Effects of interface morphology on Schottky-barrier heights: A case study on Al/GaAs(001)

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(Received 11 April 1997)

The problem of Fermi-level pinning at semiconductor-metal contacts is readdressed starting from first-principles calculations for Al/GaAs. We give quantitative evidence that the Schottky barrier height is very little affected by any structural distortions on the metal side—including elongations of the metal-semiconductor bond (i.e., interface strain)—whereas it strongly depends on the interface structure on the semiconductor side. A rationale for these findings is given in terms of the interface dipole generated by the ionic effective charges. [S0163-1829(97)01647-0]

Despite several decades of extensive experimental and theoretical work,[1,2] the key factors affecting the Fermi-level pinning at metal-semiconductor contacts have not yet been clearly assessed. In a review written almost ten years ago,[3] Tersoff identified the most relevant controversy as to whether the pinning is determined by *intrinsic* interface states which exist even at an abrupt ideal interface, or by *extrinsic* electronic states arising from native defects: this remains the main controversy to date. Unfortunately, there is essentially no experimental access to the microscopic morphology of a given interface: were this known, the actual Schottky barrier height would be unambiguosly determined by the laws of electrostatics and of quantum mechanics. For a given (and simple enough) morphology, the barrier can nowadays be accurately predicted from first principles.[4–10] Other theories and models, based on various concepts—such as the charge-neutrality level[2]—could provide a complementary useful approach, provided they are validated against some parameter-free descriptions of the same phenomena. Since real interfaces are ''complex and dirty,'' first-principles calculations performed on idealized geometries provide a deal of unique ''experimental'' information that any successful model will have to account for.

Previous theoretical work has unequivocally assessed the following facts: the barrier height depends of the nature of the metal;[4] it also depends on the crystallographic orientation as well as on the microscopic morphology of the interface.[7] The electronic mechanisms governing the value of the Schottky barrier—as well as their dependence on the microscopic morphology of the interface—have not been systematically investigated so far and are basically unknown. Here we provide a contribution in this direction, by studying the barrier-height variations induced in Al/GaAs(001) by several structural and morphological perturbations which are switched on and off in our computational framework. Our calculations provide a microscopic probe for the nature of the interface—including its ''effective'' thickness—and for the electronic response phenomena responsible for the barrier height. In a microscopic description of insulating materials, the basic constants which couple electrostatic potentials to ionic displacements go under the name of dynamical effective charges. In the present work we elucidate the crucial role of the dynamical charges of interface ions in determining the variations of the interface dipole.

The Al/GaAs(001) interface is sp bonded and almost perfectly lattice matched (1% mismatch); because of the actual growth conditions, the semiconductor is likely to be As terminated. At variance with previous first-principles work, we do not aim at a detailed modeling of the real interface; instead, we concentrate on a reference system as simple as possible, so as to evidentiate the leading effects induced by controlled variations of the interface morphology. We assume therefore a defect-free epitaxial geometry as a working hypothesis. On the same ground, we study here an ideal unstrained interface where the metal is a fictitious Al, perfectly lattice matched to GaAs, and hence retaining its cubic structure in the epitaxial overlayer. Strain effects, although quantitatively sizeable, are considered spurious in the present analysis (see, however, some considerations below).

The interfaces are modeled with periodically repeated supercells. The results for our (001) interface are obtained with a supercell where the semiconductor slab is chosen with double As termination, thus containing two equivalent junctions. In this geometry the metal and the semiconductor cubic axes are rotated by 45° around the growth direction, and the lattice-matching condition sets the ratio of the two cubic lattice constants equal to $1/\sqrt{2}$. A typical supercell, such as that used for the calculation shown in Fig. 1, contains 9 Al

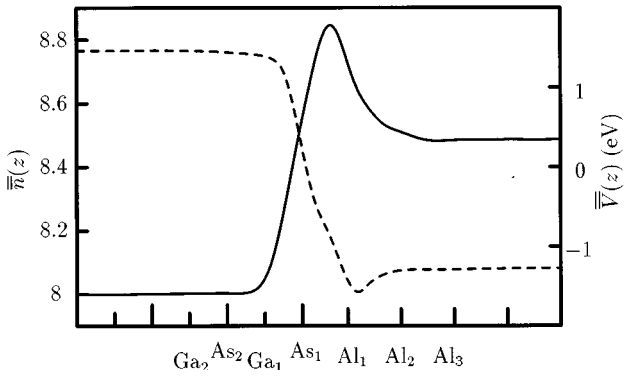

FIG. 1. One-half of the 31-atoms computational supercell modeling the (001) interface: in abscissa we have the z coordinate normal to the interface. The positions of the atomic layers are shown using vertical bars of different length: the labels identify the layers closest to the junction. The functions displayed are the macroscopic averages—defined as in Ref. 8—of the electronic density (solid line, scale at the left), and of the total electrostatic potential (dashed line, scale at the right).

layers, 6 Ga layers, and 7 As layers, for a total of 31 atoms (there are two Al atoms per layer). We focus on the barrier between the GaAs valence-band edge and the Al Fermi level, relevant for hole carriers and hence indicated as Φ_p. As usual,[11] the barrier height can be partitioned into two contributions: the electrostatic *potential lineup* across the interface ΔV, and the *band-structure term* ΔE_p. The latter is the difference between the Fermi energy of the metal and the valence-band edge of the semiconductor, each measured with respect to the average of the electrostatic potential of the corresponding crystal. The potential lineup is an interface-specific property and therefore must be extracted from supercell calculations; the band-structure term is the difference between bulk properties of the two constituents, and hence it is obtained from independent calculations for crystalline GaAs and Al. The calculations have been performed within density-functional theory in the local-density approximation, using pseudopotentials[12] and plane waves (with a kinetic-energy cutoff of 18 Ry); reciprocal space integrations are performed on a Monkhorst-Pack special-point grid,[13] using the smearing technique of Ref. 14 (see also Ref. 15). The 31-atom supercell calculations are well converged using a (10,10,2) grid and a smearing parameter $\sigma = 0.01$ Ry.

Typical results are shown in Fig. 1. The solid line is the macroscopic average[11] of the electron density, in units of (valence) electrons per semiconductor cell. In these units the bulk density of the semiconductor is 8, whereas the one of the bulk Al reaches the value of 8.485, which is 6 (number of electrons in one periodicity of Al) times $\sqrt{2}$ (ratio between the periodicity in the GaAs region and the one in the Al region). Because of symmetry, we show only one half of the supercell. It is easily realized that the actual density reaches its bulk value very close to the junction, thus showing that the supercell is large enough to model the isolated (and neutral) interface. Solution of the Poisson equation for the *total* charge (electronic and ionic) yields the macroscopic average of the electrostatic potential, shown in the same figure as a dashed line. The lineup between the plateaus in the two bulks coincides with the ΔV discussed above: its value for this calculation is 2.74 eV. Two independent self-consistent calculations for the individual bulks are then performed: we find that the electrostatic-potential average is 8.65 eV below the Fermi level in bulk Al, while it is 5.17 eV below the valence-band top in bulk GaAs. Putting these three figures together, we get the value $\Phi_p = 0.74$ eV for the Schottky barrier at our ideal junction between GaAs and fake Al. When we compare different (001) calculations among themselves, as extensively done below, our estimated numerical accuracy for Φ_p is 0.01 eV: we stress that this is a *relative* accuracy for a given set of technical ingredients. We now investigate how our calculated value of Φ_p depends on different perturbations which alter the interface morphology.

First of all we insert a thick layer of vacuum between the metal and the semiconductor: the calculated value of the barrier becomes thus equal to the difference between the work functions of the metal and of the semiconductor. Technically, we perform the calculation in the same geometry as in Fig. 1, but *removing* the Ga_1 and As_1 layers. We find in this way a barrier of -0.24 eV, very much different from the previously calculated value of $\Phi_p = 0.74$ eV. This result provides further evidence (if any was needed) that the early Mott-Schottky model—where the identity of the two quantities was postulated—is invalid.

We consider then a very *thin* layer of vacuum: instead of breaking the Al–As bond, we gently elongate it while keeping the rest of the structure rigid (the length of the supercell is elongated accordingly). Such a displacement is commonly referred to as *interfacial strain*. The Schottky barrier is found to depend very weakly upon interfacial strain: it takes in fact a strain as large as 3% in order to vary Φ_p by 0.01 eV, our estimated numerical accuracy. With the (enormous) value of 10%, Φ_p varies by about 0.04 eV.

Next we perform an analogous 10% elongation, but on the Ga–As bond nearest to the interface: we get in this case the much larger variation of 0.09 eV. We give below a simple rationale for such a different dependence of Φ_p on different local strains: we will see that the dynamical charges of interface ions play a major role.

The next step is to consider the effect of *bulk* strain on the metal side. Of course in the epitaxial geometry only uniaxial tetragonal strain is allowed, where the Al lattice constant along the growth axis is elongated by a factor $1+\epsilon$. The calculated Φ_p is completely insensitive to ϵ: a calculation performed for $\epsilon = 0.01$ gives a Φ_p variation of 0.01 eV. The ϵ value of 1% corresponds to the actual mismatch-induced relaxation of an epitaxial Al slab (when we choose the Al bulk equilibrium lattice constant equal to the theoretical one). This finding is rather unexpected, since—according to previous theoretical work—the barrier for a given semiconductor seems to vary with the nature of the metal.[4] Instead we find that the barrier is unchanged in the special case considered, namely two metals having the same chemical composition but different lattice parameters, hence different electronic densities.

We elaborate a little bit more about these findings, which give insight into the robustness of Φ_p and shed some light on the very important—although disturbingly vague—concept that the barrier is formed extremely close to the semiconductor.[1] Imagine an ideal double interface, where the semiconductor is joined to a first metal, and then the first

metal is joined to a second metal. The barrier forms at the semiconductor/metal interface, and then—if the middle slab is thick enough—remains constant through the second interface, since the Fermi level is aligned across any metal/metal contact. This *transitivity rule* is not expected to hold when the thickness of the middle slab is reduced. Instead, in our case study a macroscopic slab is not needed—not even a microscopic one—in order for the barrier to be robustly established. As a double check of our transitivity finding, we scrutinize the two contributions ΔV and ΔE_p separately: while their sum turns out to be ϵ independent, their individual variation is sizable. With the above value of $\epsilon=0.01$, the calculated ΔE_p varies by -0.10 eV: we wish to compare this to the ΔV value at an ideal strained/unstrained metal homojunction. To this aim, a supercell calculation is unnecessary: ΔV is a pure volume effect, and we get it by calculating the deformation potential[16] of bulk Al, i.e., the linear variation of the Fermi energy, measured with respect to the average of the electrostatic potential. We find in this way $\Delta V=-0.11$ eV, in very good agreement with the above value.

The next probe we are going to use in order to test the robustness of the barrier height, is the displacement of individual atoms, while the rest of the structure is kept fixed. The basic quantities measuring the response of the electronic system to such perturbations are the effective charges for lattice dynamics. Consider a displacement of an ionic plane in the bulk semiconductor by an amount u: this creates a dipole per unit area, inducing a potential lineup of $\Delta V=8\pi e^2 Z_T^* u/(\varepsilon_\infty a^2)$, where a is the cubic lattice constant, ε_∞ is the dielectric constant, and Z_T^* is the Born (alias transverse) dynamical charge of the given ionic species.[17] Given the composite nature of our heterostructure, it proves better to deal with Z_T^* and ε_∞ altogether: we focus then on the *longitudinal* dynamical charges $Z^*=Z_T^*/\varepsilon_\infty$. The bulk GaAs value appropriate to our computational framework is $Z^*=\pm 0.18$, while in any bulk metal Z^* vanishes due to perfect screening.[18] The calculation of the dynamical effective charges of the different ions across the junction gives a way to monitor the transition between the two bulk materials and provides a very meaningful measure of the interface thickness. In fact, a structural distortion may affect (to linear order) the electrostatic lineup—and hence the barrier Φ_p—only if it displaces ions whose Z^* is nonvanishing.

Our calculations follow Ref. 17, with a typical u value of 0.03 a.u.; a conservative estimate[18] of the numerical accuracy of our Z^*'s is 0.01. When approaching the interface from the semiconductor side, our calculated Z^* values are: $+0.18$ (Ga_2), -0.15 (As_2), $+0.14$ (Ga_1), -0.07 (As_1). Entering into the metal, the calculated Z^* drop rapidly to their (vanishing) bulk value. Since there are two nonequivalent Al atoms per plane, we displace each of them at a time. We get ± 0.01 for Al_1, and -0.01, $+0.02$ for the Al_2 atoms. These figures (also shown in Fig. 2) have been rounded to 0.01: their apparent differences being of the order of our numerical accuracy. One important message emerging from our calculated Z^*'s is that—as far as the dynamical charges are concerned—the interface is very sharp on the metal side, while instead a semiconductor ion ''feels'' the presence of the metal up to a depth of a few layers: the closest cation

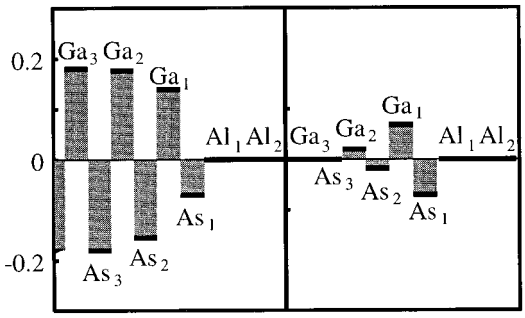

FIG. 2. The left panel shows the calculated dynamical charges in the form of a hystogram; the darkest regions indicate our numerical accuracy in the calculation. The right panel is the macroscopic average of the left one: it shows the averages of the Z^*'s over a segment, centered at a running point, and whose length equals the periodicity of the bulk semiconductor region. The plot illustrates the dynamical neutrality of the interface, and also shows that the interface region is more extended on the semiconductor side than on the metal one.

(Ga_1) is already strongly ''nonmetallic,'' though not yet bulklike. Although Z^* is a *linear* property of lattice distortions, our calculations indicate that a structural defect on the metal side—even very close to the junction—would have a little effect on Φ_p; while on the contrary a defect on the semiconductor side is likely to have a sizeable effect. Of particular importance to the barrier height are therefore the detailed arrangements of the semiconductor atoms closest to the metal (given that noncentrosymmetric structural defects deep in the semiconductor can be ruled out). This sensitivity of the barrier height to the morphology of the first few semiconductor layers is in qualitative agreement with the findings of other authors,[4,6,9] who have considered chemical defects in an otherwise undistorted structure.

We have recently discovered a novel sum rule for the dynamical charges at the surface of a semi-infinite crystal,[19] which is easily generalized to the case of an interface between a pair of semi-infinite crystals. The present (001) geometry is a particularly simple example, where the meaning of our sum rule can be made clear without any formal derivations. We first observe that the usual acoustic sum rule[20] (ASR) requires the sum of all Z^* in the supercell to vanish: in fact, our calculations comply with ASR within a few times 0.01. The sum rule can be interpreted as a ''dynamical neutrality'' of the supercell as a whole: since our supercell contains two equivalent interfaces, the ASR obviously implies the dynamical neutrality of each of them separately. We may assume each of the interface regions to be one half of the supercell, and clearly the sum of the Z^* vanish in each of them. The key point is that our semiconductor slab has n cations and $n+1$ anions ($n=6$ in the actual calculation), and therefore the central anion must be reckoned with weight *one half* in summing the dynamical charges of each interface. One arrrives therefore at the important conclusion—which applies in general to any *isolated* (001) metal/semiconductor interface—that the sum of the dynamical charges Z^* in the interface region equals *one-half* the bulk dynamical charge of the semiconductor (with the appropriate sign). As a corollary, the semiconductor ions in the interface region *cannot* have the same dynamical charges as in the bulk. All this is in

perfect agreement with our computational findings.

The dynamical charges are very closely related to the lineup induced (to linear order) by interface strain, as first shown in Ref. 21 for the similar case of a semiconductor-semiconductor heterojunction. In the present case we have independently calculated the effect of interface strain (see above) and found that it is very small. More precisely, we find zero Φ_p variation (within our computational tolerance) when the bond-length elongation is comparable to the one used in calculating the Z^*'s. The explanation for this finding lies in the fact that all the dynamical charges on the metal side are extremely small. Let us think of an isolated junction between two semi-infinite bulks: the interface strain amounts to a rigid relative translation. Suppose first that the semiconductor is kept fixed, and that the metal is displaced: by linearity, the lineup induced by the displacement of the semi-infinite metal is the sum of the lineups induced by the displacement of individual metal planes, and this sum is close to zero using our calculated Z^* values. We wish to recover an identical result when we keep the metal fixed, and we displace the semiconductor instead: this looks less trivial, since the dynamical charges oscillate indefinitely in the semiconductor bulk. We have shown in Ref. 19 how to regularize such an indeterminate sum using the appropriate physical criterion: to the present purposes, it suffices to say that the dynamical neutrality of the interface, discussed above, is the crucial property ensuring the correct result.

In conclusion, we have shown that the dynamical effective charges Z^* in the interface region are the key quantity for rationalizing morphology-induced variations of the Schottky barrier. A detailed study of these charges show which distortions affect (or do not affect) the barrier height. Actual calculations performed for As-terminated Al/GaAs(001) show that the semiconductor Z^* converge to their bulk value rather slowly: the actual thickness of the interface region, when monitored by means of Z^*, is definitely larger than an analysis of the mere static electronic charge would suggest. Finally, owing to our sum rule,[19] the sum of all Z^* in the interface region equals one half the bulk Z^* value.

We thank S. de Gironcoli for several illuminating discussions and for invaluable technical help. We also thank A. Baldereschi and N. Binggeli for providing copies of their papers before publication and for useful discussions. We acknowledge the ''Iniziativa Calcolo Parallelo'' of INFM.

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