in Al (1.0 $eV^{-1}\Omega^{-1}_{GaAs}$). In spite of that, in the energy window of the GaAs fundamental gap the LDOS of the GaAs region closest to the metal (region IV) is slightly larger in the Au/GaAs junction than in the Al/GaAs junction. This suggests a non-negligible influence of the $P_{z,As}$ interface states on the Au/GaAs LDOS spectrum.

C. Discussion

Our results show that there is indeed a qualitative difference between the interface-band structure in Al/GaAs and Au/GaAs(100) epitaxial junctions, consistent with Heine's suggestion. The calculated PBS's indicate that no localized state may exist in the GaAs band gap at the Al/GaAs(100) interface, whereas truly localized states may occur near the Fermi energy at the Au/GaAs(100) interface. In fact, from our interface-state study we find that intrinsic localized states do occur near the Fermi energy at the abrupt As-terminated Au/GaAs(100) junction, and it is thus reasonable to extrapolate that some other local interface atomic configurations—including, e.g., defects—will induce also other (extrinsic) interface states in the GaAs band gap.

It should be stressed, however, that the common-gap region of the PBS's near the center of the 2D BZ, where truly localized interface states can exist, is not very large.[34] This results from the folding of the Au PBS associated with the $c(2\times2)$ reconstruction. In the presence of larger interface unit cells, corresponding to more complex interfacial geometries, additional foldings will take place, which will decrease the common gap region and hence the probability of finding truly localized interface states. Nevertheless, our results for the resonant interface states of the As-terminated Au/GaAs(100) interface suggest that Au/GaAs junctions are more likely in general to exhibit interface states, even in the presence of such foldings, than Al/GaAs junctions.

Experimentally, interface states have been observed recently at buried epitaxial Au/GaAs (100) interfaces, grown by molecular-beam epitaxy, using nonlinear optical spectroscopy.[20] These measurements revealed a sharp midgap interface-state peak in As-rich Au/GaAs(100) junctions. The position of these interface states is consistent with those of the localized $P_{z,As}$ interface states we find at the As-terminated Au/GaAs junction. The observed peak, however, could also be due to interface states induced by some local perturbations, e.g., by defects, in the midgap region.[18,35]

IV. CONCLUSIONS

Using a first-principles approach, we have investigated the existence of interface states in epitaxial Al/GaAs and Au/GaAs(100) junctions. The calculated PBS's reveal that truly localized interface states can exist in the GaAs fundamental band gap at Au/GaAs(100) junctions, whereas no such states are allowed at the Al/GaAs(100) interface. Our study of the interface-band structures shows the existence near the Fermi energy of bridge-bond-localized states in the As-terminated Au/GaAs(100) junction, which derive from frustrated covalent bonds at the interface. Localized interface states also exist in the ionic valence gap of GaAs, and below the As-*s* band, both in the Al/GaAs and Au/GaAs(100) junctions. The latter states are localized by the attractive electrostatic potential in the semiconductor near the interface, and derive mainly from the 4*s* orbitals of the As and Ga atoms at the interface.

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