Self-consistent calculation of the electronic structure of the (110) GaAs-ZnSe interface

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The abrupt (110) interface of GaAs-ZnSe is studied using the self-consistent pseudopotential method. No interface states are found in the fundamental gap, but interface states do split off from bulk states in some other regions. The band-edge discontinuity found in the present calculation does not satisfy the simple electron affinity rule; the calculated discontinuity of the conduction-band minima is 0.7 eV compared with the electron-affinity difference of 0.02 eV. The role of ionicity in the electronic structure of the interface is discussed.

I. INTRODUCTION

Self-consistent pseudopotential calculations[1,2] for the (110) interfaces of Ge-GaAs, AlAs-GaAs, and Ge-ZnSe have raised the question of whether interface states arise from the semiconductor-semiconductor ionicity difference or from the crystal symmetry change across the junction (or from both). Since the lattice mismatch is negligible (< 0.2%) in the systems studied and the junction is assumed to be perfectly smooth and abrupt, symmetry and ionicity differences are presumed to be the two possible causes for the existence of interface states. For the AlAs-GaAs interface, the ionicity changes by a very small amount, and the symmetry does not change at all (zinc blende-zinc blende) across the interface, and no interface states are found in the calculation. For Ge-GaAs and Ge-ZnSe interfaces, both the ionicity and the structural symmetry (diamond-zinc blende) change, and interface states are found. The GaAs-ZnSe interface considered here represents a prototype of a heterojunction between a III−V and a II−IV compound semiconductor where the ionicity changes across the interface without a corresponding change in symmetry (zinc blende-zinc blende). This system, therefore, should be useful in probing the questions raised above. Furthermore, by comparing the three systems (i.e., Ge-GaAs, Ge-ZnSe, and GaAs-ZnSe), we are able to extract interesting trends of the electronic structure of semiconductor-semiconductor interfaces as a function of ionicity difference.

Although there is a paucity of published experimental work on the GaAs-ZnSe interface, this system has been thought to be a good candidate for solar cell devices because of its high conversion efficiency.[3,4] Another attribute of this system is that a small lattice mismatch (0.2%) of the system (which is crucial in heterojunction devices) makes it possible to ignore effects due to dislocations or faceting and to focus on the variation in the potential across the interface.

For our calculations, we assume an abrupt (110) GaAs-ZnSe interface and use self-consistent pseudopotential techniques together with a superlattice geometry. This method has been described extensively elsewhere.[1,2,5] Our unit cell consists of seven layers of GaAs and seven layers of ZnSe. The atomic positions near a (110) interface in GaAs-ZnSe are shown in Fig. 1. As each (110) plane contains two
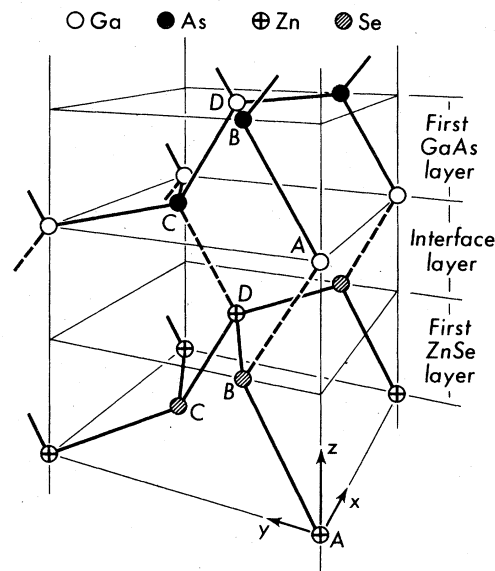

FIG. 1. Atomic positions near the GaAs-ZnSe (110) interface. Bonds are denoted by heavy solid lines except bonds across the interface which are shown as heavy dashed lines. The chains *ABAB* and *CDCD* are the two independent bonding chains perpendicular to the interface, containing the Ga-Se and As-Zn bonds, respectively. *z* is the direction perpendicular to the interface.

TABLE I. Ionic pseudopotential core parameters a_i for Ga, As, Zn, and Se entering Eq. (1) in the text. The potentials are normalized to a volume of 152.9 a.u. (Ref. 3) corresponding to a lattice constant $a_c = 10.696$ a.u. With q given in atomic units, the potential is in Rydbergs. (The Ga potential is accurate only for $q \leq 3$ a.u.)

Potential Parameters	Ga	As	Zn	Se
a_1	−0.338 45	−0.704 51	−0.303 7	−2.293 0
a_2	1.330 50	1.044 80	1.340 0	0.530 0
a_3	0.456 60	0.166 24	0.082 0	−0.570 0
a_4	0.007 05	−0.015 12	−0.008 6	−0.032 0

atoms per unit cell, the unit cell contains 28 atoms and two interfaces. Each interface is separated by seven layers; tests show that this distance is large enough to prevent significant interaction between interfaces. The lattice constants (a_c) are assumed to be 10.696 a.u. for both materials; this is a reasonable approximation because of the small lattice mismatch mentioned above. Relaxation or any other reconstruction is not incorporated in the geometry. Relaxation is presumably very small for nonpolar (110) interfaces compared to other low-index polar interfaces like (100) and (111) planes. Our idealized geometry yields a semiconducting interface in agreement with experiment.

The core pseudopotentials used in the calculation are parametrized in the form

$$V_{ps} = \frac{a_1}{q^2} (\cos a_2 q + a_3) e^{a_4 q^4} , \qquad (1)$$

and the values (Table I) of the a_i's have been obtained[1,2] by fitting bulk band structures. We have used the same pseudopotentials as Refs. 1 and 2 to facilitate comparison of the present results with previous calculations and to determine trends among the different systems. Approximately 350 plane waves are used in the basis set, and an additional ~900 plane waves are included via a second-order perturbation scheme. The $X\alpha$ method is used for calculating the exchange potential ($\alpha = 0.794$). The ionic pseudopotential is screened by the electrostatic potential of the electrons and the exchange potential. The degree of convergence and the self-consistency are approximately the same as in Refs. 1 and 2. When self-consistency (up to 10^{-3} Ry) is achieved, the average (total) potential on the ZnSe side is ~0.3 eV higher than the average on the GaAs side. The results calculated from this self-consistent potential are presented in Sec. II.

II. RESULTS

The self-consistent valence charge density for the (110) GaAs-ZnSe interface is shown in Fig. 2. The charge density is shown for two planes perpendicular

to the interface; one plane contains the Ga-Se, and the other contains the As-Zn bond across the interface. The charge density on each side, at a distance which is more than an atomic layer from the interface, reproduces the respective bulk charge density. This indicates, at least qualitatively, that the interface shown is effectively "isolated" from the other interfaces. A significant charge redistribution occurs within two layers of the interface. In a very simplified chemical valence picture, (Zn, Ga, As, Se) contribute (2, 3, 5, 6) electrons to their four tetrahedral
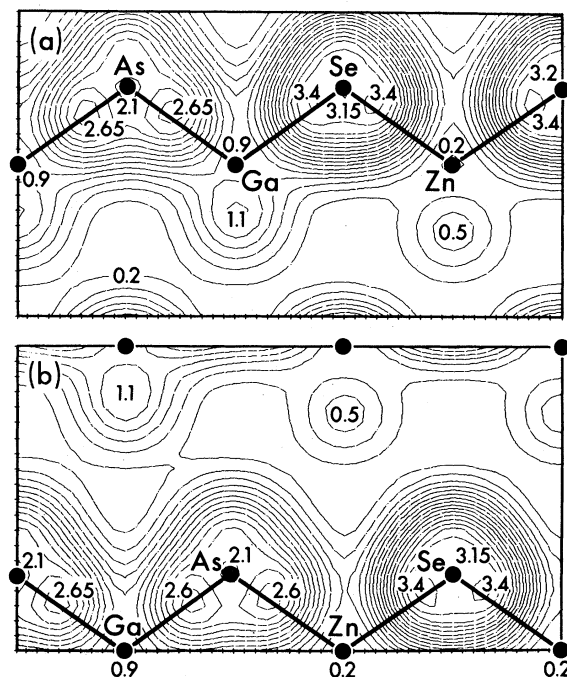

.FIG. 2. Contour plots of the total self-consistent valence charge density of GaAs-ZnSe, pictured in the planes perpendicular to the interface containing the $ABAB$ (a) and $CDCD$ (b) chains of Fig. 1. Only five layers of the unit cell, centered at the interface, are shown. The average charge density is normalized to unity; multiplication by 8 gives the number of electrons per bulk unit cell. Successive contours are separated by 0.2 units.

bonds; i.e., they contribute (0.5, 0.75, 1.25, 1.5) electrons/bond. This leads to an initial estimate of 2.25 and 1.75 electrons for Ga-Se and Zn-As bonds, respectively. To calculate the bonding charge at the interface, the unit cell is decomposed into regular parallelepipeds such that each region contains a single bond and the (pseudo) valence charge in the region is integrated. We have found Ga-Se and Zn-As bonds across the interface contain 2.27 and 1.73 electrons, respectively, showing that the argument above based on valency is verified to within our calculational accuracy ($\sim 1\%$).

The spectrum of interface states is shown in Fig. 3 together with the (110) projected band structures (PBS) of GaAs and ZnSe. *No interface states exist in the gap between the conduction band and the valence band.* The absence of interface states in this gap in the ideal junction is significant. This result is in contrast to the case of Ge-GaAs or Ge-ZnSe where interface states are found[1,2] in the gap. The existence of interface states in the gap can be related to band-gap lineup, which is a crucial characteristic of the heterojunction. From Fig. 3, the discontinuity of the valence-band maximum ($\Delta E_v = E_v^{GaAs} - E_v^{ZnSe}$) is ~ 2.0 eV. In previous calculations, $\Delta E_v \sim 0.4$ eV and ~ 2.0 eV for Ge-GaAs and Ge-ZnSe. An unusual feature of the present result is that ΔE_v is rather large in view of the ionicity difference across the interface. The ionicity difference across the interface for GaAs-ZnSe is approximately the same as that for Ge-GaAs and is one-half of the Ge-ZnSe value. For the Ge-GaAs interface, interface states split off from the upper valence band and are pushed up into the gap because of the difference between the Ge-Ga potential and the Ge-Ge potential. The splitting of the state and the movement into the gap is possible because the separation of the valence-band edges of the PBS between Ge and GaAs is small[1] (~ 0.4 eV at Γ). The separation of the valence-band edges of the PBS between Ge and ZnSe is large (~ 2.0 eV at Γ), but the ionicity difference is also large in this case. The influence of the Zn potential is stronger than that of Ga (strong enough to compensate for the wide separation of bands), and the interface states again appear above the Ge bulk valence band.[2] In the present case, the separation of the PBS near the valence-band maximum between GaAs and ZnSe is large while the ionicity difference (or, equivalently, potential difference) is equivalent to that of Ge-GaAs. Therefore, we only have interface *resonances* *below* the fundamental gap. In other words, the perturbation caused by the potential difference is not large enough to split off the interface resonances from the valence-band continuum.

The calculated value for ΔE_v seems to violate the simple electron affinity rule (EAR).[6] The electron affinities of GaAs and ZnSe are 4.07 and 4.09 eV,[3] while the band gaps of these materials are 1.53 and

───── GaAs-ZnSe interface states
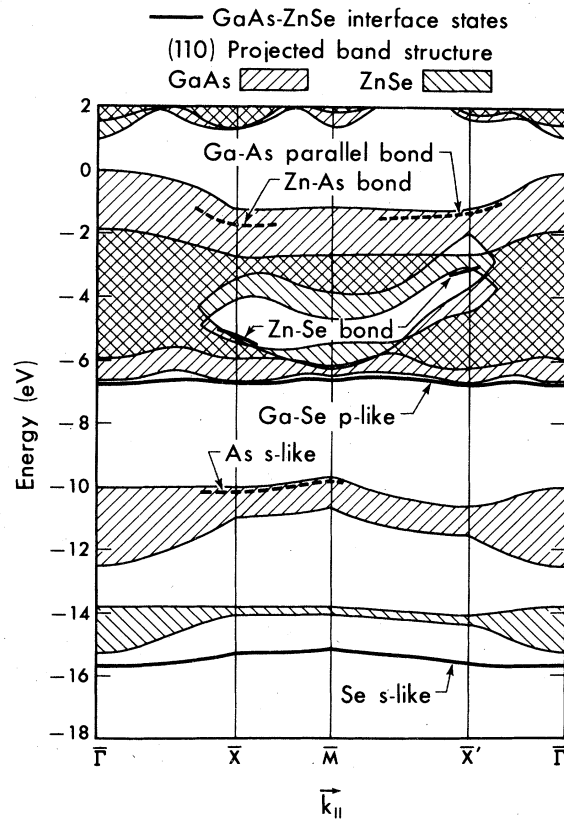(110) Projected band structure
GaAs ⬚⬚⬚   ZnSe ⬚⬚⬚

FIG. 3. Interface states of (110) GaAs-ZnSe relative to the projected band structures of bulk GaAs and ZnSe from self-consistent calculations. The dispersion of the interface states is denoted by heavy solid lines; heavy dashed lines indicate interface resonances.

2.80 eV (at 0 °K)[7] respectively. The EAR would predict $\Delta E_c = 0.02$ eV and $\Delta E_v = 1.29$ eV; the calculation yields $\Delta E_c \sim 0.7$ eV and $\Delta E_v \sim 2.0$ eV. The self-consistent charge redistribution can significantly alter the results obtained by the EAR. However, Frensley and Kroemer[8] estimated the correction due to the charge-transfer dipole to be only ~ 0.1 eV. Our results strongly indicate the free-surface dipoles can vary for different materials, and they do not, in general, cancel out when a heterojunction is formed. The concept of the "cancelling interface" providing the theoretical justification for the EAR does not seem to be quantitatively valid.

Anaylzing our data for Ge-GaAs, Ge-ZnSe, and GaAs-ZnSe, we have found that a consistent explanation for the band-edge lineup is possible if we assume that the surface dipole of GaAs (namely, vacuum-GaAs interface) is stronger by ~ 0.6 eV than that of Ge (therefore, the average bulk potential of GaAs relative to vacuum level is *lower* than that of Ge by ~ 0.6 eV) and stronger by ~ 1.0 eV than that of ZnSe. Charge redistribution of the heterojunction
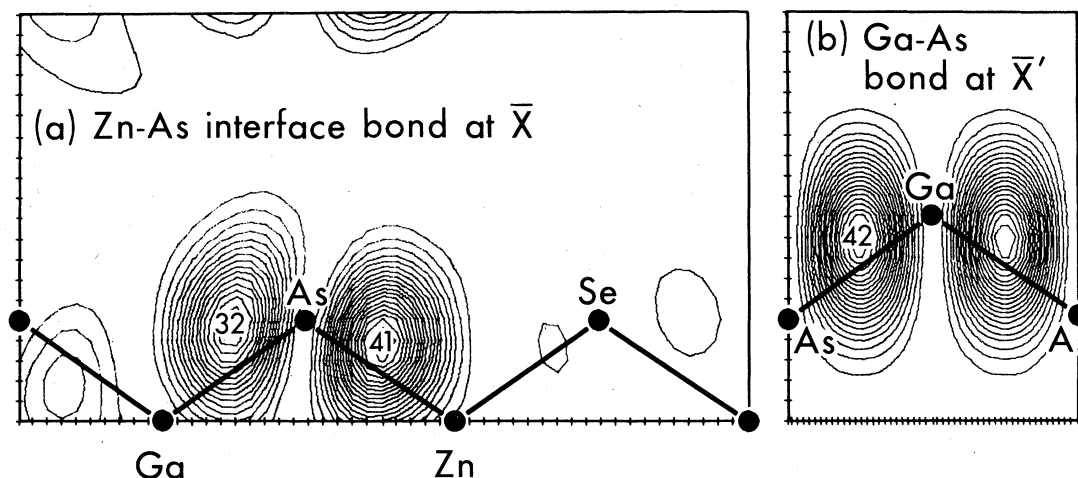
FIG. 4. Contour plots of the charge density of the interface resonances in the upper valence band. In (a) the charge density of the state at $\bar{X}(-1.5$ eV) is plotted in the plane perpendicular to the interface while (b) illustrates the charge density of the state at $\bar{X}'(-1.0$ eV) in the plane parallel to the interface containing Ga and As. The charge density is normalized to unity in the unit cell and the contour spacing is 2.

tends to reduce such a large dipole mismatch. The potential difference we actually get is ~ 0.2 eV rather than ~ 0.6 eV for the GaAs-Ge interface, ~ 0.3 eV rather than ~ 1.0 eV for the GaAs-ZnSe interface, and ~ 0.2 eV rather than ~ 0.4 eV for the Ge-ZnSe interface. As the free-surface dipole mismatch deduced from our calculation is biggest for the GaAs-ZnSe interface, it is not surprising that the electron affinity rule breaks down badly in this system while the deviation is small for the other two systems. The difference mentioned above (0.3 vs 1.0 eV for GaAs-ZnSe, for example) measures how much the calculated results differ from the EAR. The above argument, however, hinges on the ability of the local pseudopotential scheme to produce correct surface dipole potentials. For example, our pseudopotential should reproduce the work function within a tenth of an eV. More stringent tests on the pseudopotential calculations should resolve this question.

The interface resonances near $\bar{X}$ and $\bar{X}'$ are shown in Fig. 4. They are of different character; the interface resonance near $\bar{X}$ is a Zn-As p-like state whereas the resonance near $\bar{X}'$ is a Ga-As parallel bond state (parallel to the interface). While no interface states are found in the gap, we do find true interface states in other regions of the PBS as illustrated in Fig. 3. Because of the lineup of the bottoms of the upper valence bands of GaAs and ZnSe, Ga-Se p-like interface states do split off from the bulk PBS throughout the Brillouin zone. A careful experiment should be able to detect these states in the *ionic* gap. The character of these states is shown in Fig. 5(a). Another interface state, which was also found in the Ge-ZnSe
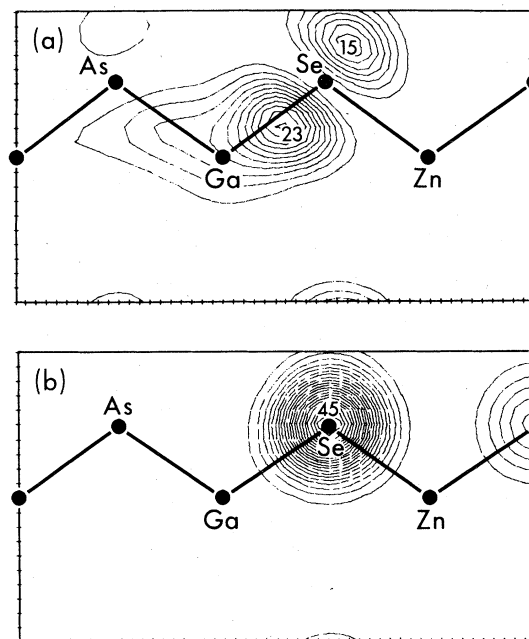

FIG. 5. Contour plots of the charge density of the interface states. In (a) the charge density of the Ga-Se p-like state at $\Gamma(-6.6$ eV) is shown in the plane perpendicular to the interface. The antibonding lobe is also seen in the figure and the interface state tails toward the GaAs side. In (b) the charge density of the Se s-like state at $\Gamma(-15.5$ eV) is plotted in the plane perpendicular to the interface. The charge density is normalized to unity in the unit cell and the contour spacing is 2.

interface,[2] is the Se *s*-like state below the ZnSe lower valence band. The localization of the charge at the Se site is very strong [Fig. 5(b)], and the state exists throughout the Brillouin zone.

Interface resonances (or interface states) are also found in the stomach gap (in the middle of the upper valence band) in Fig. 3. They exist near $\bar{X}$ and $\bar{X}'$, both at the top and the bottom of the stomach gap. They appear in a narrow region of the Brillouin zone and can very easily move into the bulk region to become resonances depending on small changes in the lineup of the PBS's. Their character is mainly Zn-Se *p*-like (parallel to the interface). We also found As *s*-like interface resonances in the lower valence band, but its contribution to the density of states is insignificant.

III. DISCUSSION

One immediate conclusion we can draw from the above results is that the ionicity change across the interface (without involving symmetry change) can give rise to interface states if the change in ionicity is large enough. This was not evident in the previous study on the GaAs-AlAs system because the ionicity difference was too small to split off observable interface states. The existence of *specific* interface states is sensitive to the details of the projected band structure and the strength of the potentials involved as discussed in Sec. III. The possibility of the existence of interface states arising solely from symmetry change was discussed elsewhere.[2] The study of the interface between the (111) zinc blende and (0001) wurtzite ZnS or ZnSe could resolve this question. Because the lattice can be made to match exactly between these two structures, the only possible cause for the interface states would be the symmetry change across the interface (from the *ABCABC*-type of zinc-blende slabs to the *ABAB*-type of wurtzite slabs).

We have found that Ga-Se and Zn-As bonds across the interface contain 2.27 and 1.73 electrons in agreement with the simplified valence approximation predicting 2.25 and 1.75 electrons. This is also consistent with the previous calculations for Ge-GaAs and Ge-ZnSe interfaces; Ge-As and Ge-Ga bonds contain 2.23 and 1.77 electrons while Ge-Se and Ge-Zn bonds contain 2.46 and 1.54 electrons, respectively. The charge transfer appears to be linear in ionicity. This result supports the linear charge-transfer dipole model employed by Frensley and Kroemer[8] although the amount of charge transferred per bond in their calculation is smaller than our calculations would suggest. This does not mean that the *net* calculated charge transfer across the heterojunction is large. On the contrary, the self-consistent calculation shows that the average potential difference between the two sides of the interface is relatively small (~ 0.3 eV for the present system). A possible relaxation would be a contraction of the Ga-Se bond and a stretching of the As-Zn bond thereby inducing slightly more charge transfer per bond. This prediction is based on the observation that stronger bonds have shorter bond lengths if other conditions are similar. Since the Ga-Se bond has more electrons than the As-Zn bond, a shorter Ga-Se bond can result in a net gain in exchange energy (equivalently, the Ga-Se bond feels a net inward exchange force). On the other hand, previous studies on the relaxation of the Ge-GaAs interface[9] showed that relaxation has a minor effect on the interface dipole or on the band-edge lineup.

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