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# Band offsets in heterostructures with thin interlayers

N. E. Christensen and L. Brey*
*Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65,*
*D-7000 Stuttgart 80, Federal Republic of Germany*

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The valence-band offsets in lattice-matched semiconductor heterostructures are calculated from first principles by means of the self-consistent, relativistic linear-muffin-tin-orbital method applied in *supercell* geometries. The influence of the interface structure on the offset value is examined by performing calculations for systems with ultrathin interlayers introduced at the [nonpolar (110)] interface between the two constituents. For a wide class of systems it is found that the offset is surprisingly *in*sensitive to the inserted interlayer, although, for a given pair of heterostructure constituents, different interlayers cause vastly different charge distributions in the atomic layers close to the interface. In these cases the *dipole* and thus the offset remain essentially the same as for the system without interlayer. A particular, presumably small, class of semiconductor interlayers are able to affect the offset clearly. These are the semiconductors that in their bulk form introduce deviations from the "transitivity rule" (CuBr) in binary heterostructures.

## I. INTRODUCTION

The electronic structures of semiconductor superlattices have attracted much interest during the last few years due to the great technological importance of such systems. In particular the discontinuities in the band edges at the interface between two semiconductors, the valence- and conduction-band offsets, are important quantities, and reliable predictions of their magnitudes from theoretical points of view is considered to be a significant part of what may be called theoretical *materials design* for such systems. In this context it is interesting to examine how modifications of the nature of the interface may affect the offset values. One obvious way of performing this kind of band-gap engineering would consist in trying to modify the interface by adding an additional (thin) layer of another material. It is the purpose of the present paper to present examples of such calculations. For the examination of the interlayer effects we have chosen here to consider only nonpolar (110) interfaces.[1] The examples included here suggest that in these cases very little in the direction of offset "design" can be achieved. The offsets turn out to be those obtained without interlayers. This somewhat disappointing result does, however, have interesting consequences, as it suggests that the offset values are essentially governed by *bulk* properties of the individual semiconductors. This gives further support to *model theories* that are based on the assumption of a (partial) alignment of particular energy levels, *charge-neutrality* levels as the interface is formed.[2-5]

There are exceptions, though, to the rule stated above about the insensitivity of the offset to the interlayers. We show that these occur when the interlayer consists of a semiconductor which, when used as one component of a binary heterostructure, causes a noticeable deviation from the "transitivity rule." CuBr is an example[6] of such a compound.

The results of the calculations for superlattices with the thin interlayers are presented and discussed in Sec. II. In this study we also include the academic example of a "vacuum" interlayer, and is argued that a vacuum behaves similarly to CuBr in the sense of causing nontransitivity. In order to discuss this in more detail we present in Sec. III the results of superlattice calculations for AlAs(110) and GaAs(110) surfaces, neglecting relaxation. Section IV contains the conclusions, and in an Appendix we briefly discuss definitions of "interface-induced" dipoles.

## II. RESULTS AND DISCUSSION

The results which are described here are all derived from self-consistent band-structure calculations using the linear-muffin-tin-orbital (LMTO) formalism[7] in supercell geometries. The same method was earlier applied to similar problems.[8] We use the local-density approximation (LDA) to the density-functional theory. The LDA functional constructed by Ceperley and Alder[9] is applied in Perdew and Zunger's parametrized form.[10] The relativistic corrections suggested by MacDonald and Vosko[11] are included. More details of the method are given in Ref. 8. Here we just mention that the outer corelike cation *d* states, where necessary (Cd,Ga,In) are treated as fully relaxed band states, and all supercell calculations, even those where there are no low-lying *d* states to be treated as band states, are iterated to self-consistency using two energy panels. This ensures the optimum description of the anion *s* states. Also, as usual when the LMTO method is applied to zinc-blende-type semiconductors, two "empty spheres," located at the interstitial positions, are in included for each formula unit in the cell. These are treated as "atoms" without nuclear charge ($Z=0$).

The self-consistent charge distribution in the supercell may be illustrated by displaying the excess number of electrons in each layer parallel to the interface, i.e., the total number of electrons in the four atomic spheres in each layer of the supercell minus the sum of the atomic numbers associated with these spheres ($Z_c$, $Z_a$, 0, 0, the cation-, anion-atoms, and the two empty spheres). In Fig. 1 this electron distribution is shown for AlAs/GaAs (110), and the effect of inserting thin layers of a third semiconductor compound is illustrated in Figs. 2–5. Interlayers of ionic compounds (Figs. 4 and 5) strongly modify the charge distributions in the AlAs and GaAs layers close to the interface. In spite of this, it turns out that the difference between the average potentials in the central layers of the AlAs and GaAs sides of the cell is very close to the value obtained for AlAs/GaAs without interlayer for all the cases represented in the graphs here. The difference between the offsets of the heterostructures with GaSb and ZnSe interlayers is 0.1 eV, but each of them differ from the "pure" AlAs/GaAs value, 0.55 eV (5 + 5 cell), by only 0.05 eV. The offsets are thus surprisingly insensitive to the insertion of an (semiconductor) interlayer. In Figs. 6 and 7 we show the valence-band profiles for two AlAs/GaAs superlattices with one and two Ge interlayers, respectively. These are obtained by the "frozen potential" method described in Refs. 8 and 6. The AlAs/GaAs offset is, as indicated in these figures, in both cases 0.58 eV, close to what was found in the supercell calculation of pure[8] AlAs/GaAs, 0.53 eV. Further, it is interesting to note that although the Ge interlayers are extremely thin, one and two monolayers, the calculations here also give the AlAs/Ge and GaAs/Ge discontinuities

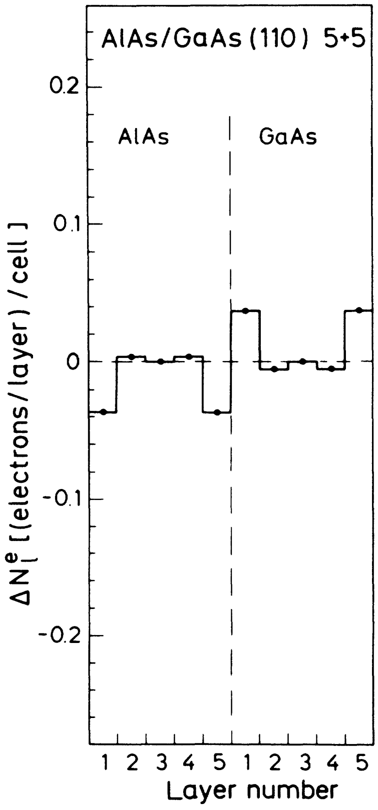

FIG. 1. Excess number of electrons in each layer of the 5 + 5 supercell for AlAs/GaAs in the (110) orientation.

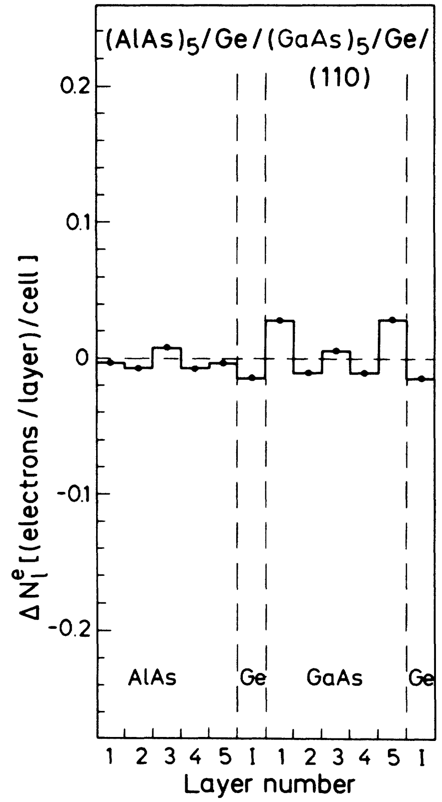

FIG. 2. Excess electron numbers on each atomic layer of the (110) cell for AlAs/GaAs with single Ge interlayer (i.e., a layer with one $Ge_2$ formula unit per cell).

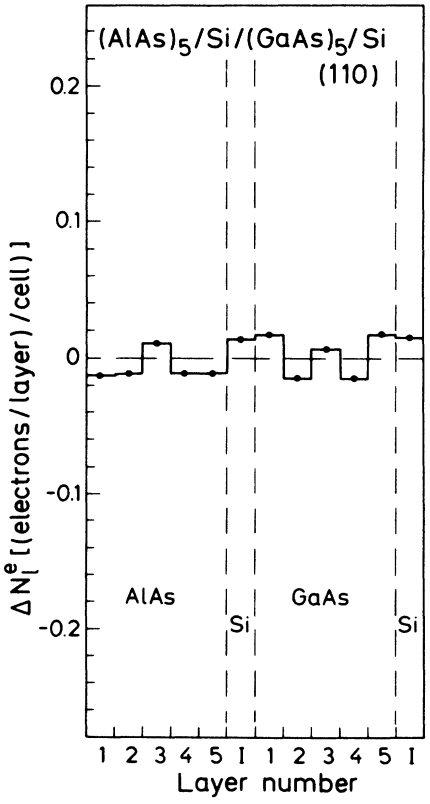

FIG. 3. Electron distribution in AlAs/GaAs (110) with a Si interlayer.

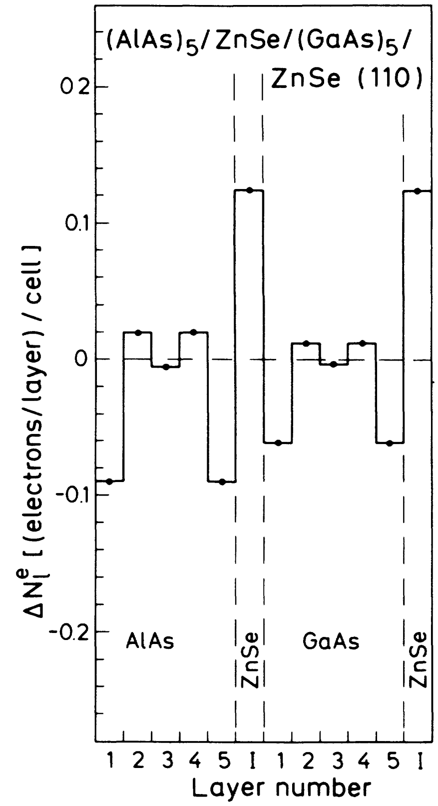

FIG. 4. Electron distribution in AlAs/GaAs with a single ZnSe interlayer.

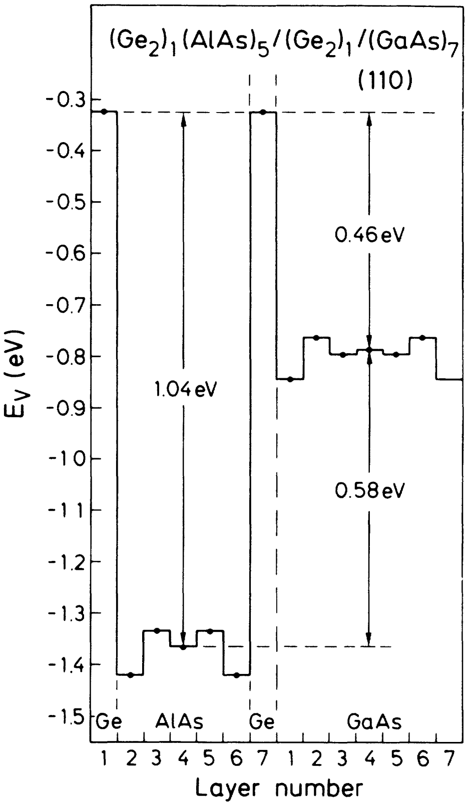

FIG. 6. Valence-band-edge profile through the superlattice of AlAs/GaAs with a monolayer of Ge deposited at the interface.

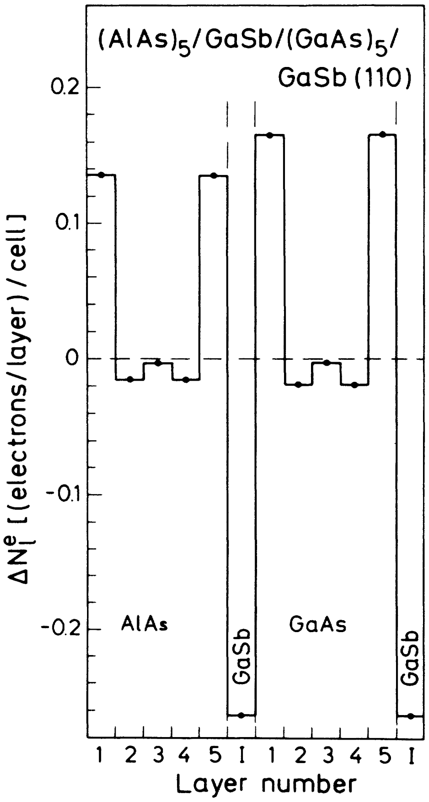

FIG. 5. Electron distribution in AlAs/GaAs with a single GaSb interlayer.

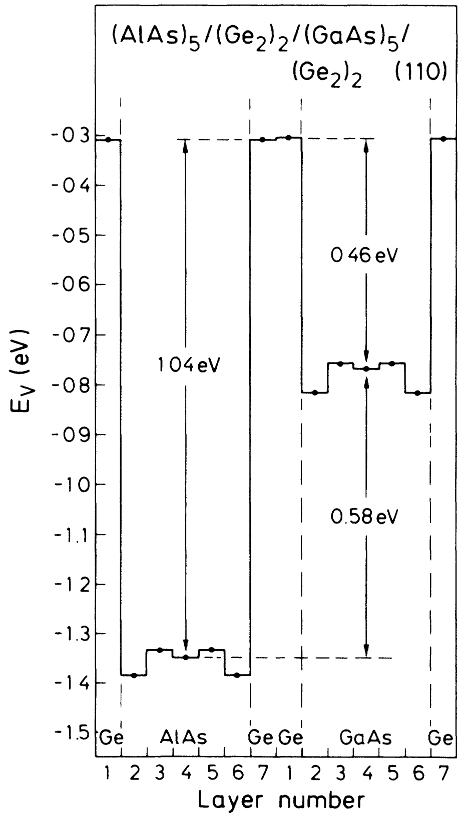

FIG. 7. Valence-band-edge profile through the superlattice of AlAs/GaAs with two Ge interlayers.

(1.04 and 0.46 eV, respectively) in close agreement with the results obtained from the $7+7$ AlAs/Ge and GaAs/Ge supercell calculations.[8] AlAs/Ge, Ge/GaAs, and AlAs/GaAs represent a series of heterostructures for which we have found[6] that the transitivity rule is fulfilled. The calculations here shows that this even holds for the extremely thin layers.

The results of the superlattice calculations including thin interlayers are summarized in Table I (see the Appendix). Disregarding shifts in $\Delta E_v$ of the order of 0.05 eV it is concluded that by far the majority of the interlayers studied here are unable to modify the offset values. The very hypothetical case where ZnSe is deposited with interchanged anion and cation sites causes a very large perturbation of the charge distribution, and a reduction, nevertheless moderate, of the offset is found. There are a few cases where a noticeable shift is predicted. These are marked with an asterisk in Table I. A CuBr interlayer reduces the AlAs/GaAs offset by 0.15 eV and that of AlAs/Ge by 0.28 eV. This compound, CuBr, was found[6] to produce nontransitivity due to the formation of localized interface states. The results here demonstrate that these also are present in the interlayer heterostructures and clearly modify the dipole. The presence of interface states has also been found by calculating layer-projected density-of-states functions. In Table I we have also included calculations where the interlayer is taken to be a vacuum layer, i.e., one single layer consisting entirely of empty spheres. Curiously enough, this does not affect the CdTe/InSb offset, but that of AlAs/GaAs is reduced by 0.18 eV. "Vacuum" behaves, when chosen as one of the constituents in a structure, similarly to CuBr. Pronounced interface states (surface states) appear, and transitivity is not fulfilled; the valence-band top in the interior of semi-infinite GaAs lies (see Sec. III) 0.82 eV above that of semiinfinite AlAs, i.e., differing appreciably from the AlAs/GaAs heterostructure band offset, 0.53 eV.

## III. SUPERCELL CALCULATIONS FOR IDEALIZED SURFACES

Although it is the purpose of the present work to examine the heterostructures with thin interlayers, it is of interest to digress to the surface calculations which were used in the discussion above. In these we neglect relaxation, and the supercell calculations are therefore performed along the same lines as used for the usual superlattices. One part of the cell is in this case just occupied entirely by empty spheres. In Fig. 8 the most important energy profiles are shown for the AlAs/vacuum $7+7$ supercell. A similar calculation for GaAs was not size converged (on the GaAs side), and therefore we used nine layers of GaAs. Referring, as in Fig. 8, energy levels to

TABLE I. Valence-band offsets and interface-induced dipole (see the Appendix) in heterostructures, $(A)_m/I/(B)_n/I/$, with interlayers $I$ all in the (110) orientation. Energies are in eV.

| $A$ | $B$ | $(m,n)$ | $I$[a] | $\Delta E_v$ | $V_{\text{dip}}$ |
|---|---|---|---|---|---|
| AlAs | GaAs | (5,5) | | 0.55 | 0.05 |
| AlAs | GaAs | (7,7) | | 0.53 | 0.03 |
| AlAs | GaAs | (5,5) | GeGe | 0.53 | 0.03 |
| AlAs | GaAs | (5,7) | GeGe | 0.58 | 0.08 |
| AlAs | GaAs | (5,5) | 2GeGe | 0.58 | 0.08 |
| AlAs | GaAs | (5,5) | SiSi | 0.61 | 0.11 |
| AlAs | GaAs | (5,5) | GaSb | 0.61 | 0.11 |
| AlAs | GaAs | (5,5) | ZnSe | 0.51 | 0.01 |
| AlAs | GaAs | (5,5) | SeZn | 0.46* | −0.04 |
| AlAs | GaAs | (5,7) | CuBr | 0.40* | −0.10 |
| AlAs | GaAs | (5,5) | *EE*[b] | 0.38* | −0.12 |
| AlAs | GeGe | (5,5) | | 1.06 | 0.33 |
| AlAs | GeGe | (7,7) | | 1.03 | 0.31 |
| AlAs | GeGe | (5,7) | CuBr | 0.80* | 0.07 |
| AlP | SiSi | (5,5) | | 0.93 | 0.00 |
| AlP | SiSi | (7,7) | | 0.91 | −0.02 |
| AlP | SiSi | (5,5) | GeGe | 0.87 | −0.04 |
| AlP | SiSi | (5,5) | AlAs | 0.87 | −0.04 |
| CdTe | InSb | (5,5) | | 1.07 | −0.03 |
| CdTe | InSb | (7,7) | | 0.93 | −0.17 |
| CdTe | InSb | (5,5) | GeGe | 1.04 | −0.03 |
| CdTe | InSb | (5,5) | *EE*[b] | 1.08 | −0.02 |

[a] The interlayer (monolayer) is specified as $I_c I_a$ where $I_c$ is the atom on the cation position and $I_a$ gives the atom occupying the anion position in the lattice.

[a] *EE* ("empty sphere–empty sphere") means a vacuum layer of the thickness of one bulk semiconductor layer.

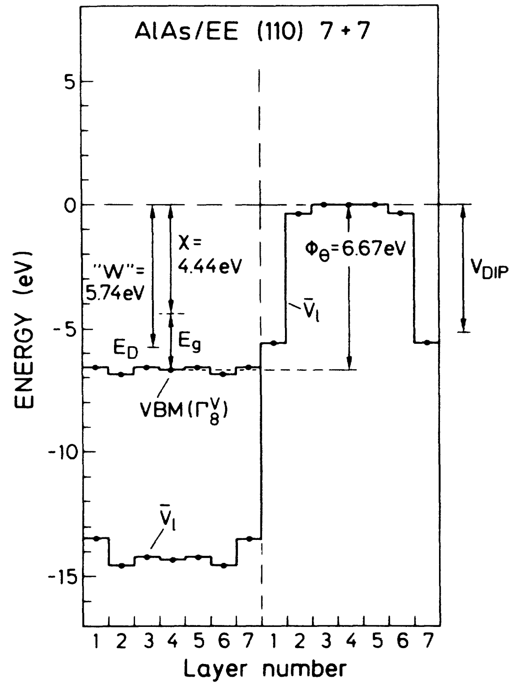

FIG. 8. Supercell calculation for idealized, unrelaxed (110) AlAs surface: Valence-band maximum in AlAs (VBM) derived for each layer by the frozen-potential method, and the layer-averaged potential at the atomic-sphere surfaces ($\bar{V}_l$) through the supercell containing seven layers of AlAs and seven layers of empty spheres (vacuum). In the figure the following quantities are indicated: the photothreshold $\Phi_\theta$, the affinity $X$, the surface dipole $V_{\mathrm{dip}}$, and the work function $W$, here defined as the difference between the vacuum level and the dielectric midgap energy $E_D$. The surface dipole $V_{\mathrm{dip}}$ is derived as described in the text (see Fig. 10).

the vacuum potential, we find the valence-band maximum (VBM) of GaAs to lie at $-6.13$ eV, i.e., the photoemission threshold is 6.13 eV. Subtracting from this the experimental gap, 1.52 eV, the electron affinity is calculated to be 4.61 eV. The experimental value given for the (110) surface in Ref. 12 is 4.4 eV, and since we have not included relaxation of the atom positions at the surface we consider the theoretical value to agree well with experiment.

The electron distribution in the AlAs/vacuum (110) cell is shown in Fig. 9. A large number of electrons spill out into the first layer of vacuum sphere, but the density is zero already in the third vacuum layer. The surface dipole, $V_{\mathrm{dip}}$, is calculated as described in the Appendix and as illustrated in Fig. 10. The profile of the layer-averaged potential shown in Fig. 8 is obtained from total potentials, i.e., the exchange-correlation contributions are included. Therefore, and since in that figure there is no subtraction of bulk quantities, the potential of the central AlAs layer is not just $-V_{\mathrm{dip}}$, but considerably lower, of course.

The level $E_D$ in Fig. 8 is the dielectric midgap energy (DME) defined as in Ref. 13 but here derived from a frozen-potential calculation using the potentials in the central AlAs layer of the supercell. We have decided to

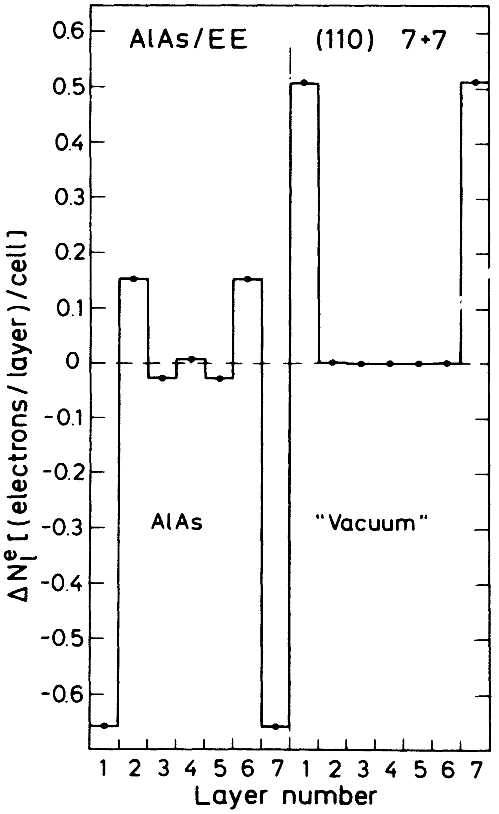

FIG. 9. Excess electron distribution in the (110) supercell representing the idealized AlAs(110) surface calculation.

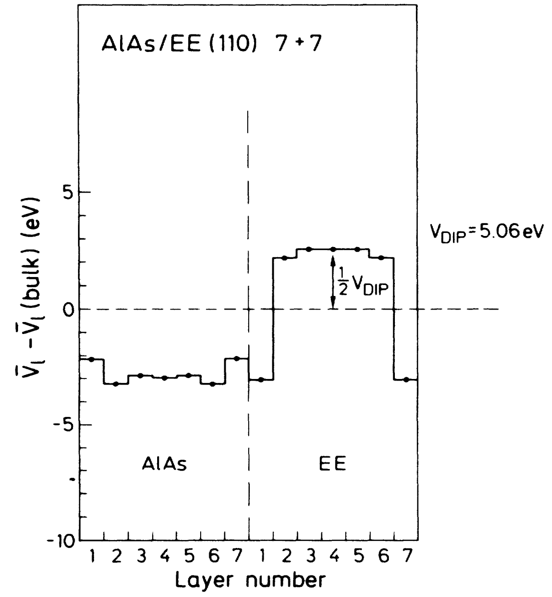

FIG. 10. Surface dipole of AlAs(110) defined as the layer-averaged potentials minus the corresponding bulk quantities (see the Appendix).

call the difference between the vacuum level and this $E_D$ the "work function," $W$. The reason is that the DME model[13] theory predicts that the Fermi level of a metal (sample holder in a spectrometer, for example) lines up with $E_D$ when brought in contact with the semiconductor.

## IV. CONCLUSIONS

The present calculations illustrate that the heterostructure band discontinuities are determined largely by polarization properties that are inherent to the bulk constituent semiconductors. This supports the model theories of the "charge-neutrality-point" type, and agrees well with the recent theory based on interface-bond polarities derived from the wave functions of the bulk crystals.[14] As in the examination of the transitivity rule, though, we also find here exceptions from this rule. There are semiconductor interfaces (and surfaces, of course) where specific electronic properties appear which modify the interface dipole by producing an anomalous charge transfer. These interface specific features cannot be described by theories that apply only to quantities related to the bulk properties of the constituents. The conclusion that was reached in that respect from calculations for the binary superlattices consisting of "thick" layers of each compound, also applies to the case of ultrathin interlayers as studied here. *A priori* it could not have been ruled out that the very thin layers would introduce new features because the charge rearrangement usually occurs over 2–4 layers near the interface.

The conclusion that only very limited possibilities seem to exist for performing a band-gap engineering by inserting interlayers is thus somewhat disappointing, and this even more so if one considers the stability of these heterostructures. Total-energy calculations have shown[15] that all GaAs/AlAs are unstable (metastable), and that the enthalpy of formation for the (110) interface is of the order of 24 meV per interface. Repeating the total-energy calculation for the system with a Ge interlayer we have found that the enthalpy increases to 446 meV per (nominal) GaAs/AlAs interface. We would therefore expect that in practice it would be even considerably more difficult to grow with, for example, the molecular-beam-epitaxy (MBE) technique, well-characterized superlattices with thin interlayers than it is to construct the usual binary systems.

We have in the present work not considered the effects of inserting thin, metallic interlayers in the heterojunctions. Some Schottky systems are known not to obey the transitivity rule (e.g., $NiSi_2$/Si), and in view of the discussion here of the relation between nontransitivity and offset modification, we would expect that also certain metallic interlayers might affect the VBM offsets.

It should be emphasized that although the band offsets are in most cases not affected by insertion of a semiconductor interlayer this does not imply that the band structures of ultrashort-period superlattices are unmodified. The offset values refer to the relative band-edge positions far away from the interface. The actual band structure of a $(GaAs)_7/(AlAs)_7$ superlattice is clearly changed if a Ge interlayer is inserted. This can even change the nature of the fundamental gap, from spatially indirect to direct, for example. Such modifications can be achieved, though, also simply by varying the ratio $m/n$ for the thin $(A)_m/(B)_n$ superlattices. The total-energy calculations indicate that this method in practice would be better than the application of interlayers since these increase the instability of the superlattice.

## APPENDIX

In the last column of Table I we have included the interface-induced dipole, $V_{\rm dip}$. A variety of definitions of "the dipole" exists. One, which is frequently applied, in particular in connection with first-principles pseudopotential calculations, starts with a calculation of the difference between the the supercell- and bulk-electron densities, $\rho(z)$ averaged in layers parallel to the interface, and as a function of the distance $z$ from the interface. This function is then, by means of Poisson's equation, used to derive "the interface-induced dipole." The dipoles derived in that way, however, are not unambiguous since the charge-difference function which is used depends critically on where the mathematical surface that is representing the interface is chosen. This means that comparison of the dipoles for different interface orientations for a given compound makes little sense when this definition is used. We prefer to consider directly the potentials in the interior of the two sides of the supercell, and avoid in that way the ambiguity related to the lack of definition of a mathematical interface. We may define a *total* dipole, for example, as the difference between the average of the potentials at the atomic-sphere surfaces in the central layer on the $B$ side and the central layer on the $A$ side of the $(A)/(B)$ supercell. From this total dipole we then subtract the equivalent quantity calculated for the $B$ and $A$ bulk compounds, and this then gives what we define as the interface-induced dipole. This scheme is possible because the crystal potential here is always a lattice sum of atomic-sphere-approximation (ASA) potentials. We could equally well use the $B$-$A$ difference in Madelung potentials for selected central-layer atomic sites minus the equivalent bulk quantity. The induced dipole does not depend on whether a cation, an anion, or any of the two empty spheres are used in this calculation.

Although we prefer the definition of the interface dipole as given here, it is stressed that the observable quantities are the band offsets, and these are, of course, independent of how the dipole is defined formally.

[*] Permanent address: Departamento de Física del Estado Sólido, Facultad de Ciências, Universidad Autónoma de Madrid, Ciudad Universitaria de Cantoblanco, E-28049 Madrid, Spain.

[1] The present work thus examines the effects of modifying the interface electronic structure by changing boundary conditions at perfect, nonpolar interfaces without introducing changes in the dipole simply by changing the atomic arrangement. For polar interfaces, for example (001) AlAs/Ge, the band offsets depend very sensitively on the actual atomic positions in the interface regime. Interdiffusion modifies strongly the dipole and hence the offsets. Such effects are not the subject of the present work [electronic structure calculations for various AlAs/Ge (001) interfaces are discussed elsehere: N. E. Christensen (unpublished)].

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