

Theoretical study of Si/Ge interfaces

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We present a theoretical study of the structural and electronic properties of pseudomorphic Si/Ge interfaces, in which the layers are strained such that the lattice spacing parallel to the interface is equal on both sides. The self-consistent calculations, based on the local density functional and *ab initio* pseudopotentials, determine the minimum energy configurations, and the relative position of the Si and Ge bands. The presence of the strains influences the interface dipole, and also causes significant shifts and splittings of the bulk bands. For (001) interfaces we find for the top of the valence bands: $E_{v, \text{Ge}} - E_{v, \text{Si}} = 0.74$ and 0.21 eV, respectively, for the cases corresponding to Ge strained to match a Si substrate and vice versa. A discussion of these results and comparison with experiment is presented.

I. INTRODUCTION

The study of heterojunction interfaces is interesting not only from a fundamental point of view, but also with regard to technologically important device applications. For a long time attention was limited to pairs of lattice matched semiconductors. Using molecular beam epitaxy, however, it has become possible to grow dislocation-free strained layer superlattices¹ involving thin layers of materials which differ in lattice constant by several percent. The mismatch is accommodated totally by strain, so that the lattice constant a_{\parallel} parallel to the interface is equal in each layer. This leads to expansion and compression of the respective layers in the perpendicular direction. Pseudomorphic growth of this type has been demonstrated² on a Si substrate for $\text{Ge}_x\text{Si}_{1-x}$ alloys with up to 50% Ge.

In this paper we present results for strained interfaces of pure Si and Ge. Our calculations are performed on a superlattice geometry as illustrated in Fig. 1 and yield self-consistent potentials and charge densities. This provides information about the interface dipoles which determine the position of the bulk potentials. We can then determine the relative energies of the Ge and Si bands, in particular the discontinuities in the valence band edges—information which is of crucial importance for all device applications. Since the nature of the pseudomorphic interface requires the materials to be strained, we must determine the interface dipoles as a function of strain, and also include the effects of these distortions on the bulk band structures. We also examine whether a rearrangement of the atoms near the interface will occur,

and to what extent such changes will influence the dipole across the interface and the band lineups.

The calculations were performed within the framework of local density functional theory,³ applied in the momentum-space formalism,⁴ and using nonlocal norm-conserving ionic pseudopotentials.⁵ Self-consistent solutions are obtained for the charge density and the total potential, which is the sum of ionic, Hartree, and exchange-correlation potentials. The latter is calculated using the Ceperley–Alder form.⁶ In each cycle of iteration a potential is used for generating the charge density, from which a new potential can be calculated. This is then used for constructing the input for the next cycle. The first cycle requires a trial potential, for which we choose the ionic potential screened by the dielectric function of a free electron gas. Convergence of the self-consistent iterations is obtained with the help of the Broyden scheme.⁷

We examine two interface orientations [(001) and (111)]. For each value of a_{\parallel} the spacings $a_{\text{Si}\perp}$ and $a_{\text{Ge}\perp}$ are fixed by minimizing the elastic energy, using macroscopic elastic constants¹—an assumption which is checked by the work described below. For each interface orientation, we examine two extreme cases. The first one involves Si fixed in the cubic structure at $a = 5.43$ Å, with Ge compressed parallel to the interface plane such as to match the Si lattice constant ($a_{\parallel} = 5.43$ Å), and expanded in the perpendicular direction, with $a_{\text{Ge}\perp} = 5.82$ Å. This mimics a structure grown upon an infinitely thick Si substrate. The other extreme is the dual structure: cubic Ge at $a = 5.65$ Å, with Si next to it, compressed perpendicular to the interface, leading to $a_{\text{Si}\perp} = 5.26$ Å. For the (001) interface, we also examine an intermediate case with $a_{\parallel} = 5.52$ Å, corresponding to a superlattice with layers of equal thickness. In all cases, the separation d between the Si and Ge layers at the interface is taken to be the average of the layer separations in the two bulk materials.

In Sec. II, we will describe in detail the calculations performed for the (001) interface between cubic Si and strained Ge. For the other configurations, only the results will be given. Section III contains a discussion of the results.

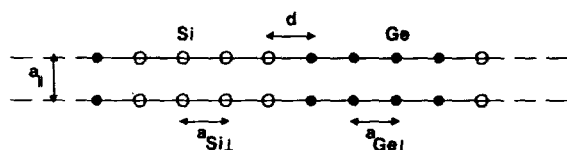


FIG. 1. Schematic illustration of a superlattice used for studying the Si/Ge interface. The supercell contains 4 atoms of each material and 2 interfaces. The lattice parameters a_{\parallel} , $a_{\text{Si}\perp}$, $a_{\text{Ge}\perp}$, and d are defined.

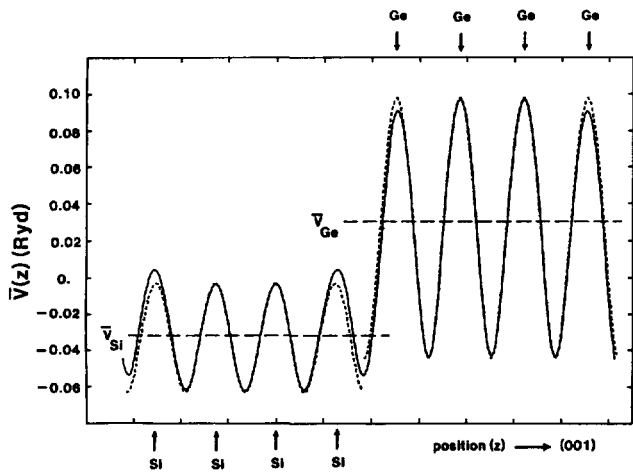


FIG. 2. Variation of the averaged $l = 1$ component of the total potential $\bar{V}(z)$ [as defined in Eq. (1)] across the (001) interface. The dashed lines represent the corresponding potentials for the bulk materials. These coincide with $\bar{V}(z)$ in the regions far from the interfaces. However, the average levels of the two bulk potentials (broken horizontal lines) are shifted with respect to each other.

II. CALCULATIONS AND RESULTS

The most detailed study was performed for the case of the (001) interface between cubic Si at $a = 5.43 \text{ \AA}$ and (001) strained Ge with $a_{||} = 5.43 \text{ \AA}$ and $a_{\text{Ge}\perp} = 5.82 \text{ \AA}$. First, we have done calculations to show that the configuration described above is the most stable one. We have carried out careful calculations of total energy and the forces on the atoms for a superlattice with 4 atoms per unit cell (2 Si and 2 Ge). The results show that the minimum energy structure is very close to that we described above, within 0.1% for d and 1% for $a_{\text{Ge}\perp}$. This checks that the simple rules for deriving the structure follow from our *ab initio* calculations. Our result that d is equal to the average of the bulk values may be an example of a more generally applicable rule. Similar results were obtained for an Al/Ge interface by Batra.⁸

For the actual interface calculations, we have used a periodic superlattice where each cell contains 8 atoms and 2 identical interfaces as shown in Fig. 1. Of course, what we are really interested in are the results for an isolated interface. These can be derived from our calculations to the extent that the interfaces in the periodic structure are well separated. We will establish *a posteriori* that this is the case, by examining charge densities and potentials in the intermediate regions, and showing them to be bulklike.

Plane waves with kinetic energy up to 6 Rydberg were included in the expansion of the wave functions (≈ 280 plane waves). Four special points are used for sampling k space. In the final self-consistent solution, a redistribution of electrons has occurred which changes the electric dipole in the interface region. The final self-consistent potential across the supercell is plotted in Fig. 2. Because the *ab initio* pseudopotentials are nonlocal, the total potential consists of different parts corresponding to different angular momenta l . We only show the $l = 1$ part of the potential here. In the plot, the variation of the space coordinate \bar{r} is limited to the component perpendicular to the interface, and values of the poten-

tials are averaged over the remaining two coordinates, i.e., in the plane parallel to the interface:

$$\bar{V}(z) = 1/(Na^2) \int V(\bar{r}) \, dx \, dy. \tag{1}$$

In the regions far from the interface, the crystal should recover properties of the bulk. Therefore we also plot (broken lines) the potentials determined separately from calculations on bulk Si and Ge (strained). One sees that already one layer away from the interface the potential assumes the form of the bulk potential. Similar results hold for the charge density. This confirms, *a posteriori*, that the two interfaces in our supercell are sufficiently far apart to be decoupled, at least as far as charge densities and potentials are concerned. The average levels of the ($l = 1$) potentials which correspond to the bulk regions are also indicated in Fig. 2. We denote these average levels by \bar{V}_{Si} and \bar{V}_{Ge} , and define the shift $\Delta\bar{V} = \bar{V}_{\text{Ge}} - \bar{V}_{\text{Si}}$.

We studied the sensitivity of our results to the procedures used. To test the dependence upon the energy cutoff, a calculation was performed including plane waves with kinetic energy up to 12 Rydberg. The effect on the shift in average potential was less than 0.04 eV. Next, an alternative verification of our assumption that the interfaces are sufficiently far apart was provided by performing a calculation on a cell with 12 atoms (6 of each material). It was found that our result for the shift in averaged potentials is not significantly affected (by less than 0.02 eV) when we include more atoms, thus confirming that a cell with 8 atoms suffices for our purposes. Finally, the effect of a rearrangement of the atoms near the interface was studied for the 12 atom cell. We displaced one plane of Ge atoms at the interface, corresponding to a 4% change in d , keeping all other atoms fixed. The resulting change in $\Delta\bar{V}$ was less than 0.02 eV. This indicates

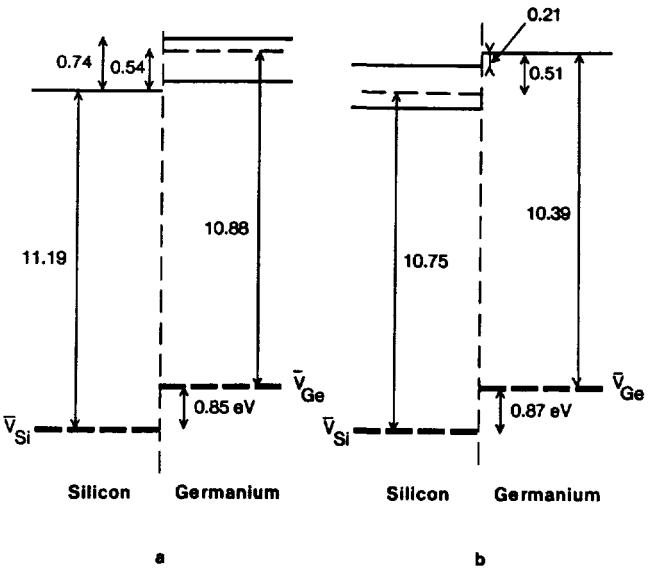


FIG. 3. Band structure discontinuities: Relative position of the average potentials \bar{V}_{Si} and \bar{V}_{Ge} , and of the Si and Ge valence bands. All values shown are derived with the $l = 1$ angular momentum component chosen as the reference potential; the band lineups, however, are unique and independent of this choice. Band splittings result from strain in the materials; in each case, the weighted average is also given. Figure 3(a) is for the case $a_{||} = 5.43 \text{ \AA}$ (cubic Si, strained Ge). Figure 3(b) is for $a_{||} = 5.65 \text{ \AA}$ (cubic Ge, strained Si).

TABLE I. Heterojunction band lineups for different Si/Ge interfaces, characterized by interface orientation and $a_{||}$. $\Delta\bar{V} = \bar{V}_{Ge} - \bar{V}_{Si}$ is the shift in the average potentials ($l = 1$) across the interface. $\Delta E_v = E_{v, Ge} - E_{v, Si}$ is the discontinuity in the top of the valence bands. $\Delta E_{v, av}$ is the discontinuity in the average energy of the Γ'_{25} valence bands.

	$a_{ }$	$\Delta\bar{V}$ (eV)	ΔE_v (eV)	$\Delta E_{v, av}$ (eV)
(001)	5.43	0.85	0.74	0.54
	5.52	0.86	0.51	0.53
	5.65	0.87	0.21	0.51
(111)	5.43	0.73	0.75	0.58
	5.65	0.78	0.27	0.56

that our results for $\Delta\bar{V}$ (and ΔE_v) are not very sensitive to the details of the structure near the interface.

To get information about band discontinuities, we still have to perform the band calculations for the bulk materials, i.e., cubic Si and Ge strained as in the superlattice layer. The bulk calculations were performed with a 12 Rydberg cutoff. Tests have shown that the choice of this cutoff is not critical for deriving the valence band lineups. We find that the valence band maximum in Si is 11.19 eV above the average potential \bar{V}_{Si} . In Ge, the strain along (001) splits the top of the valence band. The topmost valence band occurs at 11.08 eV, and the average energy of the three Γ'_{25} valence bands is 10.88 eV above \bar{V}_{Ge} . From Fig. 2, one finds $\Delta\bar{V} = 0.85$ eV. All these values are consistently obtained with the $l = 1$ component chosen as the reference potential; the band lineups, however, are independent of this choice. This leads to a discontinuity in the valence band of $\Delta E_v = 0.74$ eV (upward step in going from Si to Ge). Or, if we look at the average valence band energy: $\Delta E_{v, av} = 0.54$ eV. These results are shown in Fig. 3(a), and listed in Table I. The other extreme (001) interface is that representing the case of a Ge substrate (cubic, $a = 5.65$ Å) with strained Si ($a_{||} = 5.65$ Å, $a_{Si} = 5.26$ Å). Results for the shift in average potential and positions of the bands are given in Fig. 3(b) and Table I. Finally, we considered the (001) interface for the case corresponding to a superlattice with layers of equal thickness, with both Si and Ge subjected to tetragonal strains: $a_{||} = 5.52$ Å, $a_{Si} = 5.36$ Å and $a_{Ge} = 5.75$ Å. Table I shows the results.

We also examined the (111) pseudomorphic interface. When the materials are distorted along the (111) direction, internal displacements of the atoms will occur. These are described by the internal displacement parameter ζ . We used the values $\zeta_{Si} = 0.53$ and $\zeta_{Ge} = 0.44$, derived from recent theoretical calculations.⁹ No attempt was made to actually minimize the total energy for this structure. Based on our findings for the (001) interface, we assume that the actual positions of the atoms will be close to those found from macroscopic arguments. Our results for $\Delta\bar{V}$ and for the discontinuities in the valence bands are given in Table I.

A complete picture of the band discontinuities will require that the spin orbit splitting be included and conduction bands be considered. The former is straightforward,¹⁰ but the latter involves the well-known problem that the band gaps are not given correctly by the local density functional.

Indeed, in our calculations the Ge conduction bands are sensitive to the cutoff and are much too low near Γ .¹¹ Because of our sampling of k space by means of the special point technique, we do not expect these effects at Γ to influence our results, since none of the special points are close to that region of k space. We will present more results on valence and conduction bands in the future.¹⁰

III. DISCUSSION

Our results for the (001) and (111) interfaces, as summarized in Table I, lead to several conclusions. For the (001) interface, $\Delta\bar{V}$ and ΔE_v vary almost linearly with $a_{||}$; this justifies linear interpolation between the two extreme cases ($a_{||} = 5.43$ Å and $a_{||} = 5.65$ Å) to obtain $\Delta\bar{V}$ and ΔE_v for intermediate values of $a_{||}$. For both orientations, we notice that $\Delta E_{v, av}$ is almost constant: $\Delta E_{v, av} = 0.54 \pm 0.04$ eV. This suggests that $\Delta E_{v, av}$ might qualify as a parameter characteristic of the heterojunction, irrespective of the orientation and strain conditions. The splittings of the bands under strain are such, though, that the discontinuities as measured from the top of the valence bands vary by quite a large amount.

The Harrison theory for heterojunction band lineups¹² yields a value for Si/Ge of $\Delta E_v = 0.38$ eV. A recent theory of heterojunction dipoles by Tersoff¹³ predicts $\Delta E_v = 0.18$ eV. In either case this value is derived as the difference between certain reference energies in bulk Si and Ge—the corresponding interfaces are not pseudomorphic, and no effects of strain on the bandstructure are included. This makes a comparison with our calculations difficult.

Very few experimental results are available for band discontinuities in the Si/Ge system. In recent experiments on modulation doped Si/Ge_{0.2}Si_{0.8} heterojunctions¹⁴ it was found that $\Delta E_v \gg \Delta E_c$. These structures were grown on a Si substrate, corresponding to the case $a = 5.43$ Å. If we interpolate our result for Ge grown on Si, this leads to a value for Si/Ge_{0.2}Si_{0.8} of $\Delta E_v \approx 0.74/5 \approx 0.15$ eV, which is in good agreement. Our results also indicate that if such structures could be grown on a Ge substrate, ΔE_v would be significantly smaller.

From SXPS data for the valence band and measurements of core level shifts, Mahowald *et al.* deduce $\Delta E_v = 0.4$ eV for Ge evaporated on Si (111).¹⁵ A value of $\Delta E_v = 0.2$ eV was reported by Margaritondo *et al.* for Si/Ge¹⁶; however, they did not show that the interface was pseudomorphic. Our results indicate that an exact characterization of the structure, in terms of which material is strained and by how much, is very important in assigning a particular value of ΔE_v .

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