

Relaxation of Polar Ge-GaAs (100) Interfaces: Self-consistent Calculations of the Total Energy[†]

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The total energy and electronic properties of "compensated" polar interfaces of Ge and GaAs are calculated as a function of interface stoichiometry and relaxation. Within the averaged atom approach, we show that the relaxations are zero or very small and that the mixed $\frac{1}{2}(\text{Ge}+\text{As})$ interface is the more stable.

Interfaces between semiconductors are the subject of much current theoretical [1-5] and experimental [5-8] work. In order to understand the nature of the interface the key information is the atomic structure of the interface. Up to the present time, all detailed calculations of electronic properties [1-3] have been based upon assumed structures with atoms in idealized positions. In this paper we report some results of "first principles" calculations which predict the stable structure of Ge-GaAs (100) interfaces and their resulting properties.

We have chosen the polar (100) interface because of the interesting unanswered questions concerning the structure [4,5]. In particular, even the interface stoichiometry is unknown. It has been established from empirical energetic arguments [4,5] that the stable polar interfaces of Ge and GaAs are expected to always involve "compensated" [4] layers which are mixed Ge and Ga or Ge and As. However, the arguments have not predicted which of the possible compensated stoichiometries have lowest energy. Here we study variations of the total energy and electronic properties as a function of stoichiometry including relaxation of the interface atoms to minimize the total energy. We consider the mixed $\frac{1}{2}(\text{Ge}+\text{Ga})$ interface shown in Fig. 1 and the complementary $\frac{1}{2}(\text{Ge}+\text{As})$ case which

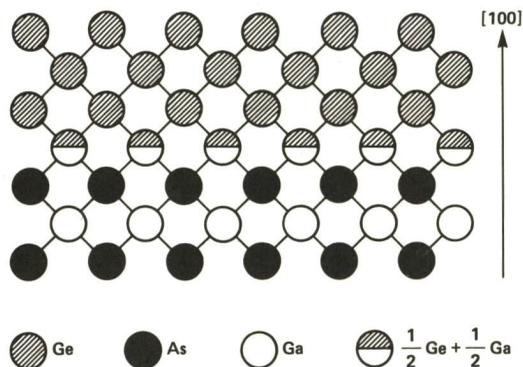


Fig. 1 Model of Ge-GaAs (100) interface viewed along the [010] direction: Here is shown the compensated $\frac{1}{2}(\text{Ge}+\text{Ga})$ interface. The other case studied is $\frac{1}{2}(\text{Ge}+\text{As})$ obtained by interchanging Ga and As. In our calculations we approximate the interface layer by "averaged atoms".

may be derived from Fig. 1 by interchanging Ga and As. These compensated interfaces do not have the energetically unfavorable accumulation of electrons or holes which occur in the idealized unmixed interfaces studied in Refs.[1]and[3].

The electronic states and total energy are evaluated as described in Refs.[9]and[10] using a pseudopotential for the interaction of the ion cores with the valence electrons and the density functional method [11] for exchange and correlation. We use the $\rho^{1/3}$ approximation with a prefactor of 0.8 and the Berkeley ionic potentials for Ge, Ga and As as given in Ref. [2]. All parameters of potentials were fitted to the bulk *bands* of Ge and GaAs; no adjustment was done to fit any other properties. The method was tested by calculating the total energy of Ge and GaAs crystals under conditions analogous to the interface calculations. The bulk properties [12] of GaAs are in excellent agreement with reality (e.g. predicted lattice constant $a = 5.64 \text{ \AA}$ compared to the experimental value of 5.65 \AA) but the calculation for Ge is much less accurate (predicted $a = 5.21$ vs. 5.66 \AA). This result for Ge is exactly like that found previously for Si [9] and the discrepancy has an important effect upon the interface calculation which will require careful treatment.

For our calculations we have used a periodic superlattice where each cell contains eight atoms and two identical interfaces. We have considered the two simplest compensated interfaces defined by $\frac{1}{2}\text{Ge} + \frac{1}{2}\text{Ga}$ layers or by $\frac{1}{2}\text{Ge} + \frac{1}{2}\text{As}$ layers. In each case the full cell contains 4 Ge, 2 Ga and 2 As atoms, so that differences in total energy result solely from differences in interface stoichiometries in the two cases. It is not known how the atoms order in the layer, therefore for our first calculations we have used the "virtual crystal approximation" (VCA) in which average atoms ($\frac{1}{2}\text{Ge} + \frac{1}{2}\text{Ga}$) or ($\frac{1}{2}\text{Ge} + \frac{1}{2}\text{As}$) are placed at the interface. We believe this will accurately describe average properties such as dipoles and average interface relaxation. However, there will be errors in the total energy. For each type of interface we have allowed the interface planes to relax keeping all other planes fixed. The calculations are described in detail elsewhere [12]. As an example, in Fig. 2 are shown the charge density $\rho(x)$, averaged in the yz plane perpendicular to the [100] direction, for the unrelaxed ($\frac{1}{2}\text{Ge} + \frac{1}{2}\text{Ga}$) interface. Comparison with $\rho(x)$ for Ge and GaAs respectively shows that the charge density has essentially recovered its bulk form in the region away from the interface so that the interfaces are effectively decoupled.

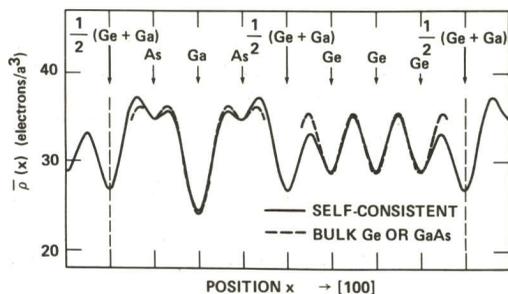


Fig. 2 Variation of the averaged electronic charge density $\rho(x)$ across the crystal containing $\frac{1}{2}(\text{Ge} + \text{Ga})$ interfaces: The self-consistent calculation on our 8-atoms unit cell (solid lines) is compared with isolated Ge and isolated GaAs (broken lines). The supercell recovers properties of the bulk in the regions far from the interfaces. Similar conclusions hold for the selfconsistent potential and for the other interface $\frac{1}{2}(\text{Ge} + \text{As})$.

The total energies as a function of relaxation are given in Fig. 3. At the top is shown the electrostatic contribution (γ^{Ewald}) which acting alone would give large opposite displacements for the two interfaces. Including all contributions to the total energy gives the displacements shown by dotted lines which is toward Ge for both interfaces. The reason for this large displacement of the interface layer towards Ge in our calculations is the ionic potential [2] of Ge, which is too attractive, as the predictions of bond lengths in the bulk have shown. Correction [9] for these spurious contributions using only information from the bulk calculations [12] leads to a linear correction term E^{SP} as indicated in Fig. 3; subtracting the spurious term E^{SP} leads to our final result that the interface energy is minimum for averaged interface atoms undisplaced, within the accuracy of the calculations. As shown in Fig. 3 our calculations find a total energy for the $\frac{1}{2}(\text{Ge}+\text{As})$ interface lower by 0.3 eV per average interface atom than the energy of the $\frac{1}{2}(\text{Ge}+\text{Ga})$ interface.

The resulting potentials for the two interfaces with the very small relaxations give shifts in the average potentials $\overline{V}^{\text{Ge}} - \overline{V}^{\text{GaAs}} = 0.57 \pm 0.01$ eV for the ($\frac{1}{2}\text{Ge} + \frac{1}{2}\text{Ga}$) case and -0.03 eV for the ($\frac{1}{2}\text{Ge} + \frac{1}{2}\text{As}$) case. Using the results for the bulk bands, this gives the relative shift of the tops of the valence bands far from the interface which are illustrated in Fig. 4. The conduction bands in Fig. 4 are determined relative to the valence bands by adding experimental band gaps.

It is interesting to note that on the non-polar (110) interface, using the same potentials, it was found [2] that $\overline{V}^{\text{Ge}} - \overline{V}^{\text{GaAs}} = 0.25$ eV, which is almost exactly the average of the above results. This finding is in agreement with Ref.[5], where it was postulated that the true (100) interface would be the average of the two interfaces considered here and that it would have an interface dipole equal to that for the (110) interface. This interpretation, however, is

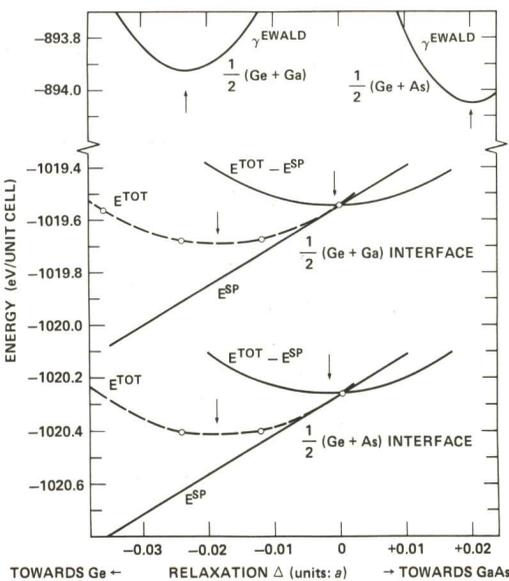


Fig. 3 Variation of total energy of the 8-atom supercell with relaxation of the (averaged) interface: Arrows indicate minima of the parabolas. Upper curves include only electrostatic terms (γ^{Ewald}). Broken lines indicate the complete calculations of total energy. These contain spurious contribution (E^{SP} , linear with relaxation) which originates in the overattractiveness of the Ge- ionic potential. When the calculated E^{SP} is subtracted, the corrected total energy (solid lines) predicts minima essentially at the unrelaxed position, within the limits of accuracy of the calculations. In the framework of our model, the total energy predicted for the averaged $\frac{1}{2}(\text{Ge}+\text{As})$ interface is lower by 360 meV per interface atom than that of $\frac{1}{2}(\text{Ge}+\text{Ga})$ interface.

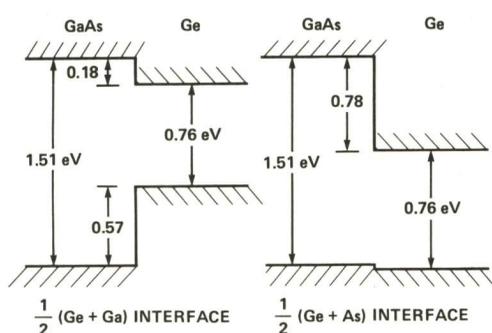


Fig. 4 Band structure discontinuities: Relative position of the Ge- and GaAs valence band maxima predicted by our model for the two averaged interfaces. The gaps are taken from experiment.

in direct conflict with our result shown in Fig. 3 that the $\frac{1}{2}\text{Ge} + \frac{1}{2}\text{As}$ interface is more stable by 0.3 eV per average interface atom and therefore would be predicted to be the true interface. We cannot say at this time whether or not this conclusion is an artifact of our use of the VCA averaging of the atoms. Therefore a firm prediction of the interface stoichiometry must await further work. Other properties of the mixed interfaces will be reported elsewhere [12].

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