

# Valence-band offsets at the $\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P-ZnSe}(001)$ lattice-matched interface

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The difficulty in making good Ohmic contact at the interfaces with  $p$ -doped ZnSe is an important problem hindering the realization of blue-light-emitting diode lasers based on the II-VI semiconductor technology. So far no metal or semiconductor material has been found to have a low enough barrier at the (001) interface with ZnSe. A possible solution to this problem is the insertion of a so-called *barrier-reduction layer* at the interface with ZnSe. We have investigated the interface formation energies and valence-band offsets at the (001) interface between  $\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}$  and ZnSe. The results of our calculations show the existence of a strong interdependence between the valence-band offset and the interface geometric structure. The interface is found to have structural and electronic similarities to the GaAs-ZnSe(001) system. The very low values obtained for the valence-band offset confirm the possibility of using this material as a major constituent of the barrier-reduction layer. [S0163-1829(97)05704-4]

## I. INTRODUCTION

Successful  $p$  doping of ZnSe by nitrogen plasma sources<sup>1</sup> has made possible the fabrication of blue-green diode lasers<sup>2</sup> based on II-VI semiconductors. In spite of the great effort expended over wide-band-gap semiconductor technology, two important problems still stand out: (i) the lifetime of the lasers is short, presumably due to dislocation growth and motion during lasing, and (ii) the devices require high operational voltages, which make them largely unsuitable for large-scale commercial applications.

The second problem is related to the very deep valence-band edge in ZnSe, about 6.4 eV below the vacuum level. Since no metal has such a large work function, an energy barrier across the  $p$ -ZnSe metal interface is formed ( $\approx 1.5$  eV), essentially preventing hole injection through the metal contact. Unfortunately, the low net acceptor density achieved so far in ZnSe also overrules the possibility to overcome the barrier through the tunneling mechanism. Recently, some improvement has been obtained using semimetallic HgSe contacts<sup>3,4</sup> or ZnSe-ZnTe pseudoternary superlattices as buffer layers.<sup>5</sup>

A radical solution to the metal contact problem is the use of an alternative configuration<sup>6</sup>  $n$ -on- $p$  instead of the customary  $p$ -on- $n$ . In the former the hole injection is achieved through the substrate and the metal contact is deposited onto  $n$  ZnSe. Due to the high- $n$ -type doping a much lower resistivity can be obtained for this interface. Customarily the substrate for this device is GaAs. However, a direct  $p$ -ZnSe/ $p$ -GaAs heterointerface is to be avoided because of the 1.2-eV valence-band discontinuity.<sup>7-9</sup> Some progress has been achieved in lowering the barrier by the insertion of thin pseudomorphic Ge layer at the interface<sup>10</sup> or using an unbiased beam pressure ratio during the ZnSe growth on GaAs by molecular-beam epitaxy.<sup>9</sup> However, up to now, no material has been found to have a sufficiently low valence-band discontinuity at the interface with ZnSe.

A preliminary investigation<sup>6</sup> has pointed out the possibility to reduce the barrier at the  $p$ -ZnSe/ $p$ -GaAs(001) interface by applying a thick barrier-reduction layer (BRL) made of a

III-V semiconductor alloy, namely,  $\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}$ . This material is especially appealing because it is lattice matched with ZnSe and based on well-established technologies. The barrier reduction should be achieved on both sides of the BRL, but it is important to point out that the band alignment is critical only on the ZnSe side, because on the GaAs side the barrier overtaking is helped by high  $p$ -doping density (about  $1 \times 10^{19} \text{ cm}^{-3}$ ) possible for both materials. The composition of the barrier-reduction layer alloy must be designed to minimize the valence-band discontinuity at the ZnSe interface. To this end it is possible to use the Al and Ga relative concentrations to get a fine tuning of the band energy keeping the lattice parameter constant. So far no investigation based on *ab initio* calculations has been made for this interface. Since heterovalent interfaces show quite complex structural and electronic properties, and experimental information is by and large missing, the present computational study is meant to establish a reference for the band offset values at this interface.

## II. COMPUTATIONAL METHODS

The calculations described below are based on density-functional theory (DFT) in the local-density approximation (LDA) for the exchange and correlation functional, using the Ceperley-Alder<sup>11</sup> form as parametrized by Perdew and Zunger.<sup>12</sup> Energy minimization and structural optimization have been performed by a modified Car-Parrinello<sup>13</sup> technique as implemented by Stump and Scheffler,<sup>14</sup> using norm-conserving ionic pseudopotentials and a plane-wave basis set. Zn 3d levels have been included in the core and accounted for by the nonlinear exchange and correlation core corrections.<sup>15</sup> The lattice parameter obtained for the ZnSe zinc-blende structure  $a = 10.6$  a.u., which compares well with the experimental value of 10.71 a.u. The theoretical value has been used as the reference lattice constant for the interface systems.

The repeated slab technique has been used to model the interface. A supercell 84.8 a.u. long, containing 64 atoms placed on 32 layers has been used for each of the configura-

tions studied. Brillouin-zone integration for the supercell has been performed by sampling over a (222) Monkhorst-Pack<sup>16</sup> mesh. The number of points has been chosen as a compromise to keep the energy cutoff (12 Ry) high enough to guarantee a reliable description of the charge distribution. Bulk calculations instead have been performed with a higher cutoff of 25 Ry to guarantee a good convergence in the band-edge energy.

The valence-band offset can be divided into three terms: (i) the difference in the averaged electrostatic potential on the two sides of the interface, (ii) the difference in the energy of the band edges of the two bulk materials calculated when the above averaged potentials are aligned, and (iii) a correction term related to spin-orbit splitting at the valence-band edge. The band offset  $\Delta E_v$  can be obtained from the equation

$$\Delta E_v = [E_v(L) - E_v(R)] + [\bar{V}_{el}(L) - \bar{V}_{el}(R)] + \frac{1}{3} [\Delta_0(L) - \Delta_0(R)], \quad (1)$$

where  $R$  and  $L$  refer to materials on the left- and the right-hand side of the interface, respectively, and  $E_v$ ,  $\bar{V}_{el}$ , and  $\Delta_0$  are, respectively, the energy of the valence-band edge, the averaged electrostatic potential, and the spin-orbit splitting in the bulk. The second term  $\bar{V}_{el}$  is extracted from self-consistent calculations for the supercell containing the interface (see below). The potential is averaged using the macroscopic sampling technique of Baldereschi *et al.*<sup>17</sup> The spin-orbit correction takes in account the effect of the spin-orbit splitting at the valence-band edge. Since our nonrelativistic self-consistent calculations do not include spin-orbit interactions, the splittings have been evaluated using experimental data for the binary and ternary compounds as in Refs. 18 and 19.

In principle, the evaluation of the conduction-band offset (CBO) requires the knowledge of the conduction-band-edge energy for both the component materials. Since the LDA conduction-band energies are underestimated and many-body calculations are outside the scope of this work, we have obtained an estimate to the CBO by means of the well-known relation between the valence-band offset (VBO) and the CBO,

$$\Delta E_c + \Delta E_v = E_{\text{gap}}(L) - E_{\text{gap}}(R), \quad (2)$$

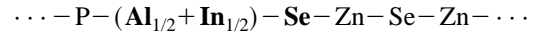
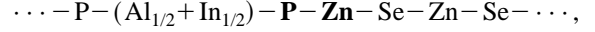
where the  $E_{\text{gap}}$  is the experimental value for the band gap.

### III. INTERFACE STRUCTURES

The band offset calculation at the junction between III-V and II-VI semiconductors requires the determination of the thermodynamically stable interface structures. Indeed, atoms at heterovalent junctions can be arranged in a wide variety of geometries that can lead to very different band alignments. An exhaustive investigation would require a large number of total-energy calculations for different kinds of interface reconstructions. The interface atomic structure of the present system is expected to be reminiscent of the GaAs-ZnSe(001) interface. The latter has been the subject to both theoretical<sup>8,9</sup> and experimental<sup>9</sup> investigations. On this basis we have focused our attention on those interface structures that are

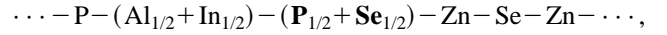
likely candidates for the greatest stability while at the same time computationally affordable.

In particular, four structures have been investigated: two abrupt interfaces and two reconstructed interfaces with an associated mixed layer. We will denote as the *acceptor* interface (A) the structure obtained bringing to contact the alloy anion-terminated (001) ideal surface with the Zn-terminated ZnSe (001) surface. The *donor* interface (D) is the conjunction of the cation-terminated alloy with the Se-terminated ZnSe. The atomic sequences are given below in the case of the  $\text{Al}_{0.5}\text{In}_{0.5}\text{P-ZnSe}(001)$  interface (atoms at the interface are marked in boldface):



(for the acceptor and donor interfaces, respectively), where the parentheses show atoms on the same layer.

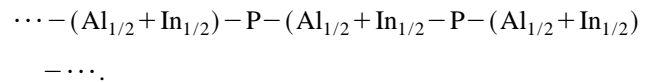
Two reconstructed interfaces have been studied: the anion-mixed (AM) interface and the interface (CM) cation-mixed. The atomic sequences of these are, respectively,



Naturally, several reconstructions are possible, all having fairly similar VBO and formation energies. In the present case we have arranged the atoms in the mixed layer according to the  $c(2 \times 2)$  reconstruction, a two-dimensional face-centered-squared lattice. This reconstruction has been taken among all the possible choices because it leads to a small unit cell with a highly symmetric structure.

In contrast to the GaAs-ZnSe(001) interface, the systems we have studied pose an additional complexity as the junction is to an alloy. The treatment of the alloys requires special care since it is not possible to study a true random distribution in the framework of periodic boundary conditions and in supercell geometry.

There are two possible approaches to model disorder in the present context. In the first, one can use a mean-field type approximation such as the virtual-crystal approximation and coherent-potential approximation methods. While these are fairly well suited for band offset calculations for semiconductors, they are not quantitatively reliable for accurate total-energy calculations. We have adopted the other possibility, where the disordered alloy has been modeled by an ordered structure in the supercell approach. The alloy has been replaced by a superlattice having  $\mathbf{a}_1 = (1,0,0)a_0$ ,  $\mathbf{a}_2 = (0,1,0)a_0$ , and  $\mathbf{a}_3 = (0,0,1)a_0$  as translation vectors and an eight-atom basis, Al (or Ga) at  $\boldsymbol{\tau}_1 = (0,0,0)a_0$  and  $\boldsymbol{\tau}_2 = (0,1/2,1/2)a_0$ , In at  $\boldsymbol{\tau}_3 = (1/2,1/2,0)a_0$  and  $\boldsymbol{\tau}_4 = (1/2,0,1/2)a_0$ , and P at  $\boldsymbol{\tau}_5 = (1/4,1/4,1/4)a_0$ ,  $\boldsymbol{\tau}_6 = (1/4,3/4,3/4)a_0$ ,  $\boldsymbol{\tau}_7 = (3/4,3/4,1/4)a_0$ , and  $\boldsymbol{\tau}_8 = (3/4,1/4,3/4)a_0$ . The atomic sequences along the (001) direction are thus



This specific geometry has the advantage of containing both cations in the same layer, thus avoiding the introduction of a

TABLE I. Formation energies for the  $\text{Al}_{1/2}\text{In}_{1/2}\text{P-ZnSe}(001)$  and  $\text{Ga}_{1/2}\text{In}_{1/2}\text{P-ZnSe}(001)$  interfaces in units of eV per  $(1 \times 1)$  interface area. For the abrupt interfaces the minimum and maximum values for the formation energy determined by the allowed range of variation for the chemical potentials are given.

Interface	$\text{Al}_{1/2}\text{In}_{1/2}\text{P-ZnSe}(001)$		$\text{Ga}_{1/2}\text{In}_{1/2}\text{P-ZnSe}(001)$	
	Minimum	Maximum	Minimum	Maximum
Acceptor	+0.21	+1.56	+0.16	+1.40
Donor	-0.09	+1.26	+0.04	1.28
AM		+0.11		+0.13
CM		+0.12		+0.14

spurious periodicity along the (001) axis. Moreover, as the cations are placed in two different sublattices forming a  $c(2 \times 2)$  structure, the alloy model has the same two-dimensional periodicity as the reconstructed interface preserving the reconstruction symmetry.

Equilibrium lattice parameters have been determined for these structures fitting to the Murnaghan equation the total energies of the fully relaxed structures for six different values of  $a_0$ . The equilibrium values of 10.63 (10.59) obtained for  $\text{Al}_{1/2}\text{In}_{1/2}\text{P}$  ( $\text{Ga}_{1/2}\text{In}_{1/2}\text{P}$ ) closely fulfill lattice matching condition with ZnSe and justify our choice for the reference parameter used in the interface calculations.

The formation energy per unit area for each structure has been calculated from the knowledge of the total energy and the constituent chemical potentials using the relation<sup>21</sup>

$$E_f^{\text{int}} = \frac{1}{2A} \left( E_{\text{tot}}^{\text{SL}} - \sum_i n^i \mu^i \right), \quad (3)$$

where  $E_{\text{tot}}^{\text{SL}}$  is the calculated total energy for the supercell,  $n^i$  the number of atoms for each element,  $\mu^i$  the relative chemical potential, and  $A$  the supercell cross-sectional area. In the present case the equation can be simplified using

$$\mu^{\text{alloy}} = \frac{1}{2} (\mu^{\text{X}} + \mu^{\text{In}}) + \mu^{\text{P}}, \quad (4)$$

$$\mu^{\text{ZnSe}} = \mu^{\text{Zn}} + \mu^{\text{Se}} \quad (5)$$

to obtain

$$E_f^{\text{int}} = \frac{1}{2} (E_{\text{tot}}^{\text{SL}} - n^{\text{alloy}} \mu^{\text{alloy}} - n^{\text{ZnSe}} \mu^{\text{ZnSe}} - \Delta n^{\text{Se}} \mu^{\text{Se}} - \Delta n^{\text{P}} \mu^{\text{P}}), \quad (6)$$

where  $X$  stands for Al or Ga,  $\Delta n^{\text{Se}} = n^{\text{Se}} - n^{\text{Zn}}$ , and  $\Delta n^{\text{P}} = n^{\text{P}} - \frac{1}{2}(n^{\text{X}} + n^{\text{In}})$ . Each supercell structure has been built with symmetric interfaces, except for the CM structure. Indeed, to contain the same number of Al (Ga) and In atoms, the supercell should be doubled in lateral size. To avoid this, an asymmetric slab has been considered, having an Al+Zn layer on one side and an In+Zn one on the other.

The formation energy for the abrupt interfaces is a function of the chemical potentials  $\mu^{\text{Se}}$  and  $\mu^{\text{P}}$ . The allowed ranges of variation for these potentials, under conditions of thermodynamic equilibrium with the bulk, are defined by the relations

$$\mu^{\text{Se bulk}} \geq \mu^{\text{Se}} \geq \mu^{\text{Se bulk}} - \Delta H^{\text{ZnSe}}, \quad (7)$$

$$\mu^{\text{P bulk}} \geq \mu^{\text{P}} \geq \mu^{\text{P bulk}} - \Delta H_f^{\text{alloy}}, \quad (8)$$

where  $\Delta H_f$  is the heat of formation for the bulk stable structure.<sup>22</sup> To prevent effects due to different  $\mathbf{k}$ -point sampling and numerical roundoff  $\mu^{\text{ZnSe}}$  and  $\mu^{\text{alloy}}$  have been calculated using the same supercell utilized for the interface system. A comparison with the fully converged bulk total energy gives a difference of  $\approx -15$  meV/atom which, although small, is not negligible in the formation energy calculation.

The calculated interface formation energies for the fully relaxed structures are shown in Table I. For each of the abrupt interfaces the minimum and maximum values for the formation energy are reported, determined by the allowed range of the chemical potentials. The results of Table I show that the acceptor interface is always energetically unstable. The donor interface has the lowest formation energy with respect to the other interfaces under extreme stoichiometric conditions related to an excess of Se and group-III elements during the growth. This last statement is subject to the uncertainties in the determination of the exact range for the Se (and P) chemical potentials. According to Ref. 23, if we define ‘‘stoichiometric’’ chemical potentials as the midpoint value of the allowed range for Se and P, we obtain for the  $\text{Al}_{1/2}\text{In}_{1/2}\text{P-ZnSe}$  ( $\text{Ga}_{1/2}\text{In}_{1/2}\text{P-ZnSe}$ ) donor interface a formation energy of 0.58 (0.66) eV per  $(1 \times 1)$  area, far above the compensated interfaces. Very likely the AM and CM compensated interfaces are the stable ones. The values reported for the formation energies show that these interfaces are nearly degenerate in energy with a very small difference of 10 meV per  $(1 \times 1)$  area in favor of the AM structure. This behavior has not been found for the  $\text{GaAs/ZnSe}(001)$  interface,<sup>8</sup> where both interfaces have the same formation energy.

We have performed an additional calculation for the  $\text{GaAs/ZnSe}(001)$  AM and CM interfaces. The results confirm the energetic degeneracy giving a formation energy of 0.20 eV/ $(1 \times 1)$  area in good agreement with other results.<sup>8</sup> A possible reason for this small difference is the higher binding energy of the P atoms, which makes the AM structure more stable than the CM one. Indeed the analysis of the relaxation at the interface (Fig. 1) shows the existence of a sensible amount of strain at the CM reconstructed interface. While in the AM interface the anion-mixed layer keeps its ideal position midway between the two neighboring bulk sides, in the CM structure the cations relax strongly towards the neighboring P layer stretching the Zn-Se bond. This stress is probably related to the lower stability of the CM structure with respect to the AM one. Since the formation energy difference is very small, in realistic conditions it is

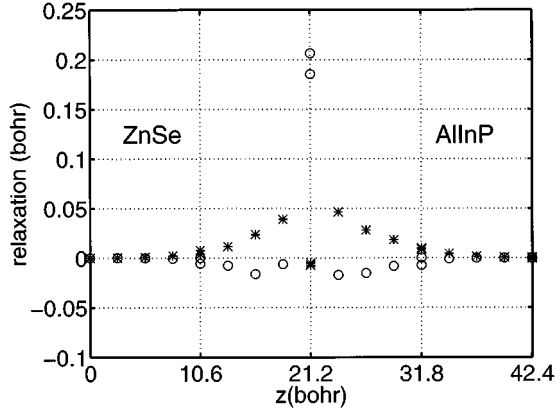


FIG. 1. Relaxation at the  $\text{Al}_{1/2}\text{In}_{1/2}\text{P}$ -ZnSe(001) interface. Circles (stars) show the longitudinal component of the relaxation in each atomic layer along the  $z$  axis for the CM (AM) reconstructed interfaces. Positive numbers are related to shift toward the  $\text{Al}_{1/2}\text{In}_{1/2}\text{P}$  alloy. The strong relaxation of the Zn and Al atoms toward the P layer is evident.

expected that there is a similar degree of mixing between the AM and CM structures with important consequences for the VBO value at the interface (see below).

#### IV. BAND OFFSETS

The main goal of this work is the investigation of the valence-band offset at the  $\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}$ -ZnSe(001) interface to establish if this alloy can be used with advantage as a BRL in between the GaAs-ZnSe junction. From the results shown in the preceding section, it appears that we are dealing with an interface having similar structural characteristics to GaAs-ZnSe(001). As for GaAs-ZnSe(001), the band offset will be different for inequivalent interfaces; in particular, the AM and CM interfaces will lead to very different values. These can be roughly estimated by resorting to the following considerations, outlined in Ref. 10. The valence-band offset  $\Delta E_v$  at a heterovalent heterojunction can be split into three contributions

$$\Delta E_v = \Delta E_v^{\text{BS}} + \Delta V_{\text{iso}} + \Delta V_{\text{hetero}}. \quad (9)$$

Here  $\Delta E_v^{\text{BS}}$  is the band-structure term,  $\Delta V_{\text{iso}}$  is the potential-energy lineup at the abrupt (110) nonpolar interface, and  $\Delta V_{\text{hetero}}$  is the additional term to the lineup related to the interface dipole at the (001) interface. The sum of the first two terms satisfies the so called transitivity rule

$$\Delta E_v(A-C) = \Delta E_v(A-B) - \Delta E_v(B-C), \quad (10)$$

where  $A$ ,  $B$ , and  $C$  are, in the present case, the  $\text{Al}(\text{Ga})_{0.5}\text{In}_{0.5}\text{P}$  alloy, GaAs, and ZnSe, respectively.

The valence-band offset at the GaAs-ZnSe(110) interface is<sup>24</sup> 1.10 eV. The VBO at the  $\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}$ -GaAs(001) junction has been measured<sup>25</sup> and its value is 0.62 (0.30) eV for  $x=0.5$  ( $x=0$ ). Using Eq. (10), we obtain 0.48 (0.80) eV as the VBO at the  $\text{Al}(\text{Ga})_{0.5}\text{In}_{0.5}\text{P}$ -ZnSe(110) interface. The additional  $\Delta V_{\text{hetero}}$  term depends on the interface microscopic structure and has its maximum and minimum values for the AM and CM structures, respectively. Its value for

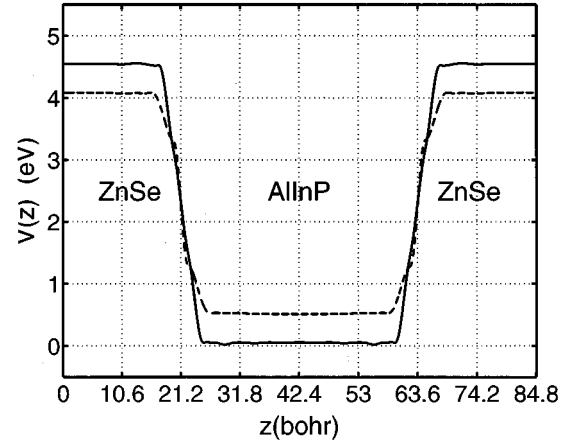


FIG. 2. Averaged (Ref. 17) electrostatic potential for the  $\text{Al}_{1/2}\text{In}_{1/2}\text{P}$ -ZnSe(001) supercell. The solid (dashed) line refers to the AM (CM) reconstruction.

these interfaces is equal to  $\pm \pi e^2 / 2a_0 \epsilon$ , where  $a_0$  is the lattice constant and  $\epsilon$  the average of the dielectric constants of the two bulk materials. In the present case ( $\epsilon \approx 10$ ) its value is about  $\pm 0.4$  eV.

Adding the  $\Delta V_{\text{hetero}}$  correction, we obtain from Eq. (9) for the  $\text{Al}(\text{Ga})_{0.5}\text{In}_{0.5}\text{P}$ -ZnSe(001) junction estimates of 0.08 (0.40) and 0.88 (1.20) eV for the VBO at the AM and CM interfaces, respectively. These extremely low values, especially for the  $\text{Al}_{0.5}\text{In}_{0.5}\text{P}$  AM structure, justify a verification by a self-consistent calculation. These values refer to the ideal zinc-blende lattice structure. In the present case there will be an additional term due to the effect of the internal relaxation in the alloy and of the interface strain emphasized in Sec. III. It is known that only the interfacial strain has an appreciable effect on the VBO; for this reason we have considered the AM and CM interfaces in both ideal zinc-blende and relaxed structures.

We have calculated the VBO using symmetric slabs corresponding to the fully relaxed structures for each of the previously studied geometries. Figure 2 displays the electrostatic *macroscopic* potential profiles for the AM and CM  $\text{Al}_{1/2}\text{In}_{1/2}\text{P}$ -ZnSe(001) interfaces. The figure confirms the perfect convergence of the potential with respect to the slab thickness.

All the results are reported in Table II. The values deduced for the conduction-band offset have been obtained using Eq. (2) and the experimental values for the alloy band gaps (1.85 and 2.33 eV) according to Ref. 19. In the third columns the net electronic plus ionic electrostatic dipoles are reported. Under braces the values for the ideal zinc-blende structures have been reported for the AM and CM structures. Indeed, the analytic estimates for the VBO based on the transitivity rule refer only to the unrelaxed structure and especially the  $\Delta V_{\text{hetero}}$  term should be compared with these last values.

With respect to the GaAs-ZnSe(001) interface, the calculated values for the present junction are very low and therefore of great technological interest. Average VBO values over AM and CM geometries have been reported on the bottom row in Table II. Since the  $\Delta V_{\text{hetero}}$  terms have opposite values the average should match the predicted values for the (110) nonpolar interface.

TABLE II. Calculated DFT-LDA valence-band offset at the  $\text{Al}_{1/2}\text{In}_{1/2}\text{P-ZnSe}(001)$  and  $\text{Ga}_{1/2}\text{In}_{1/2}\text{P-ZnSe}(001)$  interfaces. The values refer to the fully relaxed structures. The conduction-band offset values are deduced using the experimental band gaps. The averaged values over the two opposite compensated structures are reported in the last row. Values for the ideal CM and AM structures have been placed in parentheses.

Structure	$\text{Al}_{1/2}\text{In}_{1/2}\text{P-ZnSe}(001)$			$\text{Ga}_{1/2}\text{In}_{1/2}\text{P-ZnSe}(001)$		
	VBO	CBO	Dip	VBO	CBO	Dip
Acceptor	+0.15	+0.35	1.23	+0.20	+0.78	1.22
Donor	+0.96	-0.46	0.42	+1.01	-0.03	0.41
AM	+0.09 (+0.23)	+0.41	1.29	+0.32 (+0.46)	+0.66	1.10
CM	+0.89 (+1.30)	-0.39	0.49	+0.99 (+1.35)	-0.01	0.43
Average	+0.49 (+0.76)	+0.01	0.89	+0.65 (+0.90)	+0.33	0.77

The comparison between prediction and calculation shows that the values obtained for the ideal interfaces do not match exactly the results of the prediction. While the  $\Delta V_{\text{hetero}}$  term is slightly larger than predicted and such a discrepancy can be accounted for by the approximate evaluation of the average dielectric constant  $\epsilon$ , a much larger discrepancy exists between the calculated value for the (110) nonpolar interface obtained by averaging over AM and CM structures and the value obtained by means of the transitivity rule. These differences seem to suggest that  $\text{Al}_{1/2}\text{In}_{1/2}\text{P-GaAs}$  ( $\text{Ga}_{1/2}\text{In}_{1/2}\text{P-GaAs}$ ) has a VBO lower than that found experimentally. However, to compare safely experimental data with our DFT-LDA calculations we have to add the corrections due to the effect of the quasiparticle self-energy on the valence-band energy. While these corrections have been estimated by Zhu and Louie<sup>26</sup> for the III-V semiconductors, they have not been calculated for ZnSe. Since there is a good agreement between the DFT-LDA-based calculations<sup>20,10</sup> and the experimental values for the VBO at the GaAs-ZnSe(110) interface we suppose that the correction for ZnSe is small. If one uses the calculated shifts for the III-V semiconductors but assumes that the self-energy shift is zero for ZnSe, the predicted values for the VBO should be lowered by 0.28 (0.22) eV for the  $\text{Al}_{1/2}\text{In}_{1/2}\text{P-ZnSe}$  ( $\text{Ga}_{1/2}\text{In}_{1/2}\text{P-ZnSe}$ ) interface, that is, the VBO values for the relaxed (ideal) interface of -0.19 (-0.05) and 0.61 (1.02) for the AM and CM  $\text{Al}_{1/2}\text{In}_{1/2}\text{P-ZnSe}$  junction and 0.10 (0.24) and 0.77 (1.13) for the  $\text{Ga}_{1/2}\text{In}_{1/2}\text{P-ZnSe}$  are obtained, leading to better agreement with the above predictions.

## V. CONCLUSION

We have investigated the formation energies and valence-band offsets at the  $\text{Al}_{0.5}\text{In}_{0.5}\text{P-ZnSe}(001)$  and

$\text{Ga}_{0.5}\text{In}_{0.5}\text{P-ZnSe}(001)$  interfaces. For each interface four candidate structures have been considered: the so-called donor and acceptor abrupt interfaces and the  $c(2 \times 2)$  interface reconstructions containing an anion- or a cation-mixed layer. Differently from the isovalent junction, this system will have a 1-eV-wide range of variation for the VBO admitted, from -0.19 to +0.77 eV depending on the alloy composition and interface configuration. The calculation of the formation energies shows that the acceptor structure is always energetically unstable. Under extreme stoichiometric conditions (e.g., Se rich) the formation of a donor structure cannot be excluded. In normal stoichiometric conditions the  $c(2 \times 2)$  reconstructed interfaces have the lowest energy with a very small energy difference of 10 meV between them. The AM structure is stable with respect to the CM reconstruction. Even if the formation of more complex structures and a co-existence of both AM and CM interfaces is possible, the configuration for the real interface grown in Se- and P-rich conditions is likely to be the AM structure and the related VBO ranging from -0.19 to +0.10 eV according to the alloy composition. These results bear out the possibility to solve the GaAs-ZnSe contact problem by the insertion of an  $\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}$  made barrier-reduction layer.

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<sup>1</sup>R. M. Park, M. B. Troffer, C. M. Rouleau, J. M. DePuydt, and M. A. Haase, Appl. Phys. Lett. **57**, 2127 (1990).

<sup>2</sup>H. Jeon, J. Ding, A. V. Nurmikko, W. Xie, D. C. Grillo, M. Kobayashi, R. L. Gunshor, G. C. Hua, and N. Otsuka, Appl. Phys. Lett. **60**, 2045 (1992).

<sup>3</sup>Y. Lansari, J. Ren, B. Sneed, K. A. Bowers, J. W. Cook, Jr., and J. F. Schetzina, Appl. Phys. Lett. **61**, 2554 (1992).

<sup>4</sup>Z. Yang, K. A. Bowers, J. Ren, Y. Lansari, J. W. Cook, Jr., and

J. F. Schetzina, Appl. Phys. Lett. **61**, 2671 (1992).

<sup>5</sup>Y. Fan, J. Han, L. He, J. Saraie, R. L. Gunshor, M. Hagerrot, H. Jeon, A. V. Nurmikko, G. C. Hua, and N. Otsuka, Appl. Phys. Lett. **61**, 3160 (1992).

<sup>6</sup>M. Pessa, K. Rakennus, P. Uusimaa, P. Savolainen, and A. Salokatve, Phys. Status Solidi B **187**, 337 (1995).

<sup>7</sup>N. Kobayashi, Appl. Phys. Lett. **55**, 1235 (1989).

<sup>8</sup>A. Kley, and J. Neugebauer, Phys. Rev. B **50**, 8616 (1994).

<sup>9</sup>R. Nicolini, L. Vanzetti, Guido Mula, G. Bratina, L. Sorba, A. Franciosi, M. Peressi, S. Baroni, R. Resta, A. Baldereschi, J. E.

- Angelo, and W. W. Gerberich, Phys. Rev. Lett. **72**, 294 (1994).
- <sup>10</sup>G. Bratina, L. Vanzetti, L. Sorba, G. Biasiol, A. Franciosi, M. Peressi, and S. Baroni, Phys. Rev. B **50**, 11 723 (1994).
- <sup>11</sup>D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 556 (1980).
- <sup>12</sup>J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- <sup>13</sup>R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
- <sup>14</sup>R. Stumpf and M. Scheffler, Comput. Phys. Commun. **79**, 447 (1994).
- <sup>15</sup>S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).
- <sup>16</sup>H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- <sup>17</sup>A. Baldereschi, S. Baroni, and R. Resta, Phys. Rev. Lett. **61**, 734 (1988).
- <sup>18</sup>C. G. Van de Walle, Phys. Rev. B **39**, 1871 (1989).
- <sup>19</sup>M. P. C. M. Krijn, Semicond. Sci. Technol. **6**, 27 (1991).
- <sup>20</sup>A. Qteish and R. J. Needs, Phys. Rev. B **43**, 4229 (1991).
- <sup>21</sup>Guo-Xin Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **38**, 7649 (1988).
- <sup>22</sup>The calculated heat of formation for the bulk materials are (eV/pair) 1.63 (ZnSe), 1.07 ( $\text{Al}_{1/2}\text{In}_{1/2}\text{P}$ ), and 0.85 ( $\text{Ga}_{1/2}\text{In}_{1/2}\text{P}$ ). Calculated cohesive energies for the elements are (eV/atom) 4.16 (Al), 3.35 (Ga), 3.27 (In), 5.03 (P), 1.49 (Zn), and 2.88 (Se).
- <sup>23</sup>K. W. Kwak, D. Vanderbilt, and R. D. King-Smith, Phys. Rev. B **52**, 11 912 (1995).
- <sup>24</sup>J. R. Waldrop, E. A. Kraut, S. P. Kowalzyk, and R. W. Grant, Surf. Sci. **132**, 513 (1983).
- <sup>25</sup>Miyoko O. Watanabe and Yasuo Ohba, Appl. Phys. Lett. **50**, 906 (1987).
- <sup>26</sup>Xuejun Zhu and Steven Louie, Phys. Rev. B **43**, 14 142 (1991).