Pressure and alloy-composition dependence of Al/$Ga_{1-x}Al_xAs$ (100) Schottky barriers

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The dependence on hydrostatic pressure and alloy composition of the Schottky-barrier height at ideal, defect-free, Al/$Ga_{1-x}Al_xAs$ (100) junctions is investigated by means of an *ab initio* pseudopotential approach. The results reproduce closely the experimental data and, in contrast to recent proposals, demonstrate that the barrier heights can be explained without invoking interface defects. The alloy-composition dependence is understood by extending to metal/semiconductor contacts the linear-response-theory approach currently used for semiconductor heterojunctions. The pressure variation of the barriers can be obtained from the $Ga_{1-x}Al_xAs$ band-edge deformation potentials. [S0163-1829(96)52140-5]

The barrier height of metal contacts to covalent semiconductors shows a much stronger dependence on the semiconductor material than on the metal in junctions of practical interest.[1] Various models have been proposed to explain the pinning of the Fermi level which gives rise to the Schottky barrier. One class of models attributes it to intrinsic metal-induced gap states (MIGS),[2] and relates the pinning energy to a charge neutrality level.[3,4] Conversely, a second class of models associates the pinning with extrinsic gap states arising from defects near the interface.[5,6] In the specific case of contacts to GaAs, various native defects ranging from vacancies to antisites and to more complex defects such as EL2 have been invoked. It has been suggested that comparing the hydrostatic pressure dependence of the barrier height with that of extrinsic levels in the gap may help in identifying the defects responsible for the Fermi level pinning.[7]

Recent measurements[8] on epitaxial Al/$Ga_{1-x}Al_xAs$ (100) have shown that the pressure dependence of the p-type barrier, ϕ_p, is negligibly small and that of the n-type barrier, ϕ_n, coincides with that of the semiconductor band gap for both direct- and indirect-gap $Ga_{1-x}Al_xAs$. Based on qualitative arguments on the pressure dependence of the neutrality level, these results were interpreted as being in conflict with intrinsic pinning mechanisms, and as evidence of pinning due to defect states with bonding character[8] — excluding thus common defects such as antisites and EL2 centers. Similar conclusions against MIGS-related mechanisms had been proposed earlier in studies of the alloy-composition dependence of the Al/$Ga_{1-x}Al_xAs$ (100) Schottky barriers.[9,10]

In this paper, we study the pressure and alloy-composition dependence of Schottky barrier heights at ideal, defect-free, Al/$Ga_{1-x}Al_xAs$ (100) interfaces by means of first-principles pseudopotential calculations. The results show that the measured pressure and alloy-composition dependences of the barriers can be explained without postulating defect pinning mechanisms. The dependence of the Al/$Ga_{1-x}Al_xAs$ Schottky barrier height on concentration x is explained with a linear-response-theory approach in which the Al/$Ga_{1-x}Al_xAs$ interface is looked at as a reference Al/virtual-crystal junction plus a perturbation. The same approach allows us to explain the observed transitivity between the band discontinuities of Al/GaAs, Al/GaAs, and AlAs/GaAs. Finally, the variation of the barrier with pressure is interpreted in terms of the deformation potential of the semiconductor.

The *ab initio* calculations have been performed within the local-density-functional (LDF) framework using Troullier-Martins pseudopotentials and a plane-wave basis set.[11] $Ga_{1-x}Al_xAs$ alloys were dealt with using the virtual-crystal approximation. The isolated Al/$Ga_{1-x}Al_xAs$ (100) interface was modeled with supercells containing 13 $Ga_{1-x}Al_xAs$ (100) planes with As termination and 7 Al (100) planes. The Al fcc lattice was rotated 45° about the [100] axis relative to the semiconductor in order to satisfy epitaxial relations.[12] To study the effect of pressure we assumed the metallic overlayer to pseudomorphically adjust to the hydrostatic deformation of the semiconductor substrate. The small compressive strain in the Al in-plane lattice constant was accommodated by a tetragonal deformation of the Al overlayer, following macroscopic elasticity theory.[13] Atomic relaxation at the interface was found to affect little ($\sim$30 meV) the Schottky barrier heights, and was neglected.

The barrier height, ϕ_p, can be separated into two contributions: $\phi_p = \Delta E_p + \Delta V$.[12,14] The band-structure term ΔE_p is the difference between the Fermi energy of the metal and the valence-band edge of the semiconductor, each being measured with respect to the average electrostatic potential energy of the corresponding crystal. This term does not depend on the interface, and was determined from standard band-structure calculations for bulk Al and bulk $Ga_{1-x}Al_xAs$ using a kinetic-energy cutoff of 20 Ry and a (12, 12, 12) and (6, 6, 6) Monkhorst-Pack grid for Al and $Ga_{1-x}Al_xAs$, respectively.[15] The second term ΔV is the electrostatic potential-energy lineup across the interface. This term may depend on interface specific features, and was obtained from supercell calculations of the charge density in the Al/$Ga_{1-x}Al_xAs$ (100) junction using the technique of Ref. 14. The supercell calculations were carried out with a plane-wave kinetic-energy cutoff of 16 Ry, a (6, 6, 2) Monkhorst-Pack grid, and a Gaussian broadening scheme with a 0.1 eV full width at half maximum.[16] The resulting numerical convergence on ϕ_p is estimated as $\sim$20 meV.

In Fig. 1, we present the calculated dependence on concentration x of the p-type Al/$Ga_{1-x}Al_xAs$ (100) Schottky barrier together with the experimental data.[9,10] The solid line

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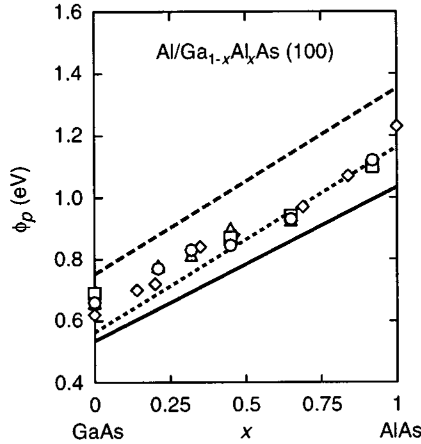

FIG. 1. Composition dependence of the p-type Al/Ga$_{1-x}$Al$_x$As (100) Schottky barrier height obtained from *ab initio* local-density calculations corrected for spin-orbit effects (solid line). The barrier heights including also the many-body corrections are given by the dashed and the dotted lines (GaAs many-body correction after Ref. 19 and Ref. 20, respectively). The symbols show the experimental data from Ref. 9 (◇, current/voltage) and Ref. 10 (△, current/voltage; ○, capacitance/voltage; □, internal photoemission).

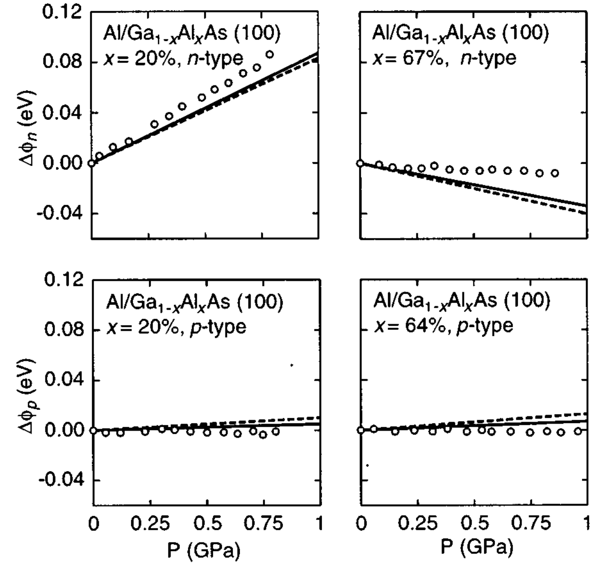

FIG. 2. Pressure dependence of the n- and p-type Al/Ga$_{1-x}$Al$_x$As (100) Schottky barriers for $x=0.20$ and $x\approx0.65$. The results of the *ab initio* supercell calculations (solid lines) are compared with the experimental data (○) of Ref. 8 and with the values obtained from the deformation potentials of the semiconductor (dashed lines).

shows the barriers obtained from the LDF calculations and corrected for spin-orbit effects.[17,18] Many-body corrections of bulk band-structure energies of Al, GaAs, and AlAs have been evaluated in Refs. 19 and 20. The correction for the Al Fermi level is $\Delta E_F^{(\mathrm{Al})}=-0.14$ eV.[19] Two values have been reported for the GaAs valence-band-edge correction: $\Delta E_v^{(\mathrm{GaAs})}=-0.36$ eV (Ref. 19) and -0.17 eV (Ref. 20). The commonly accepted value of the many-body correction for the AlAs/GaAs valence-band offset (VBO) is $\Delta E_v^{(\mathrm{GaAs})}-\Delta E_v^{(\mathrm{AlAs})}\simeq0.1$ eV.[20] Using these corrections, we obtain the two concentration dependences of ϕ_p indicated by the dashed and the dotted lines in Fig. 1, corresponding to the two reported values of $\Delta E_v^{(\mathrm{GaAs})}$.

Taking into account an estimated[19] uncertainty of ~0.1 eV on the theoretical barrier heights including many-body corrections, good general agreement is found between the calculated and measured ϕ_p. In particular, the theoretical slope agrees well with experiment. The LDF calculations slightly underestimate ϕ_p, and many-body effects tend to correct or even over-correct this trend. Since many-body corrections apply to bulk values, they do not affect the transitivity between the Al/GaAs, GaAs/AlAs, and Al/AlAs band discontinuities which, according to our results, is verified within 0.03 eV (i.e., ~ our numerical accuracy): we find VBO(AlAs/GaAs) = 0.48 eV, and $\phi_p^{(\mathrm{AlAs})}-\phi_p^{(\mathrm{GaAs})}=0.45$ eV. The transitivity is also verified experimentally, within experimental uncertainty: the measured values for $\phi_p^{(\mathrm{AlAs})}-\phi_p^{(\mathrm{GaAs})}$ range from 0.45 to 0.6 eV, and those for the VBO(AlAs/GaAs) range from 0.45 to 0.55 eV.[21]

In Fig. 2, we compare the calculated pressure dependence[22] of ϕ_p and ϕ_n to recent experimental data for contacts to p- and n-type Ga$_{1-x}$Al$_x$As samples with both direct and indirect gap.[8] The sum of the experimental p- and n-type barriers yields the experimental band gap, consistently with a unique Fermi level pinning position. Excellent agreement is found between the calculated and experimental p-type barrier heights, which show a negligible pressure variation compared to that of the n-type barriers. The LDF pressure dependences of ϕ_p and ΔV are 9 (11) meV/GPa and 16 (7) meV/GPa for Al/GaAs (Al/AlAs), respectively. The pressure variation of the n-type barriers is calculated by subtracting the pressure variation of ϕ_p from the LDF pressure variation of the energy gap calculated as $dE_{\Gamma-\Gamma}/dP=+97$ $(+103)$ meV/GPa and $dE_{\Gamma-X}/dP=-23$ (-21) meV/GPa for GaAs (AlAs). Both the experimental and the theoretical values of $\Delta\phi_n$ follow the corresponding pressure dependence of the band gap. The difference between them (i.e., ~20 meV/GPa) corresponds to the LDF error on the pressure dependence of the gap, whose experimental values are $dE_{\Gamma-\Gamma}/dP=+107$ $(+80)$ meV/GPa, $dE_{\Gamma-X}/dP=-13$ (-17) meV/GPa for GaAs (AlAs).[23] Our results thus show that the negligible pressure dependence of ϕ_p is an intrinsic property of the Al/Ga$_{1-x}$Al$_x$As interface, and cannot be used as evidence of the bonding character of the defects responsible for Fermi level pinning.

In the case of semiconductor heterojunctions, an approach based on linear-response theory has been used to demonstrate that the band offset in isovalent junctions such as GaAs/AlAs is determined only by the bulk properties of the two semiconductors.[14] The variation with alloy composition of the Al/Ga$_{1-x}$Al$_x$As Schottky barrier and the transitivity between the Al/GaAs, GaAs/AlAs, and Al/AlAs band discontinuities can be explained in a similar way. Within the linear-response-theory approach,[14] the GaAs/AlAs interface is considered as a perturbation of a reference virtual Ga$_{1/2}$Al$_{1/2}$As crystal, and the GaAs/AlAs potential lineup ΔV(GaAs/AlAs) derives from the charge density $\Delta n(z)$ induced by replacing a single plane of virtual

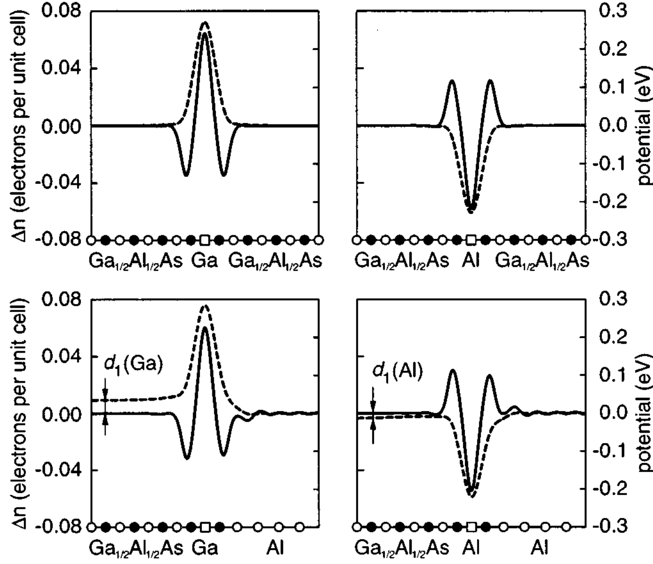

FIG. 3. Upper panels: macroscopic average of the charge (solid line) and potential (dashed line) induced in the bulk reference semiconductor $Al_{1/2}Ga_{1/2}As$ when an isolated $Al_{1/2}Ga_{1/2}$ (100) monolayer is replaced with a Ga (left) or an Al (right) monolayer. Lower panels: macroscopic charge and potential responses when the same substitutions are performed on the cation monolayer which is closest to the junction in Al/$Al_{1/2}Ga_{1/2}As$ (100). The dipolar potential lineups $d_1(\mathrm{Ga}) = -0.03$ eV and $d_1(\mathrm{Al}) = +0.01$ eV are also indicated.

$Ga_{1/2}Al_{1/2}$ cations with real Ga (Al) ions, through $\Delta V(\mathrm{GaAs/AlAs}) = -4\pi e^2(A_{\mathrm{Al}} - A_{\mathrm{Ga}})/L$, where $A = \frac{1}{2}\int z^2 \Delta n(z) dz$ and L is the distance between consecutive cation planes. The charge profiles $\Delta n(z)$ and the corresponding potential profiles are illustrated in Fig. 3 (upper panels).

Similarly, starting from a reference Al/$Ga_{1/2}Al_{1/2}As$ (100) junction, one may obtain the Al/GaAs (100) or Al/AlAs (100) systems by replacing the virtual cation planes in the semiinfinite semiconductor region with real Ga (or Al) planes. Assuming that the response of the reference Al/$Ga_{1/2}Al_{1/2}As$ junction is the same as that of the virtual $Ga_{1/2}Al_{1/2}As$ crystal, a linear superposition of the responses Δn (Fig. 3, upper panel) in the semiinfinite semiconductor region would induce a potential lineup $\Delta V(\mathrm{Al}/X\mathrm{As}) = -4\pi e^2 A_X/L$ (X=Al, Ga) across the junction, which is a bulk quantity and verifies the transitivity rule.

The response $\Delta n_i'(z)$ of the reference Al/$Ga_{1/2}Al_{1/2}As$ (100) junction to the substitution of the ith cation-plane from the interface coincides with $\Delta n(z)$ for large i. In Fig. 3 (lower panel) we show the response $\Delta n_1'(z)$ calculated with a supercell containing 21 planes of semiconductor and 7 planes of Al. Inspection of the figure shows that even $\Delta n_1'(z)$ is similar to $\Delta n(z)$ except for the presence of a dipolar asymmetry due to the proximity of the metal. The deviation from the transitivity rule is given, for a linear superposition of the $\Delta n_i'$, by the sum of the dipoles d_i corresponding to the asymmetry in $\Delta n_i'(z)$ whose values for Ga (Al) substitutions are, in eV, $d_1 = -0.03$ (0.01), $d_2 = +0.02$ (-0.03), $d_3 = +0.01$ (0.00) and $d_i \simeq 0$ for $i > 3$. The violation of the transitivity rule obtained in this way is $[\phi_p(\mathrm{Al/GaAs}) - \phi_p(\mathrm{Al/AlAs})] - \mathrm{VBO(GaAs/AlAs)} \simeq 0.02$ eV which agrees with the value 0.03 eV obtained from *ab initio* supercell calculations.

Also the pressure variation of the Al/$Ga_{1-x}Al_xAs$ Schottky barriers can be related to semiconductor bulk properties. The relevant bulk quantity in this case is the deformation potential of the appropriate semiconductor band edge (the deformation potential of the metal Fermi level being zero). We focus here on the energy E_v of the upper three valence bands of the semiconductor at Γ and on the corresponding hydrostatic deformation potential $a_v = dE_v / d\ln\Omega$, where Ω is the volume.[24] The deformation potential of the topmost Γ_8 valence bands can be obtained by adding to a_v the pressure-dependent spin-orbit corrections determined from experiment.[22]

The hydrostatic deformation potential a_v is equal to the average uniaxial deformation potential in the (100) direction $dE_{v,\mathrm{av}}/d\epsilon_{xx}$, where $E_{v,\mathrm{av}}$ is the average energy of the upper three valence bands at Γ, and can thus be computed at a strained-unstrained homojunction.[24] For a given uniaxial strain, the deformation potential in a nonpolar and nonpiezoelectric solid has been shown to be a bulk property which is related to the third linear moment of the charge induced by a single-plane displacement.[25] The $Ga_{1-x}Al_xAs$ (100) surfaces are polar, and the deformation potentials depend on the details of the surface geometry because of the presence of nonvanishing Born effective charges.[25] A procedure to obtain a bulk deformation potential which is free from effective-charge effects is to average the deformation potentials computed for two strained-unstrained homojunctions with interchanged cations and anions. With this procedure, and using a supercell containing 16 atomic planes (8 strained plus 8 unstrained), we obtain: $a_v^{(\mathrm{GaAs})} = 1.1$ eV and $a_v^{(\mathrm{AlAs})} = 1.5$ eV. We checked that one obtains the same values by averaging the third linear moments of the charges induced by a single-anion and a single-cation plane displacement. These results are in order-of-magnitude agreement with those calculated using a superposition of neutral atomic charges, $a_v^{(\mathrm{GaAs})} = 1.16$ eV and $a_v^{(\mathrm{AlAs})} = 2.47$ eV, and with experimental estimates.[24]

In Fig. 2, we compare the pressure dependences of ϕ_p and ϕ_n predicted by the hydrostatic deformation potential[22] of $Ga_{1-x}Al_xAs$ with the results obtained from the supercell calculations. The agreement is excellent, and we conclude that the observed negligible pressure variations of ϕ_p are simply due to the small value of the valence-band-edge deformation potential of $Ga_{1-x}Al_xAs$. Furthermore, using our values of the deformation potentials of GaAs, we find a +83 meV/GPa pressure variation of the Al/GaAs (110) n-type barrier. This value compares well with the recently measured value of +105 meV/GPa,[26] if one takes into account that the LDF pressure coefficient of the GaAs energy gap is 10 meV/GPa smaller than the experimental data.

In conclusion, our *ab initio* results show that the experimental pressure and alloy-composition dependences of the Al/$Ga_{1-x}Al_xAs$ (100) barriers can be fully explained without postulating a major role of defect-induced Fermi level pinning. Furthermore, we interpreted the pressure and alloy-composition variations of the barriers in terms of bulk prop-

erties of the semiconductor. Since we considered ideally abrupt interfaces, with no extensive reaction products, we would like to caution the reader that our conclusions for Al/$Ga_{1-x}Al_xAs$ (100) may not apply to other, more complex, metal/semiconductor interfaces.

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