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Electric fields and valence-band offsets in $n+n$ [001] and [110] ZnSe/GaAs, GaAs/Ge, and ZnSe/Ge superlattices

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Results for $n+n$ [001] and [110] ($n=1$–5) ZnSe/GaAs, GaAs/Ge, and ZnSe/Ge superlattices obtained from self-consistent calculations with the augmented-spherical-wave *ab initio* band-structure method are presented. The valence-band offsets are calculated with the frozen-potential method and compared with those obtained with a new method that is based on the shifts of the potentials of the individual atoms. The internal electric fields that result from the charge separation at the interfaces in the polar [001] superlattices is calculated, and its origin is traced. The valence-band offset is shown to be not affected by these fields.

I. INTRODUCTION

The knowledge of band offsets is crucial for understanding the properties of layered crystalline semiconductors. Since very few band offsets are known experimentally, many have been calculated theoretically instead. Specifically, supercell calculations based on *ab initio* band-structure methods have proven to be a powerful means of obtaining the valence-band offsets between different semiconductors along several interfaces.[1–7]

Interfaces between nonisovalent semiconductors, e.g., between III-V and VI-VI semiconductors, are particularly interesting since generally charge accumulation at the interfaces will result.[8,9] Harrison *et al.*[8] and Martin[9] have shown that a polar interface (e.g., along [001]) therefore has a tendency to form a reconstructed compensated interface. Only the non polar interface ([110]) is expected to be stable against reconstruction since it is already compensated. For this reason most calculations of the valence-band offset between nonisovalent semiconductors are performed for [110] superlattices.[1–7] It is interesting to know whether a valence-band offset can be defined sensibly for unreconstructed polar interfaces and whether it is different from that of nonpolar interfaces.

In the present work the valence-band offsets of ZnSe/GaAs, GaAs/Ge, and ZnSe/Ge along the unreconstructed polar [001] and nonpolar [110] interfaces are calculated using the augmented-spherical-wave[10] (ASW) *ab initio* bandstructure method. Moreover, we analyze the origin of the electric fields present in [001] polar superlattices. We show that the charge accumulation at the polar interfaces constitutes only a part of the total electric field. In Sec. II details of the calculation are given. In Sec. III two methods for obtaining the electric fields and the valence-band offset from the self-consistent calculations are presented and compared: the frozen potential method[2] and a method based on the shifts of the (spherically symmetric) potentials of the individual atoms. In Sec. IV the results are given and discussed.

II. SELF-CONSISTENT CALCULATIONS

The lattice constants of ZnSe, GaAs, and Ge are nearly equal: 5.668, 5.653, and 5.658 Å, respectively. Therefore the effects of strain were ignored. The lattice constants of the superlattices were taken to be the averages of those of the bulk constituents, i.e., $a=5.660$ Å for ZnSe/GaAs 5.663 Å for GaAs/Ge, and 5.656 Å for ZnSe/Ge superlattices. Furthermore, the c/a ratio in the superlattice calculations was taken to be consistent with that of the ideal zinc-blende lattice.

A self-consistent potential for the $n+n$ superlattices was generated by solving the Kohn-Sham equations[11] iteratively using the ASW basis set[10] within the local-density approximation (LDA) for the exchange and correlation functional.[11] Scalar-relativistic effects were ignored and "empty" spheres were placed at the interstitial sites.[12] The ASW basis set consisted of s, p, and d orbitals centered at each atomic site and "empty" sphere site. The Zn 3d states were incorporated as valence-band states. All atomic sphere radii were taken to be equal. The [001] and the [110] superlattices have tetragonal and orthorhombic unit cells, respectively. In both cases eight special k points in the irreducible wedge of the Brillouin zone were used. The self-consistency process was stopped when the Hankel and Bessel energies of all atoms in the superlattice changed less than 0.1 mRy per iteration.

III. OBTAINING THE VALENCE-BAND OFFSET

The particular representation of the crystal potential in the ASW method allows the valence-band offset between two semiconductors to be obtained from a superlattice calculation in several ways. One way is to employ the "frozen-potential" scheme[2] in which the potentials of the atoms and empty spheres constituting a monolayer (not too close to the interface) of either semiconductor—obtained self-consistently in a superlattice calculation—are used unaltered to calculate a *bulk* band structure for that semiconductor. The energies of the tops of the valence bands in each semiconductor are then on an absolute energy scale and can be used to obtain the valence-band offset.

Another way is to compare the self-consistently-obtained potential of the individual atoms in the superlattice with those of the corresponding atoms obtained self-consistently in a bulk calculation. For this scheme to work the potentials $V_v(r)$ of corresponding atoms in the superlattice (SL) and in the bulk (B) must be equal, apart from a constant shift ΔV_v, i.e., $\Delta V_v \equiv V_v^{\mathrm{SL}}(r) - V^B(r)$, independent of r. The energy of the top of the valence band at a specific atom v, E_v, in the superlattice is found by shifting that of the corresponding bulk system by this constant: $E_v^{\mathrm{SL}} = E_v^B + \Delta V_v$; ΔV_v is the constant energy shift at atom v. The energies of the tops of the valence bands are then, as with the frozen-potential method, on absolute energy scale. We shall call this scheme the "shifted bulk" method. The advantages of this method are that (i) the validity of employing a superlattice calculation to obtain the offset is tested directly and (ii) a more detailed picture of the form of the potential is obtained.

A practical scheme for finding the energy shift of the potential of an individual atom v within the ASW method is to calculate the differences between the so-called Hankel (H) and Bessel (B) energies $\varepsilon_{lv}^{H,B}$ (Ref. 10) obtained in the superlattice calculation and those obtained in the bulk calculation,

$$\Delta V_v = \varepsilon_{lv}^{j}(\mathrm{SL}) - \varepsilon_{lv}^{j}(B) \ . \qquad (1)$$

The Hankel and Bessel energies are the eigenvalues of the radial Schrödinger equation for the angular momentum quantum number l ($l=0,1,2,3$) with specified logarithmic derivative at the sphere of atom v. If indeed the potentials of an atom v in the superlattice and the corresponding one in the bulk differ only a constant ΔV_v, independent of r, than the difference $\varepsilon_{lv}^{j}(\mathrm{SL}) - \varepsilon_{lv}^{j}(B)$ is independent of j and l. Numbers for the scatter in ΔV_v will be given in Sec. IV.

IV. RESULTS AND DISCUSSION

Before turning to the issue of charge accumulation at the polar interfaces and its effect on the valence-band offset, we first compare the two methods.

In Figs. 1 and 2 our results for the top of the valence band and the bottom of the conduction band in 5+5 [110] and 4+4 [001] ZnSe/GaAs superlattices, respectively, are shown. The frozen-potential results for each monolayer are indicated by the closed circles. Dashed lines connect these points. The open squares and triangles denote the data as obtained with the shifted bulk method and indicate the individual cations (Zn and Ga) and the anions (Se and As), respectively. The dotted lines pass through the average values of the squares and triangles at each layer. In [001] superlattices a layer ($\simeq 1.4$ Å) contains only one type of atoms (Zn, Se, Ga, or As), whereas in [110] superlattices a layer ($\simeq 2.0$ Å) contains either both Zn and Se or both Ga and As atoms.

For the shifted bulk and the frozen-potential methods to work the potential of an atom v in the superlattice and the bulk should only differ by a constant, independent of r. The scatter of the energy shifts for the $l=0,1,2,3$ Bessel and Hankel energies for a particular atom v tests this. We find the energy shifts for $l=0,1,2,3$ and $j=\{H,B\}$ to be, at worst, equal to within 10–20 meV and 40–50 meV near a nonpolar and polar interface, re-

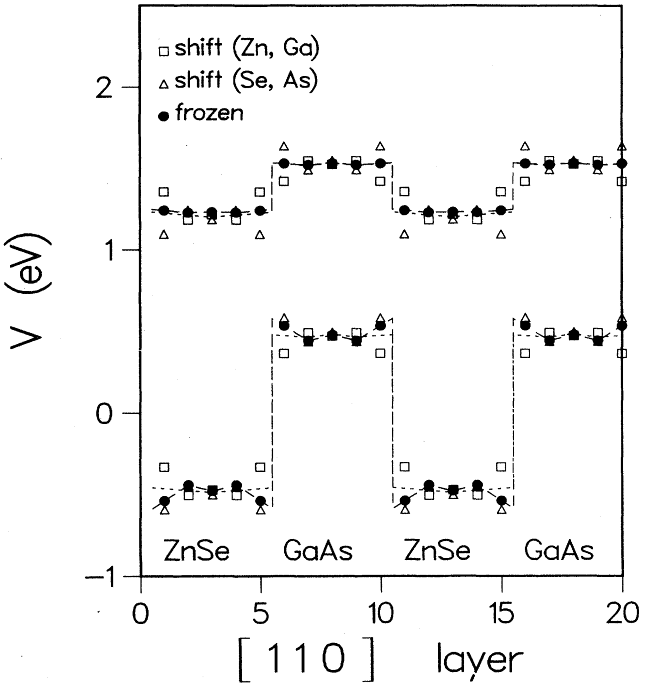

FIG. 1. Top of the valence band and bottom of the conduction band for the 5+5 [110] ZnSe/GaAs superlattice. The dashed and dotted lines connects the frozen-potential and shifted bulk results, respectively.

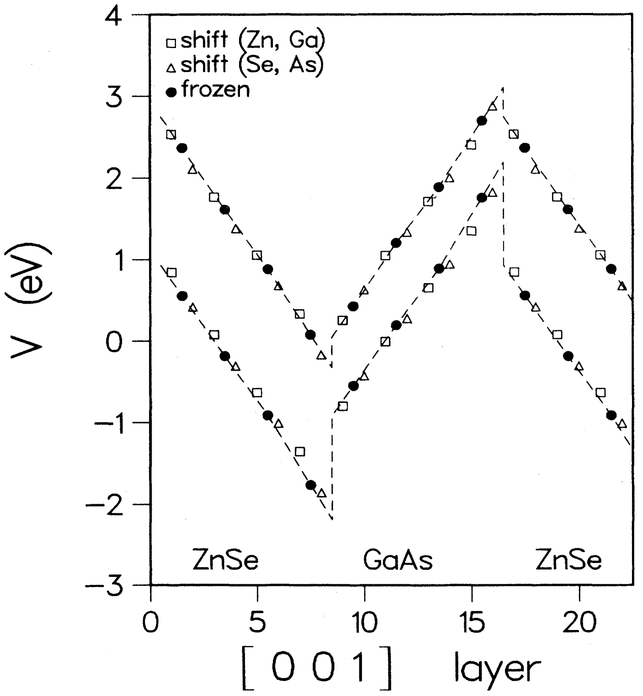

FIG. 2. Top of the valence band and bottom of the conduction band for the 4+4 [001] ZnSe/GaAs superlattice. The dashed line connects the frozen-potential results.

spectively. Away from the interfaces the potentials of the atoms in the superlattice and the bulk are more alike and the scatter decreases to 1–10 meV. This defines the accuracy levels of the shifts ΔV_v near and away from the interfaces.

Two important conclusions can be drawn from Fig. 1 and the preceding paragraph. First, away from the interface the results of the two methods are equal to within a few meV. Second, the shifts of the potentials of the atoms (□ and △) within the same interface layer are very different, e.g., $\Delta V_{\mathrm{Zn}} - \Delta V_{\mathrm{sc}} = 258$ MeV. Thus the frozen potential taken from a unit cell at the superlattice interface is, in that sense, different from that of the bulk system on an energy scale of 260 meV. However, the LDA gap, calculated using the frozen-potential scheme applied to the different layers, varies on a smaller scale: $E_g^{\text{layer 1 or 5}} = 1.78$ eV, $E_g^{(\text{layer 2or 4})} = 1.67$ eV, and $E_g^{(\text{layer 3})} = 1.71$ eV (cf. $E_g^{(\text{bulk ZnSe})} = 1.69$ eV). The valence-band offset is obtained by calculating difference of the tops of the valence bands between the middle layers of the superlattice yielding $E^{\mathrm{GaAs}} - E^{\mathrm{ZnSe}} \sim 0.9$ eV for the 5+5 [110] ZnSe/GaAs superlattice from either method.

Figure 2 shows the results for 4+4 [001] ZnSe/GaAs superlattice. The most striking feature is the presence of large electric fields with opposite signs between the polar interfaces. From Fig. 2 the strength of the electric field is found to be 0.76 eV/ML. Naively, one would expect this field to be due to a negative- and positive-charge buildup at the ZnSe/GaAs and GaAs/ZnSe interfaces, respectively. Using the expression for the electric field $\mathcal{E}_c$ between an infinite repetition of two parallel capacitor plates charged with $\pm\sigma$ electrons per unit area, $\mathcal{E}_c = 2\pi\sigma_c$ (cgs. units), a field of 0.76 eV/ML is seen to correspond to a charge accumulation of $\sigma_c = +0.048$ and $\sigma_c = -0.048$ electrons at the ZnSe/GaAs interface and the GaAs/ZnSe interface, respectively; in this paper σ will be in units of the number of electrons per area $a^2/2$ ($a = 5.660$ Å is the lattice constant). However, from the calculations the charge is found to be only $\sigma_c = \pm 0.016$ electrons at the two different interfaces, corresponding to a field of only 0.26 eV/ML. The calculated charge σ_c at an interface is defined to be equal to the accumulated charge—with respect to the bulk—in a volume with an area $a^2/2$ extending one monolayer ($a/2$) to both sides of that interface.

We will now analyze the origin of the electric fields present in the $n+n$ [001] superlattices. The major part of the electric field is due to the different layer ionicity of bulk ZnSe and GaAs along [001]: in the bulk the Zn and Se layers along [001] contain +0.211 and −0.211 electrons per area $a^2/2$, respectively, whereas the Ga and As layers along [001] contain +0.146 and −0.146 electrons per area $a^2/2$, respectively; the layer-ionicity charge is defined as $Q - Z$, where Q is the total number of electrons and Z the total nuclear charge in that layer. Note that according to this definition the layer ionicity in bulk ZnSe (or GaAs) along [110] is 0, since a plane contains both Zn and Se atoms. The charged layers may be viewed as a periodic repetition of parallel capacitor plates with charges $\pm\sigma^{\mathrm{ZnSe}}$ and $\pm\sigma^{\mathrm{GaAs}}$ in the corresponding parts of the superlattice. From simple electrostatics the magnitude of the resulting electric field, having opposite signs in the ZnSe and GaAs parts, if found to be $\mathcal{E}_i = \pi(\sigma^{\mathrm{ZnSe}} - \sigma^{\mathrm{GaAs}}) = 0.52$ eV/ML.

The sum of the fields due to the difference in layer ionicity and that due to charge accumulation at the interfaces is 0.78 eV/ML and thus almost equal to the field as obtained directly from Fig. 2.

Table I contains the data on the charge accumulation at the polar interfaces and the resulting electric fields for the $n+n$ [001] ZnSe/GaAs, ZnSe/Ge, and GaAs/Ge superlattices. Clearly, the electric field due to the difference in layer ionicity between the two semiconductors constituting a superlattice dominates the total electric field. Moreover, the charge accumulation does not seem to depend very strongly on the thickness of the superlattices, i.e., n. This is surprising since in, e.g., the 4+4 [001]

TABLE I. Charge accumulation and electric fields in the $n+n$ [001] ZnSe/GaAs, ZnSe/Ge, and GaAs/Ge superlattices. $\sigma^{A,B}$ is the charge per [001] anion/cation layer (thickness is 1.4 Å) as found from a bulk calculation. σ_c is the charge accumulation at the B/A interface as found in the superlattice calculation. $\mathcal{E}_i = \pi(\sigma^A - \sigma^B)$ is the contribution to the electric field due to the difference in layer ionicity between the two semiconductors. $\mathcal{E}_c = 2\pi\sigma_c$ is the contribution to the electric field due to charge accumulation at the interfaces. $\mathcal{E}$ is the electric field as obtained directly from the shifted bulk or frozen-potential results. All charges are in units of electrons per area $a^2/2$ where a is the lattice constant. The electric fields are in units of eV/ML.

A/B	σ^A	σ^B	σ_c	$\mathcal{E}_i$	$\mathcal{E}_c$	$\mathcal{E}_i + \mathcal{E}_c$	$\mathcal{E}$
			ZnSe/GaAs				
2+2	0.211	0.146	0.023	0.52	0.37	0.89	0.88
3+3	0.211	0.146	0.017	0.52	0.27	0.79	0.80
4+4	0.211	0.146	0.016	0.52	0.26	0.78	0.76
			ZnSe/Ge				
2+2	0.210	0.0	−0.059	1.68	−0.95	0.73	0.70
3+3	0.210	0.0	−0.072	1.68	−1.15	0.53	0.53
			GaAs/Ge				
2+2	0.147	0.0	−0.048	1.18	−0.77	0.41	0.38
3+3	0.147	0.0	−0.049	1.18	−0.78	0.40	0.40

TABLE II. Valence-band offsets determined with the shifted bulk method and the frozen-potential method for the $n+n$ [001] and [110] ZnSe/GaAs, ZnSe/Ge, and GaAs/Ge superlattices. A correction for the spin-orbit splitting has been added to our results to enable a comparison with the results of Christensen (Ref. 2). All energies are in eV.

	[001]				[110]		
	ZnSe/GaAs		GaAs/ZnSe			ZnSe/GaAs	
	shift	frozen	shift	frozen	shift	frozen	Ref. 2
1+1	1.03	1.30	−0.92	−1.30	0.98	1.32	1.25
2+2	1.09	1.17	−0.93	−1.17	0.88	0.99	
3+3	1.09	1.25	−0.96	−1.22	0.93	0.93	0.98
4+4	1.09	1.25	−0.98	−1.24	0.86	0.80	
5+5					0.90	0.87	1.07
	ZnSe/Ge		Ge/ZnSe			ZnSe/Ge	
	shift	frozen	shift	frozen	shift	frozen	Ref. 2
1+1	1.46	1.77	−1.50	−1.77	1.47	1.77	1.85
2+2	1.58	1.66	−1.52	−1.49	1.36	1.48	
3+3	1.61	1.67	−1.57	−1.59	1.34	1.26	1.39
	GaAs/Ge		Ge/GaAs			GaAs/Ge	
	shift	frozen	shift	frozen	shift	frozen	Ref. 2
1+1	0.57	0.72	−0.57	−0.72	0.57	0.72	0.66
2+2	0.62	0.65	−0.62	−0.69	0.53	0.59	
3+3	0.61	0.67	−0.62	−0.71	0.56	0.53	0.43

ZnSe/GaAs superlattice (see Fig. 2), the conduction band near the ZnSe/GaAs interface is below the valence band near the GaAs/ZnSe interface. Electrons would be expected to fill the empty states near the ZnSe/GeAs interfaces, leaving empty states—holes—behind near the GaAs/ZnSe interface. Instead, from Table I it is seen that electrons and holes are accumulated at the GaAs/ZnSe and ZnSe/GaAs interfaces, respectively, thus enhancing the electric field $\mathcal{E}_c$. This can be understood by analyzing the wave functions in some detail. It is found that the (negative) charge accumulated at the GaAs/ZnSe interface resides, for the largest part, in atomiclike s and p states of the Zn atom closest to that interface, whereas the (positive) charge accumulated at the ZnSe/GaAs interface resides in atomiclike p states of the Ga atom closest to that interface. Only the local redistribution of charge due to the difference in ionicity between the Zn, Se, Ga, and As atoms determines the charge separation. The localized nature of these states explains the small n dependence of our results. Moreover, it should be realized that both the energy gained by letting electrons and holes occupy energetically more favorable states and the energy needed to separate these electrons and holes scale with n leading to an n-independent effect.[13]

We now focus on the valence-band offset. Since the [001] ZnSe/GaAs superlattices have two different interfaces, i.e., the ZnSe/GaAs and GaAs/ZnSe interfaces, two different valence-band offsets can be expected. From the jump in the dashed line in Fig. 2 we find ~1.1 and ~1.0 eV for the ZnSe/GaAs interface and the GaAs/ZnSe interface, respectively. Despite the presence of the strong electric field, the frozen-potential method and the shifted potential method give similar results. We note that due to the difference in the valence-band offset the electric fields are only approximately equal and opposite in the different parts of the superlattice. This small effect is ignored.

In Table II we have collected all our calculated results on the valence-band offset. The difference between the valence-band offset of a [001] ZnSe/GaAs interface and that of a [001] GaAs/ZnSe interface is seen to be approximately 100 meV. Moreover, the valence-band offset for the [110] ZnSe/GaAs superlattices is smaller by approximately 150 meV than the average of those of the [001] superlattices. We also note that our results for the frozen-potential method are in reasonable agreement with those of Christensen.[2] The differences are probably due to our different treatment of the Ga and Zn $3d$ states.[14]

The valence-band offsets for the [001] superlattices obtained with the frozen-potential and the shifted bulk method are seen to differ systematically (e.g., 0.16 eV for the ZnSe/GaAs interface). This is due to the different interpolation schemes hidden in the two methods.[15] The wave functions associated with the top of the valence-band states have their largest amplitude at the anion, and it is thus expected that the frozen-potential results for the valence band follow the shifted bulk anion valence-band results (the ●'s follow the △'s closely in the valence band; see Figs. 1 and 2). In the case of the [001] ZnSe/GaAs superlattices this results in too large a frozen-potential value for the valence-band offset. Similarly, the frozen-potential results for the conduction band follow the average of shifted bulk anion and cation conduction band. This indicates that the frozen-potential scheme is less suited for [001] superlattices than the shifted bulk method.

From Table II the results from the shifted bulk method are seen to be less dependent on n than those from the frozen-potential method, certainly for the [110] superlattices. This is caused by the large energy shifts, mentioned before, between the different atoms. Also, from Table I, the charge accumulation at the [001] interfaces is seen to be more or less n independent. Apparently, the valence-band offset and the charge accumulation are completely determined at the interfaces, both for polar and for nonpolar interfaces.

Finally, we note that the conduction-band offsets should not be obtained from the results in, e.g., Figs. 1 and 2, since the LDA gaps are known to be incorrect. A much better approximation would be to obtain it from the valence-band offset by adding the difference of the experimental gaps of each semiconductor, e.g., the conduction-band offset for [110] ZnSe/GaAs becomes $\Delta E(\mathrm{VB}) + [E_g(\mathrm{GaAs}) - E_g(\mathrm{ZnSe})] \simeq 0.9 + (1.5 - 2.7) = -0.3$ eV.

In conclusion, we have shown that the valence-band offset is to a large extent orientation independent in $n+n$ [001] and [110] ZnSe/GaAs, ZnSe/Ge, and GaAs/Ge superlattices, despite the presence of large electric fields in the $n+n$ [001] superlattices. The greatest orientation dependence, $\simeq 0.25$ eV, is found for the ZnSe/Ge superlattices. The largest contribution to these fields comes from the difference in layer ionicity between the two semiconductors and not from the charge accumulation at the polar interfaces.

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[13] The total energy calculations are in agreement with this. We find the following heats of formation for the 1+1, 2+2, 3+3, and 4+4 [001] ZnSe/GaAs superlattices: −0.27, −0.38, −0.49, an −0.60 eV per unit cell, respectively. Thus, apart from a constant of approximately −0.27 eV, the heat of formation scales with the number of atoms in the unit cell. The relevant energy, the energy per atom or per interface, is n independent.

[14] We treat the Ga 3d states as core states and the Zn 3d states as valence-band states. Christensen peforms always two frozen-potential calculations, one with the corelike d states and one with higher d states included. He obtains the valence-band offset by taking the average value obtained from the two calculations.

[15] In the frozen-potential method the potentials of the anion and the cation are used to obtain one energy for, say, the top of the valence band at one position, namely, the center of the unit cell. For different states the anion and the cation potential contribute differently to the energy; e.g., the top of the valence-band state contains mainly anion character. In the shifted bulk method one energy is obtained for the anion and one for the cation at their respective positions. The energy at the center of the unit cell can be obtained by interpolating between these two. Thus the anion and the cation potential contribute equally. If the anion and cation potentials are shifted by different amounts and the state under consideration has uneven anion and cation character the two methods produce different results.