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# Atomic and electronic structure of the GaAs/ZnSe (001) interface

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We studied the atomic and electronic properties of the polar GaAs/ZnSe (001) interface using first-principles total-energy calculations. Binding energy, atomic relaxations, local electric fields, and valence-band offsets are calculated for a variety of different interface structures. The abrupt interface is found to be energetically unstable for large supercells, whereas structures with an interface consisting of one or two mixed layers are energetically more stable. Among these structures an interface consisting of one mixed layer and a $c(2 \times 2)$ structure is found to be the most stable. The valence-band offset is not explained by a single structure but in terms of a degeneracy in the interface energy with respect to polarity that results in a vanishing interface dipole moment even for polar interfaces. Based on the first-principle results we derive a simple model that explains the arrangement of atoms within the mixed layer and gives insight into the mechanisms stabilizing certain interface structures.

## I. INTRODUCTION

Recent developments of optoelectronic devices show that considerable progress has been achieved in growing III-V/II-VI heterojunctions by molecular beam epitaxy or metal-organic chemical vapor, deposition. Among these systems GaAs/ZnSe is probably the one that is investigated most intensively.[1–4] The wide band gap of II-VI zinc compounds and the well suited GaAs technique focused attention on practical applications. However, for technological applications the controlled and reproducible fabrication of high quality interface structures is fundamental.

The key to understanding the properties of interfaces is the knowledge of the atomic interface structure. Whereas surfaces are experimentally well accessible, little is known about the atomic structure of interfaces. The most direct and successful technique is transmission electron microscopy; however, the information about the atomic composition of the interface is not satisfying. Previous theoretical work on interfaces has mainly focused on calculating the electronic structure, in particular the valence-band offset.[5–7] For the system studied here, the polar GaAs/ZnSe (001) interface, the valence-band offset for different structures has been computed in a number of recent papers.[4,8] However, accurate total energy calculations are rare and mainly restricted to neutral interfaces.[7] Other approaches were based on empirical models as proposed by Harrison[9] and Martin.[10] Whereas these models have limitations in their ability to make quantitative predictions, we will show that they are useful to explain several qualitative effects at polar interfaces.

The aim of the paper is to investigate the stability of different interface reconstructions of the GaAs/ZnSe (001) interface. These investigations are performed for varying supercell sizes which will allow us to extract the interface-interface interaction which may become important for small superlattices. The case of a single isolated interface can then be extrapolated from the limit of large interface distances. We further investigate valence-band offsets and local electric fields. Throughout the paper it is assumed that each atom in the interface is tetrahedrally coordinated, i.e., interstitials, vacancies, and other defects are not considered. This should be justified for stoichiometric interfaces due to the fact that GaAs and ZnSe are well lattice matched (mismatch $<0.5\%$) and that the formation energies for these defects are so high[11,12] that the concentration of defects near the interface is too small to make significant changes. The interface structures are thus characterized by: (i) the stoichiometry, i.e., the ratio of the different chemical elements, (ii) the positions of the atoms on the ideal lattice, and (iii) small displacements around these ideal positions.

The paper is organized as follows. In Sec. II, the method is described. In particular, we discuss the role of the Zn $3d$ electrons on the atomic and, electronic properties. In Sec. III, superlattices with abrupt interfaces and, in Sec. IV, a variety of interface structures consisting of one or two mixed layers are investigated. Based on these results, we discuss applicability and limitations of existing simple empirical models.

## II. THEORETICAL METHOD

### A. Pseudopotentials and basis set

The calculations described below are based on density functional theory using the local density approxi-

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mation for the exchange-correlation functional.[13,14] The wave functions are expanded in a plane-wave basis set up to an energy cutoff of 8 Ry. An increase of the cutoff to 12 Ry changed the interface formation energies per (1×1) area by less than 0.01 eV and the valence-bands offsets by less than 0.05 eV. The electron-ion interaction is described by *ab initio* ionic pseudopotentials.[15,16] For the (1×1) supercell the Brillouin zone (BZ) integration is performed using ($8 \times 8 \times n$) Monkhorst-Pack **k** points[17] in the full BZ. $n$ ranged between 1 and 8 depending on the length of the supercells. The interface is modeled by supercells taking slabs with up to nine double layers of each material, corresponding to a total length of about 50 Å of the supercell. The supercells have up to 6 atoms per layer.

Special care is necessary to achieve a good description of ZnSe, since it is known from all-electron calculations[18] (Fig. 1) that the Zn 3$d$ band lies within the valence $sp$ bands 7.5 eV below the valence-band maximum. Treating the Zn 3$d$ electrons as valence electrons would require an energy cutoff of about 120 Ry for BHS pseudopotentials,[15] and using soft Troullier-Martins pseudopotentials[19] would still require about 60 Ry. However, the small dispersion of about 0.3 eV for the Zn 3$d$ band found in all-electron calculations indicates that the hybridization of the 3$d$ orbital is small and a correct treatment of the frozen-core approximation,[20,21] often called nonlinear core correction (NLCC), where the core charge density is used only to take the nonlinearity of the exchange-correlation functional into account, should give reliable results. Indeed, Qteish and Needs[7] showed that the valence-band offset (VBO) for the neutral GaAs/ZnSe (110) interface is then accurately described.

The pseudopotentials were also checked with respect to their ability to describe bulk properties accurately. Without taking the nonlinear core correction into account, the lattice constant of ZnSe is 9.0% too small and the bulk modulus is 143.3% too large compared to the experimental lattice constant $a_{\rm lat}^{\rm ZnSe} = 5.67$ Å (Ref. 22) and the experimental bulk modulus of 60 GPa,[22] respectively. Applying the nonlinear core correction, a remarkable improvement is observed and the lattice constant is then only 3.2% too small and the bulk modulus 11% too large.

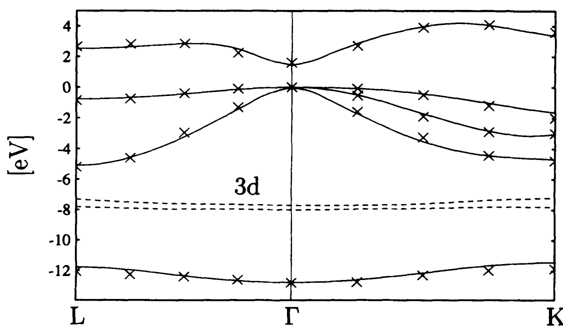



FIG. 1. Comparison of the ZnSe band structure, calculated at the experimental lattice constant $a^{\rm lat} = 5.66$ Å, using an all-electron method (Ref. 18) (crosses for the valence bands and dashed line for the Zn 3$d$ levels) and a pseudopotential approach (solid line), where the Zn-3$d$ electrons are taken into account only via the nonlinear core correction (see text).

As a further check we calculated atomic relaxations and valence-band offsets for the ZnSe/ZnS (001) interface and compared the results with a recent all-electron calculation performed for this interface by Methfessel and Scheffler.[23] We found very good agreement for binding energy differences and atomic relaxations.

The NLCC correction applied to ZnSe yields good agreement of the calculated band structure compared to the all-electron result, as can be seen in Fig. 1. Besides, we note that additional calculations without the NLCC showed that the improvement in the electronic structure stems mainly from the better description of the lattice constant. Calculating the band structure with and without NLCC for the *same* lattice constant near the experimental one causes only minor deviations of less than 0.2 eV. The main effect arises from the improvement of the lattice constant, which causes also an improvement of the bulk modulus. However, since we are interested here in the atomic structure, a good description of the bulk properties is essential and the NLCC is applied throughout the following calculations for zinc. For gallium it was not applied, because no better description of the lattice parameters was found.

The calculated lattice constant of GaAs is 1.5% too small and the bulk modulus 1.3% too large compared to the experimental lattice constant of $a_{\rm lat}^{\rm GaAs}=5.65$ Å (Ref. 22) and the experimental bulk modulus $B_0=75$ GPa.[22] For the following interface calculations the average of the theoretical lattice constants of ZnSe and GaAs $a_{\rm lat}=5.53$ Å was taken. These results are only weakly affected by small changes in the lattice constant.

For superlattices also the $c/a$ ratio has to be optimized. According to Dandrea *et al.* for lattice matched superlattices a $c/a$ ratio close to unity is expected.[24] Indeed, our test calculations for the ideal abrupt interface and interfaces with a single mixed interfacial layer showed only marginal deviations from the ideal $c/a$ ratio. Optimizing the $c/a$ ratio changes the interface energy by less than 0.02 eV per (1×1) area and the bond length by less than 5 %. Based on these results we assumed for the more complex interface structures a $c/a$ ratio of unity.

### B. The valence-band offset

To derive electric fields, charge transfer, and valence-band offsets from the electrostatic potential an averaging procedure is needed which extracts the macroscopic changes and smoothes the oscillations in the potential arising due to the atomic structure. By integrating over the Wigner-Seitz cell of the corresponding bulk system as suggested by Baldereschi *et al.*[25] it is ensured that the electrostatic potential becomes constant in bulklike regions, i.e., in regions far away from the interface. From the averaged electrostatic potential we obtain directly the shift $\Delta V_{\rm av}^{\rm el}$ in the electrostatic potential between the two bulk systems separated by an interface. To derive from this value the *valence-band offset*, a reference level is needed which relates the bulk band structure to

the supercell band structure. In an all-electron calculation the core levels of the atoms are a natural reference level. Here, using a pseudopotential approach, the averaged electrostatic potential plays the role of the reference level. We have to perform separate bulk calculations from which the difference $\Delta V_{\rm diff}^{A}$ between the averaged electrostatic potential and the top of the valence band is calculated for the bulk system $A$ and $B$. The valence-band offset is then defined by

$$E^{\rm VBO} = \Delta V_{\rm av}^{\rm el} + \Delta V_{\rm diff}^{A} - \Delta V_{\rm diff}^{B} + \tfrac{1}{3}\Delta S \ , \qquad (1)$$

where $\Delta S$ is the difference in the spin-orbit splitting between the two bulk systems $A$ and $B$. We did not include spin-orbit splitting in our density functional calculations. These effects can be added *posteriori*, by using experimental values for the spin-orbit splitting.[26] For the GaAs/ZnSe interface the difference is $\Delta S$ =0.12 eV.

### C. Formation energies and chemical potentials

To compare the stability of different interface structures we define the interface formation energy $E_f^{\rm int}$ for an interface with $(m \times n)$ structure:[27]

$$E_f^{\rm int} = \frac{1}{2}(E_{\rm tot}^{\rm SL} - \sum_A n^A \mu^A)/(n\,m) \ , \quad A = {\rm Ga, As, Zn, Se}. \qquad (2)$$

Here $E_{\rm tot}^{\rm SL}$ is the calculated total energy of the supercell, $n^A$ the number of atoms of the species $A$, and $\mu^A$ the chemical potential for this species. $(n\,m)$ is the number of atoms per layer parallel to the interface, thus the interface formation energy refers to a $(1 \times 1)$ interface. The factor 1/2 takes into account that a supercell consists of two interfaces. Thus, $E_f^{\rm int}$ is the average of the formation energies of both interfaces. In the case that the interfaces are of different structures, methods are described in the literature of separating the formation energy for each interface, such as using a local energy density[28] or separating the total energy into intracellular and intercellular interactions.[29] Whereas these methods are important for (111) interfaces, where there is an anisotropy in the [111] direction due to the different layer spacings, for the (001) interface one can find in most cases symmetric interface arrangements. The only exception we consider in this paper is an asymmetric arrangement of abrupt interfaces (Sec. III C) which is shown to be energetically unstable.

In thermodynamic equilibrium the chemical potentials are in equilibrium with the bulk, i.e.,

$$\mu^{\rm GaAs} = \mu^{\rm Ga} + \mu^{\rm As} \ , \qquad (3)$$

$$\mu^{\rm ZnSe} = \mu^{\rm Zn} + \mu^{\rm Se} \ , \qquad (4)$$

where $\mu^{\rm GaAs}$ is the chemical potential of bulk GaAs and $\mu^{\rm ZnSe}$ that of bulk ZnSe. Using these relations we can simplify Eq. (2)

$$E_f^{\rm int} = \frac{1}{2}(E_{\rm tot}^{\rm SL} - n^{\rm GaAs}\mu^{\rm GaAs} - n^{\rm ZnSe}\mu^{\rm ZnSe} - \Delta n^{\rm Ga}\mu^{\rm Ga} - \Delta n^{\rm Zn}\mu^{\rm Zn})/(n\,m) \ . \qquad (5)$$

Here $\Delta n^{\rm Ga} = n^{\rm Ga} - n^{\rm As}$ and $\Delta n^{\rm Zn} = n^{\rm Zn} - n^{\rm Se}$ give the deviation from the ideal bulk stoichiometry.

The only parameters which cannot be directly calculated in Eq. (5) are the chemical potentials for Ga and Zn. Of course, one could reduce Eq. (5) also to the chemical potentials of As and Se or any other combination. The actual value of the chemical potentials depends on the specific experimental conditions, i.e., in which form the atoms are available (molecules, atoms, etc.), in which stoichiometry. Therefore, only some general estimates are possible.

The choice of the chemical potentials is not completely free but they have to obey certain boundary conditions. A major criterion is that the chemical potential for an element $\mu^A$ is less than the chemical potential of the corresponding bulk $\mu^{A\text{-bulk}}$ since otherwise this element would form the energetically more favorable bulk structure. Using this relation and Eqs. (3) and (4) we get

$$\begin{aligned} \mu^{\rm As\text{-}bulk} &\geq \mu^{\rm As} \geq \mu^{\rm As\text{-}bulk} + \Delta H^{\rm GaAs} \ , \\ \mu^{\rm Zn\text{-}bulk} &\geq \mu^{\rm Zn} \geq \mu^{\rm Zn\text{-}bulk} + \Delta H^{\rm ZnSe} \ , \end{aligned} \qquad (6)$$

where $\Delta H^{AB}$ is the heat of formation. A negative heat of formation means that the reaction is exothermic. The corresponding bulk potentials are calculated from the bulk forms of Ga (orthorhombic),[27] As (trigonal),[30] Zn (hcp),[31] and Se (hexagonal).[32] Since the absolute values of the bulk chemical potential depend on the pseudopotential and thus have no physical meaning (only differences are physically relevant), we replace $\mu^{\rm As} \to \mu^{\rm As} - \mu^{\rm As\text{-}bulk}$ and $\mu^{\rm Zn} \to \mu^{\rm Zn} - \mu^{\rm Zn\text{-}bulk}$. The calculated values of the heat of formation:

$$\Delta H^{AB} = \mu^{AB} - \mu^{A\text{-bulk}} - \mu^{B\text{-bulk}} \qquad (7)$$

are compared with experimental data in Table I. Considering the large uncertainty in the experimental values, a good agreement is found. These values define the range where the different interface structures are thermodynamically stable with respect to segregation (Fig. 2). For the following discussion we take the values from the 8-Ry calculation, which are obviously an upper limit of the heat of formation.

In order to compare the stability of different structures we have to employ the *free energy* instead of the *total energy* which is applicable only for zero temperature. The difference between both energies is the entropy contribution $-TS$ which can be divided mainly into vibra-

TABLE I. Calculated and experimental heat of formation [eV per anion-cation pair] for ZnSe and GaAs. The theoretical values are determined with a cutoff energy of 8 and 30 Ry and for the relaxed bulk structure.

| | $E_{\rm cut}$ =8 Ry | $E_{\rm cut}$ =30 Ry | Exp. |
|---|---|---|---|
| GaAs | -1.08 | -0.76 | -0.74,[a] -0.84,[b] -0.94[b] |
| ZnSe | -1.74 | -1.34 | -1.47,[c] -1.67[d] |

[a]Reference 41.
[b]Reference 22.
[c]Reference 42.
[d]Reference 43.

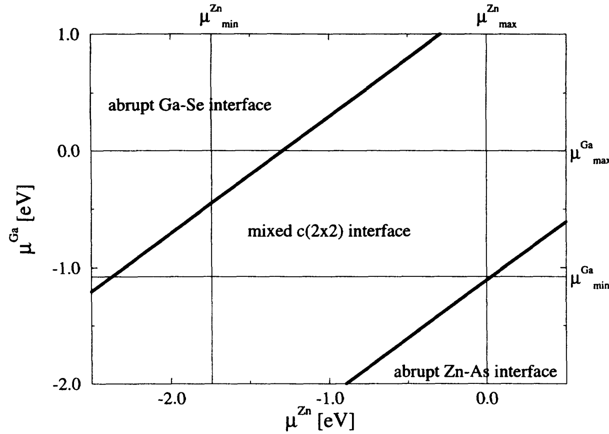



FIG. 2. Phase diagram of the energetically most favorable interfaces (among the studied) as a function of the chemical potentials of Ga and Zn for the abrupt Ga-Se, Zn-As interface and the energetically most favorable mixed interface layer (see Sec. IV). The chemical potentials $\mu^{\mathrm{Ga}}$ and $\mu^{\mathrm{Zn}}$ are referred to their corresponding bulk values.

tional and compositional entropy. Whereas vibrational entropy is typically assumed to be small, Dandrea and Duke found that compositional entropy becomes important at high temperatures for interfaces between III-V materials with considerable lattice mismatch.[33] For this case intermixing reduces the strain in the interface region, thus reducing the interface energy. Since for this mechanism the actual arrangement of atoms in the mixed layer plays only a minor role, many structures exist which are nearly degenerate with respect to their interface energy. Consequently, intermixing increases the compositional entropy.

However, for the nearly lattice matched GaAs/ZnSe interface we will show that the energy differences between the different interface structures can be understood in terms of an electrostatic interaction. Since the electrostatic interaction has a long-range character, a long range ordering occurs as will be shown in Sec. IV. Therefore, intermixing does not increases the configurational entropy and for the remaining discussions we will neglect entropy effects.

## III. INTERFACE STRUCTURES

### A. The abrupt Ga-Se interface

The simplest conceivable interface structure is an abrupt interface, where the two truncated bulk systems are put together and no reconstruction or intermixing occurs. In this case only relaxations are possible. For the system considered here, the GaAs/ZnSe (001) interface, four possible interface structures exist. We will restrict our study to those cases where cation and anion layers are continuously repeated, i.e., As-Se or Ga-Zn interfaces are excluded. Then two possible interface structures remain: (i) the Ga-Se interface and (ii) the Zn-As interface. Since we have a supercell geometry with two interfaces, which are not necessarily the same, we can distinguish between the *symmetric* case, where both interfaces are identical and the *asymmetric* case, where both interface structures (i) and (ii) occur in the same supercell. The classification into a symmetric and asymmetric arrangement of the interfaces seems to be at first glance unnecessary, since for large supercells the interfaces should be decoupled. However, for the abrupt interface our calculations show a strong interface-interface interaction.

We start with the Ga-Se interface in the symmetric arrangement. Figure 3(a) shows the averaged electrostatic potential for a supercell consisting of nine double layers of ZnSe and nine double layers of GaAs. The disturbance of the electrostatic potential near the interface decays only very slowly into the bulk which indicates that the interface induces a long-range electric field. The origin of this long-range field becomes evident if one considers the specific shape of the averaged electronic charge density [Fig. 3(b)]. Strongly localized around the interface, a remarkable increase in the averaged electronic charge density (which is eight in the bulk) is observed.

The origin of the strongly localized charge around the interface can be understood in terms of a simple bond counting model.[34] In an infinite tetrahedral lattice each atom has four nearest neighbor bonds. Since in the bulk system the number of valence electrons in the Wigner-Seitz cell, which consists of one cation and one anion, is always eight, each bond is occupied by two electrons. One can say that each atom $A$ donates one quarter of its valency $Z_v^A$ to each of its four bonds, i.e., the occupation of a bond between the atoms $A$ and $B$ is

$$f_{\mathrm{occ}}^b = (Z_v^A + Z_v^B)/4 \, . \tag{8}$$

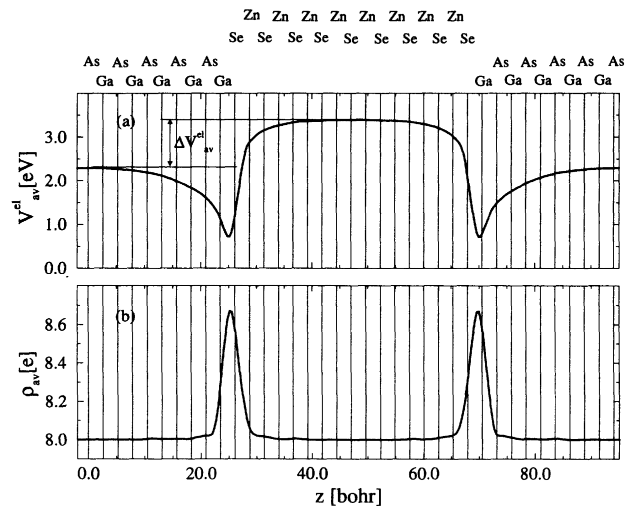



FIG. 3. (a) Averaged electrostatic potential $V_{\mathrm{av}}^{\mathrm{el}}(z)$ and (b) averaged electronic charge density $\rho_{\mathrm{av}}(z)$ of a ZnSe (001) supercell with two abrupt Ga-Se interfaces. $\rho_{\mathrm{av}}(z)$ describes the average number of electrons in a $(1\times1)$ area ranging one layer distance around $z$. The supercell consists of nine double layers of GaAs and nine double layers of ZnSe. The perpendicular lines mark the positions of the atomic layers. The averaging procedure is described in the text.

At the interface, bonds between atoms are formed where the valency sum is different from eight and thus the bond occupation $f^b_{\rm occ}$ is different from two. For the Ga-Se interface, each Ga-Se bond has an excess of one quarter electron, and for the Zn-As interface, each Zn-As bond has one quarter of an electron missing. If a bond has more than two electrons, the excess charge can either occupy the antibonding orbital (this would cost a certain amount of energy) or it may be transferred to another not fully occupied bond. In the following discussion we will call bonds with more than two electrons *donor* bonds, since they donate part of an electron, and bonds having less than two electrons, *acceptor* bonds. A system where the number of donor and acceptor bonds is equal, i.e., where the average occupation of each bond is two, is called *compensated.*[10]

Based on these definitions it is evident that the nonsymmetric Ga-Se interface, investigated above, is noncompensated since it has only donor but no acceptor bonds. The increase in the averaged electronic charge density marks then just the position of the excess electron. The fact that it is strongly localized around the interface can be understood as follows: by moving part of the excess electron away from the donating bond, the atoms forming this bond become positively charged, and thus this separation costs electrostatic energy and reduces the total energy of the system. One can say that the positively charged "defect" (the abrupt Ga-Se interface) is well screened by the excess electron. However, there exists a major difference between the interface and a "normal" point defect: The interface is a two-dimensional (2D) which causes a *qualitatively* different electrostatic interaction. According to Gauss' law the potential of a charged point defect decreases like $1/r$ with distance $r$ from the defect whereas for a charged 2D defect the potential is proportional to $r$, i.e., it causes a field which does not vanish even at infinity. This seems to contradict Fig. 3 where the field in the bulklike regions vanishes. However one has to note that in the symmetric arrangement, where both interfaces are equivalent, no charge transfer from one interface to the other occurs—the interface is for this case a neutral defect. That long-range fields may actually exist will be shown in Sec. III C.

From this simple discussion two rules can be formulated: (i) at interfaces between III-V/II-VI compounds acceptor or donor bonds are inevitable and (ii) the excess electrons or holes are strongly localized around the (generating) donor or acceptor bond. Whereas (i) was found valid for all interfaces investigated here, the second point (ii) has to be replaced by a more general rule as will discussed in connection with the asymmetric interface arrangement.

In order to calculate the binding energy of the Ga-Se interface in symmetric arrangement one has to note that the structure (the interface atoms are marked in boldface)

-As-**Ga**-**Se**-Zn-Se-Zn-**Se**-**Ga**-As-Ga-As-Ga

has one Zn and one As atom per supercell less than the stoichiometric bulk. The interface formation energy per $(1\times1)$ area according to Eq. (5), therefore, reads

$$E_f^{\rm int} = \tfrac{1}{2}[E_{\rm tot}^{\rm SL} - n^{\rm GaAs}\mu^{\rm GaAs} - n^{\rm ZnSe}\mu^{\rm ZnSe} - (\mu^{\rm Se} + \mu^{\rm Ga})] \,. \qquad (9)$$

The interface formation energy is thus a function of the chemical potentials of As and Se. The interface energy for the abrupt Ga-Se interface was compared with those of other structures, which will be discussed in the following sections. This information is summarized in Fig. 2, which shows the range of chemical potentials where each structure is energetically stable.

Some remarks on atomic relaxation: Including atomic relaxation increases the bond length between the Ga and Se layer from 2.61 bohr to 2.77 bohr and lowers the interface formation energy by 0.15 eV. Despite the slow convergence of the electrostatic potential the VBO are nearly completely converged even for a 4+4 supercell (see Table II).

According to our calculations no interface states exist. Thus, since for the abrupt Ga-Se interface only donor states are present, the energetically lowest level that the excess electrons can occupy is the bottom of the conduction band. Some of the excess electrons may of course occupy some acceptor states present in the bulk, however this is possible only for a small fraction of the excess electrons since the number of point defects near the interface is much smaller than the number of donor bonds and a transfer to defects at larger distances will cause a large electric field which prevents then the charge transfer. (The latter effect will be shown to be important for the asymmetric interface arrangement.) One can say that band bending becomes so strong that the acceptor states behind a critical distance of the interface are higher in energy than the energy of the conduction band at the interface. Thus, as opposed to point defects the interface formation energy depends only weakly on the Fermi level.

However, besides occupying states which are already present at the interface or in the bulk, a further possibility is conceivable: the donor concentration may be large enough to create native defects in the vicinity of the interface, which are acting as acceptors. Whereas this reaction was shown to be negligible in stoichiometric bulk systems[6] it cannot be excluded for the case investigated here, namely a strong nonstoichiometric interface and a donor concentration that is orders of magnitude larger than achievable in bulk. Indeed, recent experiments[2,35] that observed the formation of a $Ga_2Se_3$ interface layer

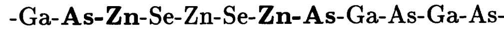
TABLE II. Calculated valence-band offsets (VBO) for the symmetric abrupt interface for the $(\text{Ga-Se})_D$ donor interface and the $(\text{As-Zn})_A$ acceptor interface. The numbers in parentheses give the VBO for the atomically relaxed interface. All VBO's are in eV. The number of layers (No. layers) is counted in multiples of double layers (4+4 means four double layers of GaAs and 4 double layers of ZnSe).

| No. layers | $(\text{Ga-Se})_D$ | $(\text{As-Zn})_A$ |
|---|---|---|
| 4+4 | 1.72 (1.86) | 0.33 (0.46) |
| 7+7 | 1.72 (1.85) | 0.35 (0.43) |
| 9+9 | 1.69 (1.83) | 0.31 (0.43) |

indicate that this process can actually become important. This possibility is disregarded in Ref. 10 since the dependence of the defect formation energies on chemical potentials was neglected.

### B. The abrupt Zn-As interface

For the Zn-As interface, where only acceptor bonds exist, the same qualitative behavior is found. A strong electrostatic field exists, and the excess holes are strongly localized around the interface. According to the interface structure



-Ga-**As**-**Zn**-Se-Zn-Se-**Zn**-**As**-Ga-As-Ga-As-

the supercell has now one excess Zn and one excess As atom compared to the stoichiometric bulk. Thus, the interface formation energy for a $(1 \times 1)$ interface reads

$$E_f^{\rm int} = \frac{1}{2}[E_{\rm tot}^{\rm SL} - n^{\rm GaAs}\mu^{\rm GaAs} - n^{\rm ZnSe}\mu^{\rm ZnSe} - (\mu^{\rm As} + \mu^{\rm Zn})] . \quad (10)$$

The dependence of the interface structure as a function of $\mu^{\rm As}$ and $\mu^{\rm Zn}$ is shown in Fig. 2. From these results we can conclude that the abrupt Zn-As interface is thermodynamically unstable against segregation.

For the acceptor interface the atomic relaxation reduces the distance between the Zn and As layer from 2.61 bohr to 2.44 bohr. This means that an acceptor state contracts the bond length, whereas a donor bond expands the bond length from 2.61 bohr to 2.77 bohr, the same tendency has been reported for the GaP/ZnS interface.[4]

### C. The abrupt asymmetric interface

As a second case of interface arrangements in supercells we will now discuss the asymmetric case of abrupt interfaces where one interface is solely built up by Ga-Se donor bonds and the other by Zn-As acceptor bonds. Since the number of acceptor bonds equals the number of donor bonds the supercell is compensated in contrast to the above discussed symmetric interface arrangement. The averaged electrostatic potential for this system is plotted in Fig. 4(a). A strong electric field is visible which does not vanish even in the bulk region. The corresponding averaged electronic charge density plotted in Fig. 4(b) exhibits a sharply localized enhancement around the donor interface and a depletion around the acceptor interface, equivalent to the abrupt interfaces in the symmetric arrangement. To discuss the interface-interface interaction, which is expected to be large for a configuration where the electric field does not vanishes, we calculated the interface formation energy for different supercell sizes. The interface formation energy for a $(1 \times 1)$ interface according to Eq. (5) simplifies to

$$E_f^{\rm int} = \tfrac{1}{2}(E_{\rm tot}^{\rm SL} - n^{\rm GaAs}\mu^{\rm GaAs} - n^{\rm ZnSe}\mu^{\rm ZnSe}) . \quad (11)$$

$E_f^{\rm int}$ contains now contributions from the different interfaces and furthermore from the interface-interface interaction. Note that for this compensated structure where the number of Zn-As bonds equals the number of Ga-Se bonds the formation energy does not depend on the atomic chemical potentials. The results for the interface formation energies as a function of the supercell size are listed in Table III and shown in Fig. 5. We note the initial rapid increase in the interface formation energy with increasing interface-interface distance which saturates for larger distances. The interfaces experience a strong short-range attractive interaction—the energetically most stable situation for this type of interfaces would be the smallest supercell. Due to kinetical barriers this does not mean that a large supercell would undergo a transition into smaller supercells, i.e., into a highly ordered structure but due to atomic interdiffusion a disordered interface structure would be formed.

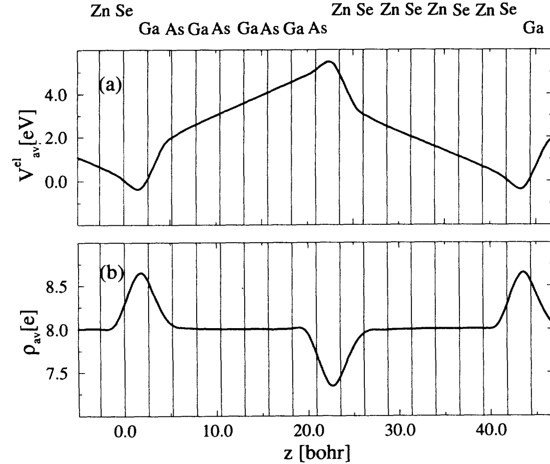



FIG. 4. Averaged electrostatic potential (a) and electronic charge density (b) for an asymmetric GaAs/ZnSe (001) supercell where one interface is formed by Ga-Se donor bonds, the other by Zn-As acceptor bonds. The supercell consists of four double layers of GaAs and four double layers of ZnSe. The vertical lines mark the positions of the atomic layers.

TABLE III. Interface formation energy $E_f^{\rm int}$ per $(1\times1)$ interface area, electric fields, charge transfer, and potentials for several supercell sizes. $\mathcal{E}^{\rm eff}$ is the effective electric field according to Eq. (12), $Q$ is the charge transfer from the Ga-Se donator to the Zn-Se acceptor interface and $\mathcal{E}^{Q}$ is the field induced by the charge transfer [Eq. (14)]. $\Delta\Phi^{\rm eff} = \mathcal{E}^{\rm eff} l/4$ is the potential difference between the two interfaces and $\Delta\Phi^{\rm comp}$ is the difference in the valence-band offsets. $l$ is the length of the supercell (5.22 bohr per double layer). The number of layers corresponds to double layers.

| No. layer | $E_f^{\rm int}$ (eV) | $\mathcal{E}^{\rm eff}$ (V/bohr) | $Q$ (e) | $\mathcal{E}^{Q}$ (V/bohr) | $\Delta\Phi^{\rm eff}$ (eV) | $\Delta\Phi^{\rm comp}$ (eV) |
|---|---|---|---|---|---|---|
| 1+1 | 0.10 | | | | | |
| 2+2 | 0.17 | 0.42 | 0.082 | 0.50 | 2.09 | 0.63 |
| 4+4 | 0.28 | 0.32 | 0.049 | 0.30 | 3.14 | 0.80 |
| 6+6 | 0.30 | 0.22 | 0.036 | 0.22 | 3.44 | 0.95 |
| 8+8 | 0.33 | 0.17 | 0.030 | 0.18 | 3.34 | 1.26 |
| 10+10 | 0.34 | 0.14 | 0.024 | 0.15 | 3.34 | 1.27 |

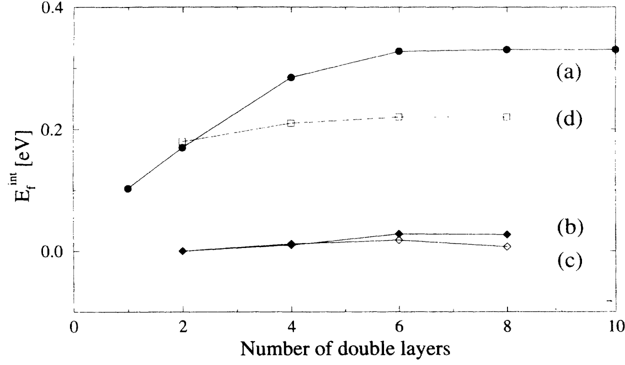



FIG. 5. Interface formation energy per (1×1) interface area as a function of supercell length $l$ for abrupt interfaces in: (a) asymmetric supercells, (b) symmetric supercells with Zn-As interfaces and (c) symmetric supercells with Ga-Se interfaces. For comparison we also included the interface formation energy for an interface structure consisting of one mixed interface layer and a $c(2 \times 2)$ structure (d). Since we are only interested here in the $l$ dependence, we choose $\mu^{\rm Ga}$ and $\mu^{Zn}$ so that $E_f^{\rm int}$ vanishes for the asymmetric (2+2) supercells (b) and (c).

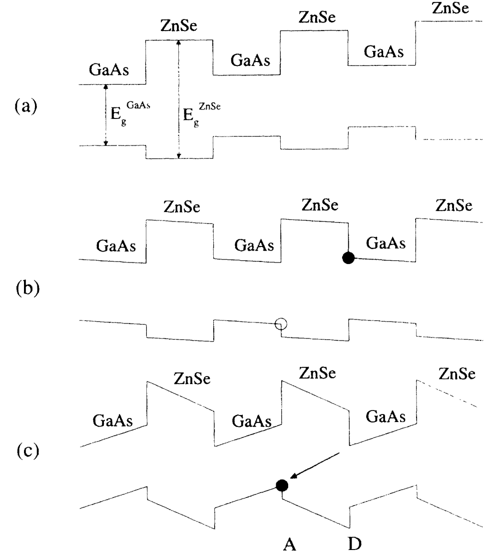



FIG. 6. Schematized dependence of valence and conduction band in real space perpendicular to the interface: (a) without periodic boundary conditions and assuming a zero field inside the bulklike regions, (b) by introducing periodic boundary conditions, and (c) additionally allowing charge transfer from the donor states to the acceptor states. $D$ and $A$ mark the donor and acceptor interface, respectively. The charge transfer, realized in (c), moves the excess electrons (marked with a filled circle) which are initially located at the donor interface (b) to the energetically lower lying acceptor states located at the $A$ interface (marked by an open dot).

The key to understanding this strong interface-interface interaction is the macroscopic electric field. We call it macroscopic since it exists even in the bulk region far away from the interface. To define this field correctly one has to consider that the absolute value of the electric field at each point depends on the boundary conditions, whereas the difference of the electric field $\mathcal{E}^{\rm eff}$ at both sides of the interface is a well defined value, depending only on the charge distribution around the interface, with

$$\mathcal{E}^{\rm eff} = \mathcal{E}^{\rm GaAs} - \mathcal{E}^{\rm ZnSe} , \qquad (12)$$

where $\mathcal{E}^{\rm GaAs}$ and $\mathcal{E}^{\rm ZnSe}$ are the electric fields extracted from the averaged electrostatic potential midway between the two interfaces, i.e., in a region where the slabs are nearly bulklike. From the averaged charge density we obtain the charge transfer $Q$ from the donor interface to the acceptor interface. Both are listed in Table III. Obviously, both the macroscopic electric field and the charge transfer decrease with increasing interface-interface distance. Another interesting aspect is that if one considers the potential difference between the two interfaces, which is $\Delta\Phi^{\rm eff} \approx \mathcal{E}^{\rm eff} l/4$ ($l$ is the length of the supercell perpendicular to the interface), it converges with increasing supercell size (Table III). Furthermore, superlattices with more than three double layers become metallic.

To explain this puzzling behavior let us consider the shape of the valence and conduction bands in real space along the growth axis perpendicular to the interfaces (Fig. 6). For the following discussion it is important to note that one forms a superlattice with two different interface structures (a donating and an accepting interface) so that the valence-band offset is different for the left and right side of each material (see Fig. 6). If we assume that there is no macroscopic field in the bulk region [Fig. 6(a)] one finds that the bands diverge with increasing supercell size. The divergence vanishes if one considers that a supercell obeys periodic boundary conditions, i.e., the bands have to be translationally invariant with respect to the supercell lattice vector. The periodic boundary conditions are inherent in a plane-wave method as used here, and the resulting bands are shown in Fig. 6(b). An electric field is induced which exactly compensates the constant electric field that caused the divergence in (a)

$$\mathcal{E}^{\rm comp} = \Delta\Phi^{\rm comp}/l , \qquad (13)$$

where $\Delta\Phi^{\rm comp} = \Phi_A^{\rm VBO} - \Phi_B^{\rm VBO}$ is the difference of the valence-band offsets at both interfaces. Similar effects were discussed in Ref. 36.

Another field contribution arises due to the fact that one interface acts as a donor (it has excess electrons), the other as an acceptor. This implies that the excess electron which is located in the conduction band around the donor interface is transferred to the acceptor interface. However, due to this electron transfer $Q$ the donor interface becomes positively charged, the acceptor interface negatively charged, and a strong electric field $\mathcal{E}^Q$ is built up as follows:

$$\mathcal{E}^Q = \frac{Q}{4\pi\epsilon_0 A} . \qquad (14)$$

$A$ is the area of the supercell parallel to the interface. The electric fields in the GaAs and ZnSe slab are given by

$$\mathcal{E}^{\mathrm{GaAs}} = \mathcal{E}^{\mathrm{comp}} + \frac{l^{\mathrm{ZnSe}}}{l}\mathcal{E}^{Q} ,$$

$$\mathcal{E}^{\mathrm{ZnSe}} = \mathcal{E}^{\mathrm{comp}} - \frac{l^{\mathrm{GaAs}}}{l}\mathcal{E}^{Q} . \quad (15)$$

Here $l^{\mathrm{GaAs}}$ and $l^{\mathrm{ZnSe}}$ are the lengths of the GaAs and ZnSe slabs, respectively. From Eq. (15) the compensating field and via Eq. (13) the difference $\Delta\Phi^{\mathrm{comp}}$ in the VBO between the GaAs and ZnSe interface can be calculated. The results are listed in Table III. For an asymmetric supercell consisting of 10+10 double layers the difference is 1.27 eV (Table III), which agrees well with the 1.40 eV difference of the VBO for symmetric supercells (Table II).

From Eq. (14) it is obvious that if the charge transfer $Q$ is constant, which would be the case if all excess electrons would be transferred to the acceptor interface, then the electric field will be constant which implies that with increasing supercell length $l$ the potential and thus the total energy diverges. This argument was used by Harrison *et al.*[9] to show that the abrupt charged interface is energetically unstable. The effect of charge transfer is shown in Fig. 6(c): the one particle energies are increased around the donor interface and decreased around the acceptor interface. Therefore, if the distance between the two interfaces becomes too large the valence band near the acceptor interface becomes higher in energy than the conduction band around the donor interface and a back charge transfer from the acceptor to the donor interface occurs. A negative energy gap results, as pointed out by Bylander and Kleinman[37] for polar Ge/GaAs superlattices. Thus, at a certain thickness $l_{\mathrm{crit}}$ of the supercell the system becomes metallic and due to the back charge transfer the electric field decreases. Due to the decreasing electric field the total energy converges to a fixed energy as shown in Fig. 5. For the interface structure considered here the critical thickness is $l_{\mathrm{crit}} = 15$ bohr. The reason for the unusual back transfer of electrons from acceptor states to donor states is that the interfaces correspond to a 2D delta-doped system. As opposed to the "normal" case where donors and acceptors are randomly distributed, this specific atomic arrangement causes a *macroscopic* electric field between the interfaces which finally makes the system metallic.

We like to note that the above discussion is different from that given by Eppenga[8] for the same system. Analyzing rather small superlattices, Eppenga came to the conclusion that the charge transfer is less important and the field arises mainly due to the difference in the layer ionicity between the two semiconductors.

We conclude, that an abrupt interface *may* exist for small asymmetric superlattices (interface distance small). A symmetric arrangement of abrupt interfaces, which is highly noncompensated, is thermodynamically unstable against segregation. In the next section, we will discuss whether these interfaces are stable with respect to intermixing, i.e., we will address the question whether the formation of an intermixed layer can reduce the interface energy.

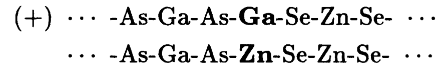
## IV. MIXED INTERFACES

### A. Mixed interfaces with one mixed layer

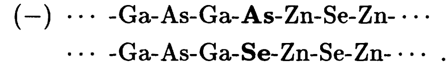
Whereas for the case of abrupt interfaces the number of possible interface structures was restricted, in the case of mixed interfaces there exist an infinite number of possibilities. We, therefore, focus in this section on the case of compensated interfaces. A second reason for this choice is that for uncompensated interface structures one would expect strong reconstructions with probably exotic structures as indicated by the formation of a $Ga_2Se_3$ interface layer.

In order to reduce the number of possibilities further we concentrate on interfaces having only one or two mixed interface layers and on some selected structures parallel to the interface (see Fig. 7). At the end of this section, we will show that the main effects that cause the interface arrangement are very short range so that these assumptions are justified.

We start with the case of the interface being formed by only one mixed layer. Since, as was mentioned in the last section, we allow only the replacement of cations by cations and anions by anions, we can either form a mixed layer consisting of Ga and Zn atoms or of As and Se atoms. These two cases will be labeled (+) if the mixed layer is formed by cations




or (−) if it is formed by anions:




The atoms marked boldface are the elements in the mixed layer and the bold marked connection lines mark the position of a donor or acceptor bond. Since we will consider

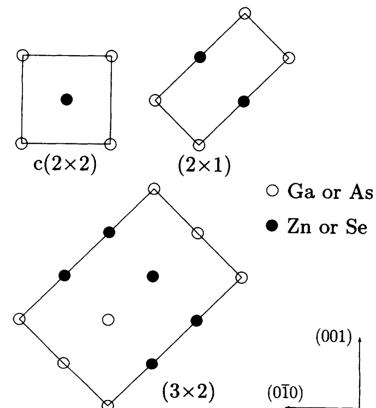



FIG. 7. Lateral atomic arrangement for interfaces consisting of one mixed layer. The pictures show the positions of the atoms in the mixed layer for a $c(2\times2)$, $(2\times1)$, and $(3\times2)$ structure. For a (+) interface the mixed layer consists solely of cations (Zn and Ga) and for a (−) interface of anions (As and Se).

here only compensated interfaces where the number of donor and acceptor bonds is the same, the mixed layer is either formed by 50% Ga and 50% Zn atoms [case (+)] or by 50% As and 50% Se atoms [case (−)]. The only remaining degree of freedom is then how the atoms are arranged laterally in the mixed layer. We calculated the interface formation energy for several structures (see Fig. 7). The structures were chosen such that the atoms in the mixed interface layer have different *in-plane coordination numbers* $C_n^{\rm plane}$. Here $C_n^{\rm plane}$ is the number of nearest neighbor atoms that an atom has in the mixed interface layer and that are of the same species as the atom itself. The structures we studied are: (i) a $c(2\times2)$ structure where each atom has no in-plane nearest neighbor atoms of its own species ($C_n^{\rm plane}=0$), (ii) a $(2\times1)$ structure where atoms of one species form a linear chain ($C_n^{\rm plane}=2$) and (iii) a $(3\times2)$ structure where the atoms form a more complex pattern ($C_n^{\rm plane}=2.5$).

The interface formation energy for these structures is listed in Table IV. The binding energies were calculated for several supercell sizes with different interface-interface distances. Contrary to the case of the ideal (compensated) interface we observe a rather weak interface-interface interaction. An interface separation of about 10 bohr (which corresponds to 4 monolayers) was found to be sufficient to describe the binding energy and the valence-band offset with an error less than 2%. A similar convergence distance of $\approx 10$ bohr has been reported for neutral interfaces.[7,38]

The reason for the short-range interface-interface interaction becomes obvious if one considers the averaged electrostatic potential (Fig. 8). The deviation of the potential from the bulk value is strongly localized around the interface layer, and the next layer already experiences mainly the bulk potential. At a distance of 5 bohr the potential is bulklike within less than 0.5%.

The calculations find all compensated systems to be semiconducting. The interface formation energies, listed in Table IV, exhibit several interesting properties. First they are nearly degenerate with respect to the polarity, i.e., whether the interface layer solely consists of cations [((+) interface) or anions ((−) interface)]. This indicates

TABLE IV. Interface formation energies per $(1\times1)$ surface area for interfaces built up by one mixed layer for both polarities. $E_f^+$ gives the interface energy for the (+) interface, where the mixed layer consists only of the cations Ga and Zn and $E_f^-$ is the interface energy for the (−) interface which consists only of the anions As and Se. The interface energies were calculated for three different lateral structures differing by the in-plane coordination number $C_n^{\rm plane}$ (see text). The numbers in parentheses are the interface energies without atomic relaxation. Note that for compensated interface structures as considered here the formation energy is independent of the atomic chemical potentials according to Eq. (11). All energies in eV.

| Structure | $C_n^{\rm plane}$ | $E_f^+$ | $E_f^-$ |
|---|---|---|---|
| $c(2\times2)$ | 0 | 0.22 (0.24) | 0.22 (0.23) |
| $(2\times1)$ | 2 | 0.27 (0.30) | 0.26 (0.30) |
| $(3\times2)$ | 2.5 | 0.36 (0.45) | 0.35 (0.44) |

FIG. 8. Averaged electrostatic potential (a) and electronic charge density (b) for a GaAs/ZnSe(001) supercell. The interfaces consist of one mixed layer where As and Se are arranged in a $c(2\times2)$ structure. The supercell consists of four double layers of GaAs and four double layers of ZnSe.

that the atomic arrangement is mainly originated by an electrostatic interaction, where the sign of the charge plays no role. From the electrostatic point of view it is unimportant whether the interface layer is built up by anions or cations. Interface stress, where the chemical properties of the atoms are directly involved, is thus expected to play only a minor role. Second, the interfaces become less stable (their interface energy increases) if one occupies the nearest neighbor sites around a given atom with atoms of the same species. The origin of this repulsion is again of electrostatic nature. If two atoms of the same species are placed next to each other one has also two donor or acceptor bonds with excess electrons or holes close to each other. This would require a charge transfer over larger distances, which increases the electrostatic Madelung energy of the system and makes it energetically less favorable. Thus the $c(2\times2)$ interface, where each donor bond is surrounded by four acceptor bonds and vice versa is energetically preferred. In all other cases donor or acceptor bonds become nearest neighbors, the interface energy increases and the system becomes less stable.

If the atoms are allowed to relax, the energy differences between the different interface structures are reduced (for some structures more than 30%), but the general trend remains unchanged. This indicates again the dominance of the electrostatic interaction: it drives the relaxation, however, since it is the origin of the relaxation it changes not the preference between two different structures. The conclusion, that the electrostatic Madelung energy dominates the interface energy for nearly lattice-matched interfaces is consistent with a simple quantitative model proposed by Dandrea *et al.*[24] which was derived from first-principal results and successfully applied for IV/III-V superlattices.

The valence-band offsets are summarized in Table V. The interesting point is that they are nearly degenerate

TABLE V. Valence-band offsets for interfaces consisting of one or two mixed layers for both polarities [(+) and (−) interfaces, see text]. For interfaces consisting of one mixed layer three different lateral structures (see Fig. 7) were considered and for two-layer mixed interfaces two structures according Fig. 11. The numbers in parentheses give the VBO if atomic relaxation is allowed. All energies are given in eV. The experimentally measured VBO for the GaAs/ZnSe(001) interface is $1.22 \pm 0.01$ eV (Ref. 3) and $1.25 \pm 0.07$ eV (Ref. 35).

| Structure | $E_{\mathrm{VBO}}^{(+)}$ | $E_{\mathrm{VBO}}^{(-)}$ |
|---|---|---|
| $c(2 \times 2)$ | 1.75 (1.72) | 0.72 (0.79) |
| $(2 \times 1)$ | 1.72 (1.53) | 0.72 (0.65) |
| $(3 \times 2)$ | 1.74 (1.65) | 0.72 (0.70) |
| $(2 \times 2)^a$ | 1.13 (1.03) | 1.32 (1.25) |
| $(2 \times 2)^b$ | 1.22 (1.07) | 1.26 (1.15) |

with respect to the underlying lateral structure. This picture changes slightly if one allows atomic relaxation, but the differences are still small (less than 0.2 eV) and clearly smaller than the large difference between a cation (+) interface layer ($E^{\mathrm{VBO}} \approx 1.7$ eV) and an anion (−) interface layer ($E^{\mathrm{VBO}} \approx 0.7$ eV). The insensitivity of the valence-band offsets with respect to the lateral atomic arrangement is simply related to the fact that the averaged dipole moment perpendicular to the interface is independent to the actual atomic arrangement. It depends only on the stoichiometry and the polarity of the elements which form the interface layer. In the same way one can also explain the large difference in the valence-band offsets between the (+) and (−) interface layer. For the (+) interface the acceptor bonds lie towards the ZnSe and the donor bonds toward the GaAs (see Fig. 9). Due to the electron charge transfer from the donor to the acceptor bonds a strong dipole moment towards the GaAs is built up (the dipole moment is directed toward the positive charge). This dipole moment increases the valence-band offset. For the (−) interface exactly the same argumentation but with opposite sign (the charge is transferred towards the GaAs) explains the lowering of the valence-band offset. One can say that the actual valence-band offset is the sum of a "neutral band offset" (which one would get, e.g., for neutral interfaces) and a potential induced by the interface dipole moment. This is in agreement with the fact that the average of both VBO's is about 1.26 eV (1.24 eV for the unrelaxed interface) and very close to the result for the neutral GaAs/ZnSe(110) interface [$E^{\mathrm{VBO}} = 1.10$ eV,[39] 1.07 eV,[38] 0.99–1.27 eV,[7] 1.42 eV (Ref. 5)].

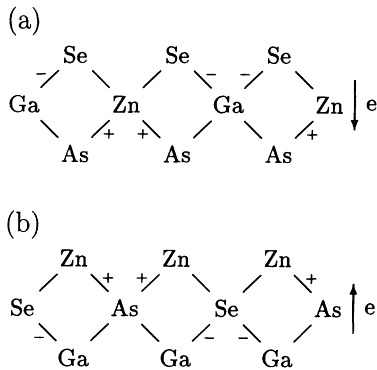
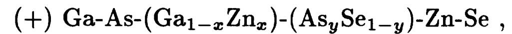


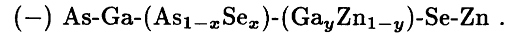

FIG. 9. Schematic arrangement of the donor and acceptor bonds around a (+) interface (a) and a (−) interface (b). Due to the charge transfer of the excess electrons from the donor states to the acceptor states a dipole moment is induced pointing toward the GaAs (a) and the ZnSe (b). Note that the number of Zn-As, Zn-Se, Ga-As, and Ga-Se bonds is the same for both polarities, i.e., in a simple bond counting model the two polarities are energetically degenerate.

### B. Interfaces with two mixed layers

Having discussed the influence of the *lateral* atomic arrangement on the stability and the valence-band offset of the interface we now discuss the influence of the atomic arrangement *perpendicular* to the interface. We will focus on compensated interfaces which consist of two mixed layers. Similar to interfaces with one mixed layer we can distinguish two cases, different only in polarity



$$(+)\ \text{Ga-As-}(\text{Ga}_{1-x}\text{Zn}_x)\text{-}(\text{As}_y\text{Se}_{1-y})\text{-Zn-Se}\ ,$$



$$(-)\ \text{As-Ga-}(\text{As}_{1-x}\text{Se}_x)\text{-}(\text{Ga}_y\text{Zn}_{1-y})\text{-Se-Zn}\ .$$

The notation (+) means here that the acceptor bonds (Zn-As bonds) are outside the mixed layer and (−) means that the donor bonds (Ga-Se bonds) are outside (see also Fig. 10). To impose compensation the stoichiometric parameters $x$ and $y$ cannot be chosen independently but have to obey the relation: $y = 1/2 - x$. Under this relation the number of donating Ga-Se bonds equals the

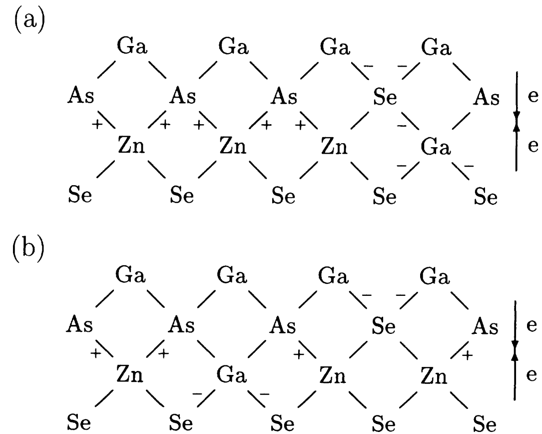



FIG. 10. Schematic arrangement of donor and acceptor bonds in a two-layer mixed interface with a (a) $(2 \times 2)^a$ and (b) $(2 \times 2)^b$ structure (see Fig. 11). Note, that in structure (a) additional donor and acceptor bonds are formed between the mixed layers. In both cases the charge transfer is symmetric with respect to the interface plane, i.e., the total interface dipole moment should be small.

number of accepting Zn-As bonds. The special cases $x = 0$, $y = 1/2$ and $x = 1/2$, $y = 0$ yield the case of one mixed layer which we investigated in Sec. IV B. Another distinct case is $x = y = 1/4$. This stoichiometry realizes the highest symmetry and it is the geometry where one would expect the lowest dipole moment, as pointed out by Harrison.[9]

The smallest possible interface supercell with this stoichiometry consists of four atoms per atomic layer and has a $(2 \times 2)$ structure (see Fig. 11) [a $(4 \times 1)$ structure is possible as well, but was not considered]. Besides the polarity there is for the $(2 \times 2)$ interface one additional free structural parameter, namely where to position the exchanged atom in the second layer (see Fig. 11). To make this more clear let us consider the $(-)$ interface, which consists in the first interface layer of 25% Se and 75% As and in the second layer of 25% Ga and 75% Zn. In structure (a) the Ga atom bonds to one Se and one Ga atom, in (b) to two Se atoms. The backbonds are the same in both cases. The complete supercell used in the calculations consists of 20 monolayers.

The calculated binding energies (Table VI) exhibit several features, which are similar to those obtained for a one-layer mixed interface. First, they are nearly degenerate with respect to polarity [$(+)$ and $(-)$ interface]. Second, the atomic relaxation reduces clearly the differences in the binding energies, but again without changing the order. The structures are found to be energetically less favorable than the "best" one-layer interface, the $c(2\times2)$ structure (see Table IV). To explain the relatively large energy difference between the two structures (a) and (b) let us consider both structures in a more schematic picture. From Fig. 10 it is evident that the main difference between (a) and (b) is the number of donor and acceptor bonds per unit cell. Structure (a) exhibits 5/4 more acceptor and donor bonds than structure (b), where the two exchanged atoms (the Ga and Se atom) are maximally separated. At first glance it seems surprising that the structure with more donor and acceptor bonds should be the energetically more favorable one. However, the argument we used to explain the stability of the $c(2 \times 2)$ interface holds here, too: the interface structure with the lowest Madelung energy becomes the most stable. Since structure (a) has more acceptor and donor bonds, the

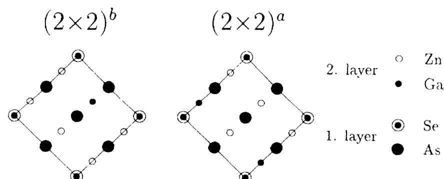



FIG. 11. Atomic geometry in an interface with two mixed layers. The pictures show the lateral arrangement of the first (atoms are marked by small filled and unfilled circles) and the second mixed layer (atoms are marked by large filled and unfilled circles) for a $(2\times2)$ structure. The structures (a) and (b) are different in the position of the exchanged atom in the second layer. The elements are given for a $(+)$ interface. The other polarity [the $(-)$ interface] is obtained by interchanging the cations Ga, Zn and the anions As and Se.

TABLE VI. Interface formation energies per $(1\times1)$ interface area for interfaces consisting of two mixed layers for both polarities. $E_f^+$ is the interface energy for the $(+)$ interface, where the acceptor bonds are outside the mixed layers, and $E_f^-$ is the interface energy for the $(-)$ interface where the donor bonds are outside. The interface energies were calculated for two different structures (see Fig. 11). The number in parentheses are the interface energies if atomic relaxation is not allowed. All energies are given in eV.

| Structure | $E_f^+$ | $E_f^-$ |
|---|---|---|
| $(2\times2)^a$ | 0.29 (0.30) | 0.28 (0.30) |
| $(2\times2)^b$ | 0.34 (0.43) | 0.35 (0.45) |

distances between them are shorter and the electrostatic energy due to charge transfer is thus smaller.

The calculated valence-band offsets are summarized in Table V. One striking feature of these VBO is that they are close to the "neutral" VBO.[39] The reason becomes evident if one notes in Fig. 10 that the resulting perpendicular dipole moment should be small since the charge transfer is (nearly) symmetric with respect to the centerplane of the interface: the charge transfer occurs from both sides outside the interface layer into the mixed layer. This specific property of the $x = y = 1/4$ stoichiometry minimizing the dipole moment was first pointed out by Harrison.[9] Using the fact that experimentally there is no evidence for large VBO differences between neutral and polar interfaces of the Ge/GaAs(110) and (001) interface, he concluded that the interface should have a vanishing dipole moment. The simplest interface structure which is dipole free is the two-layer mixed interface with $x = y = 1/4$.

However, our calculations predict, at least for GaAs/ZnSe interface, a different structure. The structure with the lowest interface formation energy consists of one mixed layer with a $c(2 \times 2)$ structure. This structure is energetically degenerate with respect to polarity, i.e., the energy does not depend on whether the mixed interface layer consists of anions or cations, and builds up a positive or negative dipole moment. Thus, under normal growth conditions and in thermodynamic equilibrium one expects that both polarities occur in a ratio of about 1:1. This implies that the dipole moment of the interface nearly vanishes, although for a given polarity the dipole moment is large and may cause a shift of about 0.4 eV of the VBO (see Table V). The resulting VBO is then the *average* of those for both polarities, which is $\approx 1.25$ eV, and close to the "neutral" VBO of $\approx 1.10$ eV.[39] The averaged VBO is also in good agreement with the experimental result for the GaAs/ZnSe(001) interface of $1.22\pm0.1$ eV (Ref. 3) and $1.25\pm0.7$ eV.[35] The degeneracy of the interface formation energy with respect to polarity (which itself is caused by the dominance of the electrostatic energy) causes a vanishing total dipole moment in the interface and realizes the empirically noticed fact that the VBO is only weakly dependent on the interface orientation. More complicated interface structures with two mixed layers, which also realize a vanishing dipole

moment, are found to be energetically less stable.

Under realistic growth conditions at a finite temperature we expect that not only the $c(2 \times 2)$ mixed interface is formed but also some other structures that are energetically slightly less favorable. However, since we found for *all* investigated structures that the interface energy is nearly degenerate with respect to polarity and thus with respect to the sign of the interface dipole moment, the total interface dipole moment should vanish and thus the VBO will be close to the "neutral" VBO. This picture explains why the VBO is nearly independent of interface orientation as found experimentally.[3,39] Furthermore, the fact that the interface dipole vanishes, allows us to estimate the VBO with simple methods that were originally only developed for neutral interfaces, such as the tight-binding approach of Harrison and Tersoff[5] or the model solid approach of Van de Walle and Martins.[6]

For several technical applications it would be interesting to modify the VBO simply by modifying the growth conditions without adding new materials. Which modifications of growth conditions could do this? First, one could think about kinetic effects (different diffusion barriers, specific preparation of the surface, etc.). However, from our results we cannot predict anything in this direction, since we studied exclusively the final structure and not the reaction path. Another possibility would be the modification of the chemical potentials, e.g., by changing the stoichiometry. But since both structures are compensated and thus independent of the chemical potentials [see Eq. (10)], the chemical potentials cannot discriminate between the two polarities. Varying the chemical potentials will probably only result in an enhanced defect formation. Another possibility is conceivable: a discrimination of the two polarities by applying an electric field. This could be realized by a strong external electric field during the growth or by adding some electrolytes or alkali metals which would increase the local electric field. In any case it would be highly interesting to find experimental growth conditions which could use the potentially large range (for GaAs/ZnSe between 0.7–1.7 eV) to change the VBO for polar interfaces.

After completion of this work Nicolini *et al.* reported a novel method to vary the VBO for the GaAs/ZnSe (001) interface from 0.58 eV to 1.20 eV. The basic idea is to change the Zn/Se flux ratio during the early growth stage of ZnSe on GaAs. Due to the low growth temperatures (290 °C) the kinetic barriers are so large that the first layer remains unchanged. Thus, if the first layer consists mainly of Se, a (−) interface is formed whereas if the first layer consists mainly of Zn a (+) interface is formed. Other structures, although energetically degenerate, are kinetically hindered. In the same paper[40] also first-principle calculations for the VBO's were presented which are in excellent agreement with our results.

## V. SUMMARY

We discussed in detail density-functional theory supercell calculations for various interface configurations of the polar GaAs/ZnSe (001) interface. Different interface arrangements as well as a large number of abrupt and mixed interfaces were studied.

Our calculations predict that abrupt interfaces are thermodynamically unstable. Only for small supercells in an asymmetric arrangement or low growth temperatures they can be metastable. Whereas the abrupt Zn-As interface is unstable against segregation under all stoichiometric conditions (see Fig. 2), the Ga-Se interface might occur. However, experimental observations indicate that this interface is unstable against the formation of a defect-rich $Ga_2Se_3$ layer.

Under normal stoichiometric conditions mixed interface layers are energetically most stable. For these our calculations predict an interface consisting of one mixed layer where the atoms are arranged in a $c(2 \times 2)$ structure to be energetically most stable. All investigated structures have one feature in common: they are nearly degenerate in energy with respect to polarity. This is explained in terms of a simple electrostatic model. The degeneracy of the interface formation energies is shown to have important consequences on the valence-band offset. Since interfaces with the same structure but different polarity have opposite dipole moments, the total interface dipole moment vanishes in thermodynamic equilibrium since the probability for both polarities is the same. The resulting VBO is consequently close to the "neutral" VBO. If growth conditions could be found which discriminate between the two polarities the VBO could be adjusted within a large range from 0.8 eV to 1.7 eV.

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