PHYSICAL REVIEW B VOLUME 41, NUMBER 5 15 FEBRUARY 1990-I

Modification of heterojunction band offsets by thin layers at interfaces: Role of the interface dipole

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(Received 5 September 1989)

We have carried out *ab initio* self-consistent calculations to investigate the extent to which the band offset can be modified by polar layers. The cases studied are double layers of Ge in bulk GaAs (for which the offsets are totally due to induced dipoles) in (100) and two distinctly different (111) geometries. The (111) double layer with the maximum number of Ge—Ge bonds is found to be energetically the most stable and to have the smallest dipole, but it is still large (0.7 eV) compared to typical band offsets in semiconductors. We argue that this demonstrates the potential possibility of providing a mechanism for band-offset engineering using thin layers at interfaces.

I. INTRODUCTION

The interfaces between different semiconductor materials have been extensively studied both experimentally[1] and theoretically[2,3] over the past quarter of a century. This effort was clearly justified because of the importance of these heterojunctions in many novel solid-state devices. In the past ten years progress in heterojunctions research has provided new growth techniques based on molecular-beam epitaxy (MBE) and metallo-organic chemical vapor deposition (MOCVD),[4] and many new classes of materials have been developed,[5] such as superlattices, graded-composition structures, staircases, etc.

The heterojunction band discontinuities are key design parameters of these devices because the valence- and conduction-band offsets, ΔE_v and ΔE_c, determine the transport and confinement properties at the interface. The possible control of the band discontinuity has become a fundamental objective for technology and basic research. Recently two series of experiments established that band lineups can indeed be modified and potentially controlled. As a result of this, the concept of band-offset engineering has gradually emerged.[6] One mechanism proposed by Capasso *et al.*[7] suggests the possible modification of band offsets using doping interface dipoles (DID). The other one proposed by Margaritondo *et al.*[8] is based on the deposition of ultrathin interlayers between the two semiconductors which modifies the charge distribution creating an interface dipole.

In this paper we study the theoretical possibility of band-offset engineering in semiconductor heterostructures. We investigate the atomic scale control of the interface composition and the resulting changes in the electronic properties. There are mainly two effects that may be used to explain the control of the band discontinuities: (i) the electrostatic interface potential resulting from dipoles at the interface, and (ii) the effect of strain at the interface. The latter has been studied with *ab initio* self-consistent calculations by Van de Walle and Martin,[9,10] who showed that the offset depended significantly on Si-Ge strained interfaces. We will concentrate on the first effect of the interface dipole. Recently Christensen[11] using the linearized muffin-tin-orbital (LMTO) method studied a similar problem with nonpolar (110) interfaces showing that, except in two extreme cases, the dipole contribution to the band offset was unimportant. The same result was obtained by Muñoz *et al.*[12,13] in a more simplified self-consistent tight-binding (SCTB) calculation. In a recent paper, Martin[14] suggested that the most likely place to search for changes in the offset is the polar interfaces. We will concentrate our efforts on polar and lattice-matched interfaces.

We will report results for a double layer of Ge in bulk GaAs, which is an example of a thin layer at an *A*/*B* interface where, in this special case, materials *A* and *B* are both GaAs. Any offset between the two regions of GaAs across the interlayer will be due solely to the change in the stoichiometry at the interface. This idea can be applied to a general *A*/*B* interface, but extracting the same information would be more difficult. These materials are important from both a theoretical and an experimental point of view: (i) both GaAs and Ge are of technological importance in electronic devices, (ii) GaAs/Ge polar interfaces are the prototype examples of heterojunctions between III-V and IV compounds[1] and we can expect important dipole effects, (iii) due to the similar crystal structure and lattice matching with $a_0 = 5.65$ Å, we can study more carefully the effect of geometry and composition at the interface (lattice mismatch could give other effects but we wish to study the simplest case), (iv) from our results we can obtain theoretical information about the more stable structures, so we can predict the possibility of making these heterojunctions, and (v) this example may be of interest in itself since quantum wells in GaAs with ultrathin layers could be technologically important.

The GaAs/Ge polar interfaces have been studied by many authors[4-24] with variations in the dipole (up to ~ 1 eV for the abrupt junction) showing that polar interfaces can produce changes in the offset. In Refs. 21 and 24 ideal metallic interfaces were considered, whereas in Refs. 17 and 18 and later in Refs. 15, 19, and 20 it was argued that insulating interfaces with mixed stoichiometries should be more stable.

In a simple picture due to Harrison[17] the double layer of Ge in GaAs may be thought of as arising from the transfer of protons from a layer of As atoms to an adjacent layer of Ga atoms at the interface in bulk GaAs. For polar cases this double layer permits the possibility of producing a dipole in a natural way. The Ge atoms in Fig. 1 are clearly inequivalent to each other and the net effect is to produce a dipole sheet in bulk GaAs. This establishes the fact that such interfaces should produce dipoles, but the magnitude of the dipole may not be quantitative and this model does not address the energy to create such interfaces.

In Sec. II we describe the problem and the method of calculation. In Sec. III we report results for the three interfaces that we studied, and in Sec. IV we present our conclusions.

II. METHOD

We assume an ideal crystal form with abrupt changes in the chemistry at the interface and we consider the polar (100) and (111) orientations. We distinguish between two different (111) interfaces corresponding to a minimum number and a maximum number of Ge—Ge bonds as shown schematically in Fig. 2. These interfaces also correspond, respectively, to a maximum distance of $(\sqrt{3}/4)a_0$ between the Ge planes and a minimum distance of $(\sqrt{3}/4)a_0/3$; we will refer to these as the (111)-far and the (111)-near interfaces.

We employ first-principle total-energy calculations using a norm-conserving, nonlocal Kerker[25] pseudopotential within the local-density approximation (LDA) with the Ceperley-Alder[26] form for the exchange and correlation energies. The double layer of Ge embedded in bulk GaAs reduces the translational symmetry, which is essential for the reciprocal space formulation of the problem. To this end we use a supercell geometry with 12 atoms per unit cell and we apply periodic boundary conditions in the z direction which results in a sawtoothlike potential with the periodicity of superlattice. The Kohn-Sham equations[27] are solved in reciprocal space[28] in a plane-wave basis with kinetic-energy cutoffs of 6 and 12 Ry, ($\sim$500 and $\sim$1300 plane waves, respectively). The Brillouin $\mathbf{k}$ integration is done using the special points technique[29] and convergence is facilitated by utilizing the Broyden[20] scheme.

The final self-consistent potential $V(\mathbf{r})$, which is the sum of the Hartree potential, the exchange-correlation potential, and the $l=2$ local component of the ionic pseudopotential, is plotted in Fig. 3 for the (111)-near configuration for the 12-Ry calculation. The variation of the r-space coordinate is limited to the component perpendicular to the interface, and values of the potential are averaged over the remaining two coordinates, i.e., in the xy plane parallel to the interface

$$V(z)=\frac{1}{Na^2}\int dx\,dy\,V(\mathbf{r})\ .$$

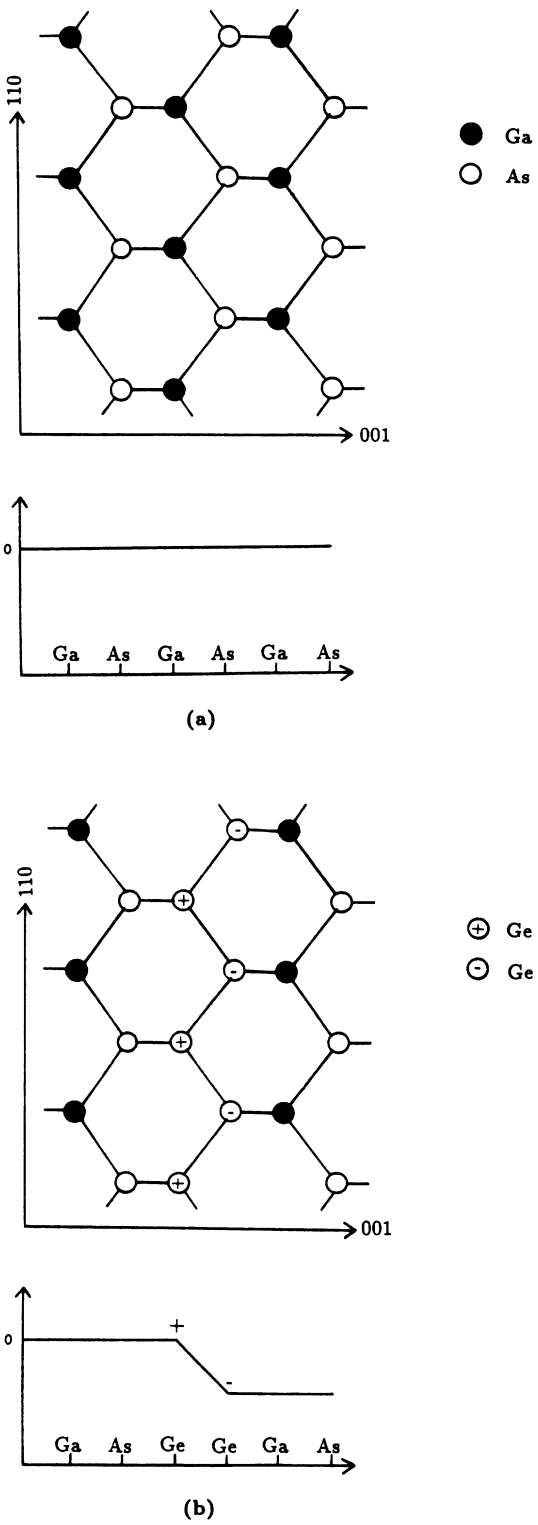

FIG. 1. Schematic representation of Harrison's theoretical alchemy model for the polar (100) direction. (a) The transfer of protons from a layer of As atoms to an adjacent layer of Ga atoms in bulk GaAs results in (b) a double layer of inequivalent Ge atoms. The net effect is to produce a dipole sheet in bulk GaAs. The planar-averaged potential V, which is obtained by integrating the Poisson equation from left to right, shifts across this dipole layer.

From this quantity we find the slowly varying one-dimensional macroscopic average defined by Baldereschi *et al.*[31] for lattice-matched heterojunctions

$$\bar{V}(z)=\frac{1}{\alpha}\int_{z-\alpha/2}^{z+\alpha/2}dz'V(z')\ ,$$

where α is the shortest period defined by the crystal orientation in the z direction. Figure 3 also shows the resulting macroscopic electric fields with microscopic variations at the interface for the (111)-near configuration. The discontinuity of the self-consistent potential across the double layer of Ge is $\Delta\bar{V}$; note that because we have GaAs on both sides of the interface, this dipole is exactly the band offset induced by the thin interlayer of Ge—the relative positions of the valence- and conduction-band edges of GaAs shift by this amount.

We define a similar macroscopic average for the charge density $n(\mathbf{r})$

$$\bar{n}(z)=\frac{1}{\alpha}\int_{z-\alpha/2}^{z+\alpha/2}dz'n(z')\ ,$$

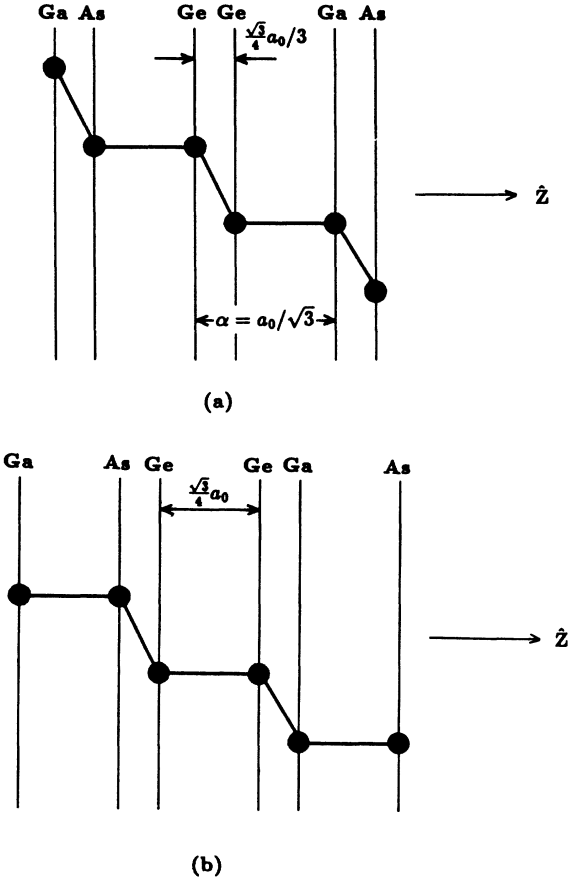

FIG. 2. (a) The (111)-near interlayer with a maximum number of Ge—Ge bonds. The distance between the Ge plane of atoms is $(\sqrt{3}/4)a_0/3$, and $\alpha=a_0/\sqrt{3}$ is the shortest period defined by the (111) orientation. (b) The (111)-far interlayer with a minimum number of Ge—Ge bonds. The distance between the Ge plane of atoms is $(\sqrt{3}/4)a_0$.

where $n(z)$ is the averaged charge density in the xy plane. An inspection of the $\bar{n}(z)$ in Fig. 4 for the (111)-near configuration is representative of our calculations and shows *a posteriori* that the 12-atom unit cell is sufficiently large to attain the bulk properties of GaAs because the charge density $\bar{n}$ is equal to the bulk value of 48 electrons per cell only a few atomic layers away from the interface.

III. RESULTS AND DISCUSSION

The results of our calculations for the 12-atom unit cell are presented in Table I for kinetic-energy cutoffs of 6, 9, and 12 Ry. We use 13 special **k** points for the (111) geometries, and 9 points for the (100) cell. We used the experimental lattice constant of 5.65 Å for both GaAs and Ge so that the atoms are on the sites of an ideal lattice.

The discontinuity in the potential, viz., the dipole, is derived from the one-dimensional macroscopic average of the final self-consistent potential as discussed in the previous section. This potential is comprised of a rapidly varying part due to the dipole at the Ge double layers plus a slowly varying part which is equivalent to an average macroscopic electric field ($\sim 10^8$ V/m). The latter is essential in our superlattice calculations where the potential is required to be periodic. Harrison's[17] theoretical alchemy model for the double interlayer gives the change in the potential as $\Delta V a_0\epsilon/4\pi e=1$, $\frac{1}{3}$, and $\frac{1}{2}$ for the (111) far, (111) near, and (100) interfaces, respectively, where ϵ is the dielectric constant. We see from Table I that these ratios are reasonably satisfied so that Harrison's model provides a good zeroth-order picture. There is a redistribution of the electrons due to the redistribution of the protons so that we may associate an effective charge $q=e/\epsilon$ with the Ge atoms assuming a capacitor model for the double layer. The results for the 12-Ry calculations give an average value of 15.4 for ϵ. Since the actual dielectric constant of GaAs is 10.9, this means that the dipoles are in reasonable quantitative agreement with the simple model.

We consider now the total energy E_{tot} and the formation enthalpy ΔH which is defined as

$$\Delta H=E_{\text{tot}}-(5E_{\text{GaAs}}^{\text{bulk}}+2E_{\text{Ge}}^{\text{bulk}})\ ,$$

where E^{bulk} is the bulk total energy per species. In each case we find the difference in the energies on the right-hand side of the above equation by subtracting energies calculated for exactly the same supercells, number of **k** points, and cutoffs, thus minimizing the errors in the difference. We tested cells of various sizes for the bulk (2–12 atoms per cell) and with different numbers of **k** points, and we conclude that the systematic errors in ΔE are less than 0.05 eV per pair of interlayer atoms. The results show that the energetically most favorable interface corresponds to the Ge interlayer in the (111)-near configuration and it also has the smallest dipole of the three cases. The (111)-far geometry with the largest dipole is least energetically favorable and it has a broken gap, i.e., the dipole is bigger than the gap. There are fewer number of dissimilar bonds (i.e., As—Ge and Ga—Ge) in the (111)-near cell compared with the (111)-

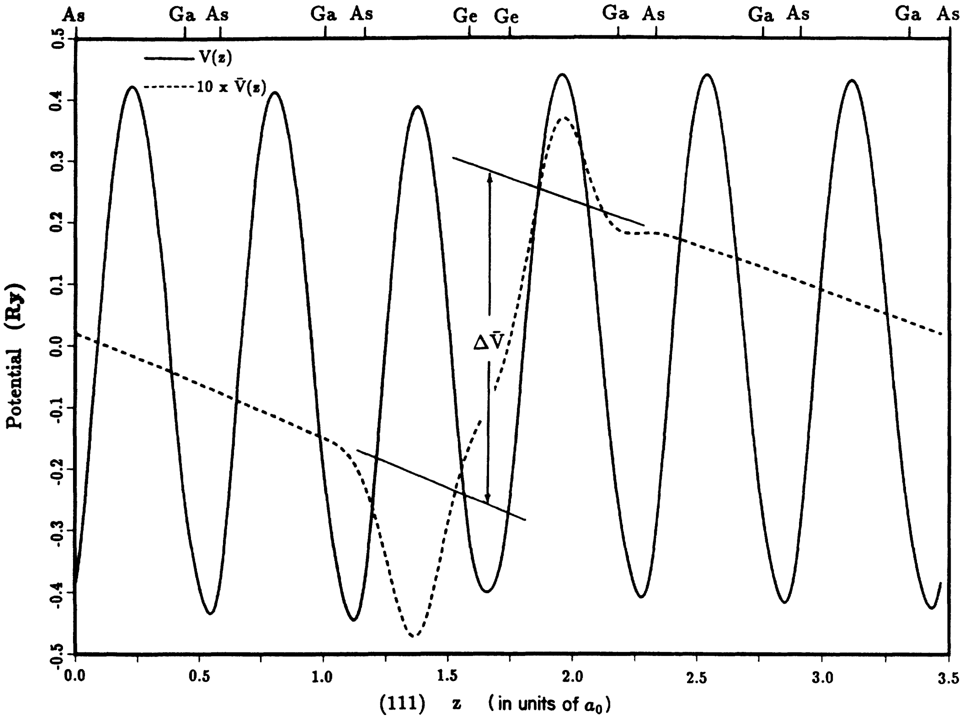

FIG. 3. The planar-averaged self-consistent potential $V(z)$ for the $(GaAs)_5(Ge)_2$ (111)-near case for a 12-Ry calculation. The macroscopic average of the potential $\bar{V}(z)$ shows the macroscopic electric field with microscopic variations at the interface; the discontinuity $\Delta\bar{V}=0.74$ eV across the double layer of Ge is the dipole.

far case; the polarization of the charge is therefore minimized resulting in a smaller dipole. We performed calculations with different kinetic-energy cutoffs and we found that the 12-Ry results were sufficiently converged with an accuracy better than 0.1 eV for the dipole [e.g., for the (100)-near case for cutoffs of 6, 9, and 12 Ry the dipole was found to be 1.13, 0.83, and 0.74 eV, respectively]. We did not carry out the large 12-Ry calculations for the (111)-far supercell because the 6-Ry calculations show that it is the least physically realistic.

The formation enthalpies ΔH for these structures given in Table I are positive but small and, in the case of the (111)-near configuration, only 120 meV per pair of interfaces. This may be compared with the recent work by Bylander and Kleinman,[21] who used a self-consistent relativistic pseudopotential calculation to arrive at a formation enthalpy of 390 meV per cell for the known metastable nonpolar $(GaAs)_3(Ge)_6$ (110) interface, and a smaller result of 236 meV for the (111) polar interface. Their calculations also show huge electric fields ($\sim 10^9$ V/m) for the ideal polar (100) and (111) GaAs/Ge heterojunctions and they argue that the (111) interface is more stable against reconstruction than the (100) case, in agreement with our conclusion that the (111)-near configuration is energetically most stable. It is worthy to note here that in the study of thin overlayers of GaAs on a Si(111) substrate Northrup and coworkers[32] find the lower energy structure to correspond to the GaAs in the "near" configuration in an As terminated surface.

Our results show, assuming an ideal abrupt interface for the polar heterojunctions, that large interface dipoles result (0.7–1.0 eV) compared with the GaAs/Ge

TABLE I. Results for a Ge double layer in GaAs. Calculations are done on a superlattice consisting of $(GaAs)_5Ge_2$ with lattice constant $a_0=5.65$ Å and with kinetic-energy cutoffs of 6, 9, and 12 Ry. E_{tot} is the total energy, ΔH the formation enthalpy, ΔV the dipole, and q the effective charge. The number of **k** points for each calculation is designated by **k** pts. The maximum uncertainties in ΔH and ΔV are 0.05 and 0.1 eV, respectively.

	(111) far	(111) near			(100)	
cutoff (Ry)	6	6	9	12	6	12
k pts	13	13	13	13	4	9
ΔH (eV)	1.61	0.19	0.16	0.12	0.53	0.48
ΔV (eV)	1.97	1.13	0.83	0.74	1.51	0.97
q (e)	0.061	0.105	0.077	0.069	0.094	0.061

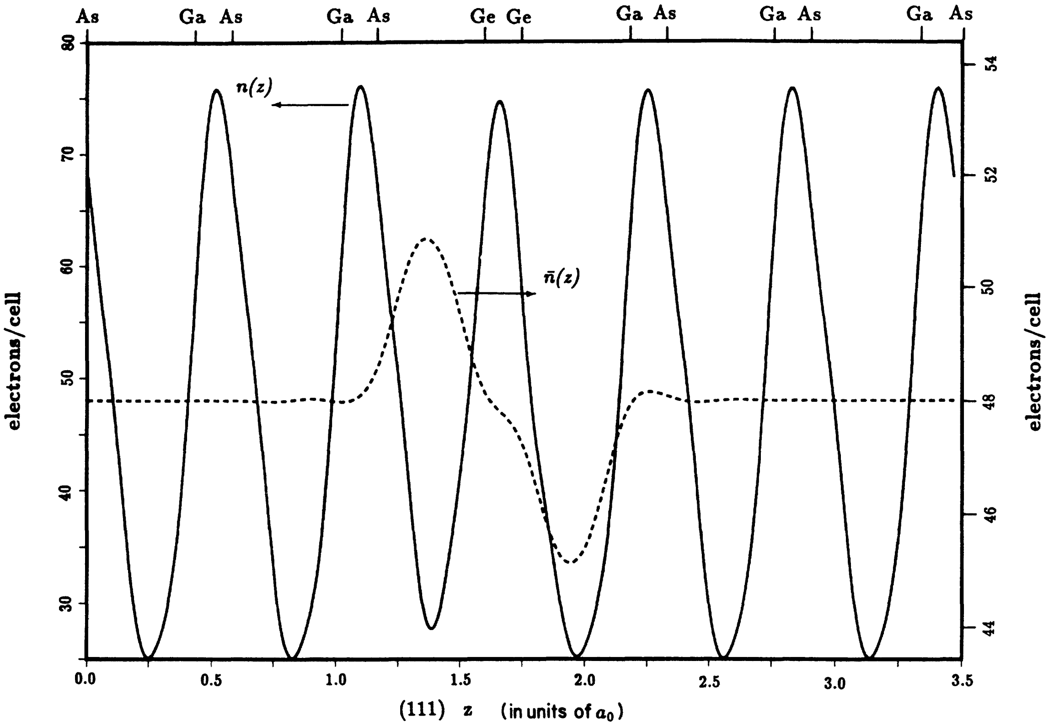

FIG. 4. The planar-averaged self-consistent charge density $n(z)$ for the $(GaAs)_5(Ge)_2$ (111)-near case for a 12-Ry calculation. The macroscopic average $\bar{n}(z)$ converges to the bulk value of 48 electrons per cell only a few atomic layers away from the interface.

valence-band offset of 0.56 eV. Today it is possible to grow high-quality materials using MBE or MOCVD.[1] If these interfaces can be grown, then our results demonstrate the potential possibility of providing a mechanism for band-gap engineering using thin layers at interfaces. Capasso *et al.*[7] have shown that band offsets can be tuned using doping interface sheet dipoles grown by MBE (~50 Å thick). Our work investigates the limit of such dipoles in atomically thin layers. The planes in the [100] direction are equidistant and we therefore expect that positive and negative dipoles would occur with equal probability during the growth process thus averaging the net effect to zero. Our best candidate to experimentally display the orientation dependence of the dipole is the (111)-near interface. For the (111) case there is a difference between the +[111] and −[111] directions; thus the dipole should not be zero by symmetry. Furthermore, the near case has the lowest enthalpy and therefore should be most stable. It is remarkable that the energy is only slightly higher than separated GaAs and Ge. To our knowledge it is the lowest-energy state yet found for GaAs and Ge and opens the possibility that some variation of this state may actually be a new stable compound of Ga, As, and Ge.

Finally, we address the failure of the transitivity rule. There has been a belief in the past that the band offset was a bulk property independent of the orientation and details at the interface. Model calculations all attempted to relate offsets to the intrinsic properties of the two materials.[2] A consequence of this assumption is the transitivity rule which has been established both theoretically and experimentally for the restricted class of lattice-matched nonpolar (110) interfaces. Our results show the breakdown of transitivity for the polar orientations since we have been able to impose a step potential in bulk GaAs with the double layer of Ge. Our work is in agreement with Capasso and others,[7] who noted that dipoles may indeed occur at polar heterojunctions causing orientation-dependent band discontinuities thus invalidating transitivity. Earlier Kunc and Matin[15] had demonstrated interface-specific dipoles for the two different polar (100) interfaces in compensated GaAs/Ge, and on a similar note Van de Walle and Martin[10] showed that strained Si/Ge exhibited orientation-dependent offsets but in their work the dipole remained unchanged. In the same vein Flores *et al.*[22] introduced the concepts of intrinsic and extrinsic charge neutrality levels to study the dependence of the band offset on metal interlayers in semiconductor heterojunctions, and recently Baroni *et al.*[23] using linear-response theory found nonzero dipoles for nonisovalent polar interfaces.

IV. CONCLUSIONS

The present calculations illustrate the possible band discontinuity control by a double layer of Ge embedded in GaAs. Using *ab initio* calculations we analyzed three different polar interlayers for which the band offset is totally due to the dipoles. We found that for these abrupt interfaces large dipoles result (0.7–1.0 eV) with a broken gap situation in the (111)-far case. All cases considered have stoichiometries with no excess electrons or holes. Our total-energy calculations show that the enthalpies of formation of these interfaces are positive but small (few hundreds of meV). Our results also show that the interface dipole has an orientation dependence.

Based upon our results, we propose that thin interlayers can be used for the control of band offsets at interfaces. Of course in real interfaces one can expect some diffusion across the interface and consequently a reduction of the dipole. From this effect we conclude that for the (100) interface the final average dipole could be zero because positive and negative dipoles could occur equally during the growth process. The asymmetric (111)-near configuration has the lowest enthalpy of formation and the smallest dipole, and we argue that even if diffusion reduces the dipole it will still be nonzero by symmetry. We suggest that this configuration is our best candidate for tuning the band offsets. Our results support the idea that control of the interface dipole can provide a mechanism to perform band-offset engineering at a general A/B interface by deposition of thin polar interlayers at the interfaces. Finally we argue that the transitivity rule fails for cases where there are significant changes in the polarity of the interface.

ACKNOWLEDGMENTS

Thanks are due to Karel Kunc, Richard J. Needs, and Ole H. Nielsen, who developed the programs that we have used. We are grateful to James Annett and Giulia Galli for invaluable support, and one of us (A.M.) is indebted to the NATO Scientific Committee for financial aid and to Consejeria de Educacion del Gobierno Autonoma Canario. This work was supported in part by the U.S. Department of Energy under Contract No. DE-AC0276-ER01198.

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