Valence-band offset of the lattice-matched β-$FeSi_2$(100)/Si(001) heterostructure

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Ab initio pseudopotential calculations have been carried out to determine the valence-band offset across the interface of $FeSi_2$ grown on a silicon substrate. The structure of the β-$FeSi_2$[010]‖Si⟨110⟩ matching interface is also obtained. The lattice parameters of the β-$FeSi_2$ epilayer defining the interfacial plane were constrained to those of silicon. The valence-band offset was found to be about 0.39 eV with the Si side of the interface having the higher potential.

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I. INTRODUCTION

β-$FeSi_2$ has recently received considerable attention due to the fact that it is a semiconductor with band gap of ~0.83–0.87 eV,[1] which corresponds to the minimum absorption window of silica based fibers, and also because it can be grown epitaxially on Si.[2] This clearly indicates that β-$FeSi_2$ is a potential material for integrating optoelectronic devices such as light-emitting diodes and near IR detectors within silicon technology. In fact, a light-emitting device operating at a wavelength of 1.5 μm that incorporates β-$FeSi_2$ into a conventional silicon bipolar junction, by growing a barrier β-$FeSi_2$ epilayer on a Si(001) substrate, has been successfully fabricated.[3]

Until recently, there was controversy over the nature of the semiconducting band gap in $FeSi_2$. Photoluminescence experiments[4,5] suggested that the material is a direct band gap semiconductor while theoretical calculations[6,7] on bulk β-$FeSi_2$ have generally shown the presence of an indirect band gap a few hundredths of an eV below the direct gap. However, in a more recent publication[8] we have shown that the band gap of β-$FeSi_2$ in the heteroepitaxial relationship β-$FeSi_2$(100)/Si(001), which has two lattice matchings, (type-A) β-$FeSi_2$[010]‖Si⟨110⟩ and (type-B) β-$FeSi_2$[010]‖Si⟨100⟩,[9] is highly sensitive to its lattice parameters and therefore to the orientation at which the material is grown on silicon, with the type-A orientation more favorable to a direct band gap.

The properties of interfaces between semiconductors in electric or optoelectronic devices govern characteristics such as charge transport through the devices. Within the device, the electronic band gap plays a crucial rule, but the valence-band offset is also critical. Therefore, when β-$FeSi_2$ grown on a silicon substrate is used in the construction of semiconductor devices, as in all heterostructures, it is important to know the band alignment at the interface. We have been motivated to study the band alignment for the β-$FeSi_2$(100)/Si(001) heterostructure due to its potential importance for devices. We have chosen the type-A orientation since, energetically, it is a more favorable structure than type-B,[8] and it also has a direct gap and consequently is more interesting for optical applications.

In this paper we present results of *ab initio* plane wave calculations of the structure of the β-$FeSi_2$(100)/Si(001) heterostructure and its valence-band offset. The β-$FeSi_2$ epilayer is constrained to the Si substrate. We have used the model developed by Baldereschi, Baroni, and Resta,[10] which works extremely well for matched interfaces such as this.

II. DETAILS OF THE CALCULATION

Knowledge of the band structures of the two bulk materials forming a heterostructure (as obtained from separate band structure calculations) is not sufficient information to obtain the difference in the band edges across the interface. This is because the band energies are determined with respect to a macroscopic average potential in the solid ($\bar{\bar{V}}_{tot}^{bulk}$), the absolute value of which can be considered arbitary in bulk pseudopotential calculations. To determine how the average potentials of the two semiconductors are positioned with respect to each other at an interface, it is therefore necessary to perform a supercell calculation in which both materials are present. To this end we define first a microscopic planar potential along the perpendicular direction (we choose this to be the z axis) to the interface, $\bar{V}_{tot}(z)$, by averaging the sum of the Hartree, exchange-correlation, and ionic potentials in the plane parallel to the interface. Clearly $\bar{V}_{tot}(z)$ is a one-dimensional quantity, which still exhibits periodic variations in the direction perpendicular to the interface. The macroscopic average $\bar{\bar{V}}_{tot}(z)$ is accomplished by averaging this function using a moving slab technique:

$$\bar{\bar{V}}_{tot}(z)=\frac{1}{\lambda\lambda'}\int_{z-\lambda/2}^{z+\lambda/2}\int_{z'-\lambda'/2}^{z'+\lambda'/2}\bar{V}_{tot}(z'')dz''dz', \qquad (1)$$

where λ and λ' are the lengths of a single period of the microscopic average on each side of the interface that lies normal to the z axis. Full details of the microscopic and macroscopic averages can be found in Ref. 11. The difference in potential line up across the junction, $\Delta\bar{\bar{V}}_{tot}$, is calculated from the difference in macroscopic averages of the potentials of the two sides of the interface that was not affected by the junction.

As illustrated in Fig. 1, the valence-band offset ΔE_v is then given by

$$\Delta E_v=(\bar{\bar{V}}_{totL}+E_{VBML})-(\bar{\bar{V}}_{totR}+E_{VBMR}) \qquad (2)$$

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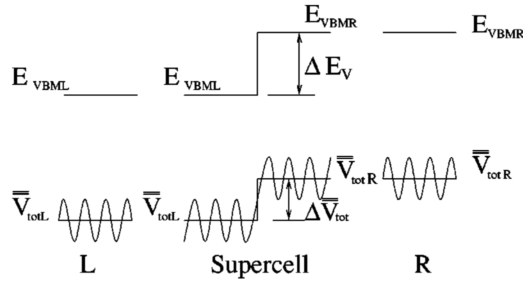

FIG. 1. Schematic representation of a band structure line-up problem at heterojunctions. L and R represent the bulk materials forming the left and right hand sides of the interface, respectively. E_{VBMR} and E_{VBML} (the maximum valence-bands of R and L cells, respectively), which are obtained from separate calculations of the two materials, are measured relative to an arbitrarily defined macroscopic average of the potential. The average potential of the whole supercell obtained from *ab initio* calculations ensures that the total potentials of both materials are expressed with respect to the same reference, and allows direct extraction of $\Delta\bar{\bar{V}}$. The separation between the relative E_{VBMR} and E_{VBML} then determines the valence-band offset.

or

$$\Delta E_v = \Delta\bar{\bar{V}}_{tot} + \Delta E_{VBM}, \tag{3}$$

where we have added a subscript L and R to indicate the left or right side of the junction. ΔE_{VBM} is the difference in the energies of the valence-band maxima of the two bulk materials measured with respect to their respective bulk potentials $\bar{\bar{V}}_{tot}^{bulk}$ defined above.

In the construction of an infinite interface, periodic boundary conditions in the directions parallel to the interface (a and b directions in this case) are used. However, the plane wave basis set calculations that will be used here (described below) require periodic boundary conditions in all three directions. Therefore in the c direction perpendicular to the interface we require a unit cell sufficiently large that the interface is isolated from its periodic images through the bulk Si and $FeSi_2$. It was found that a large supercell (described below) containing 80 Si atoms and 20 Fe atoms (corresponding to eight atomic layers on the Si side and 14 atomic layers on the $FeSi_2$ side) results in converged calculations. This ensured that the electronic distribution in the center of the two sides of the supercell could be considered as ‘‘bulklike.’’[12,13]

Following the notation of Ref. 8, the type-A interface of β-$FeSi_2$[010]||Si⟨110⟩ matching in a heteroepitaxial relationship β-$FeSi_2$(100)/Si(001) is the subject of the present investigation. To build the supercell for this system, we first defined a new larger Si tetragonal cell of the diamond structure with crystal translational vectors a', b', and c' such that $a'=(1,-1,0)a$, $b'=(1,1,0)a$, and $c'=(0,0,2)a$ (a being the conventional cubic axis of Si and equal to 5.43 Å). For the other side of the supercell we used β-$FeSi_2$ unit cells, which have the $Cmca$ space group and lattice parameters $a=9.863$ Å, $b=7.884$ Å, $c=7.791$ Å.[8,14] The two unit cells were then joined together at the Si(001) and β-$FeSi_2$(100) interfacial planes. They are very well matched when the β-$FeSi_2$ cleavage plane that leaves a layer of eight Si atoms on the surface is used (see Fig. 2). The b and c lattice parameters of the β-$FeSi_2$ unit cell (the overlayer) were both constrained at 7.7692 Å, equal to the Si cell a' and b' parameters. An illustration of the interface used in the calculations is given in Fig. 2. The type-B interface is also shown in the figure, for comparison.

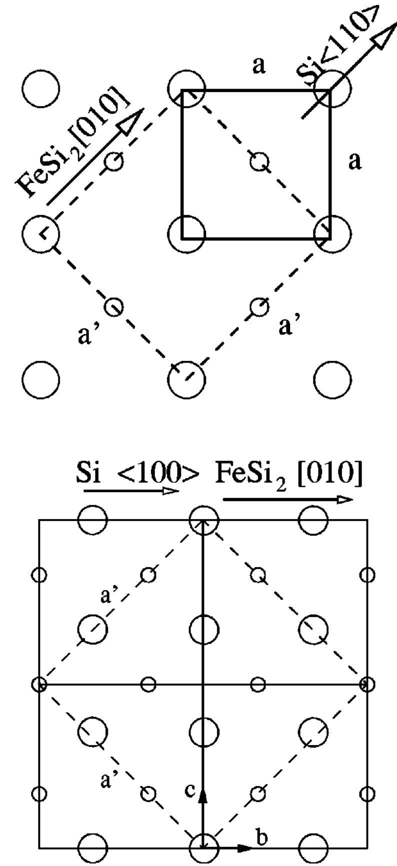

FIG. 2. The diagram shows two of the possible orientations of the heteroepitaxial relationship β-$FeSi_2$(100)/Si(001). The circles indicate the Si atoms in the (001) plane (the larger circles are the layer of Si atoms at the interface and the smaller circles show the Si layer below). The type-A (β-$FeSi_2$[010]‖Si⟨110⟩) matching is illustrated in the top diagram. The β-$FeSi_2$ cell (dashed lines) is chosen to coincide with the Si conventional cell, given a 45° rotation around the direction perpendicular to the substrate. For completeness we also illustrate, in the bottom diagram, the type-B (β-$FeSi_2$[010]‖Si⟨100⟩) interface (Ref. 8). The full lines represent 2×2 conventional β-$FeSi_2$(100) surface cells. The lattice parameters b' and c' of the smaller β-$FeSi_2$(100) common unit mesh (dashed line) are given by $b'=(0,1,1)b$ and $c'=(0,-1,1)c$.

Details of the computational technique are as follows. The CASTEP code[15] has been used for our calculations. They have been carried out within the density functional formalism using the local density approximation for the exchange and correlation potential. The electron-ion interaction was described using Vanderbilt's ultrasoft pseudopotentials[16] for both Si and Fe. In the case of the Fe atoms, the d electrons were not frozen in the ionic core, but were instead treated as valence electrons, which we found necessary to obtain reli-

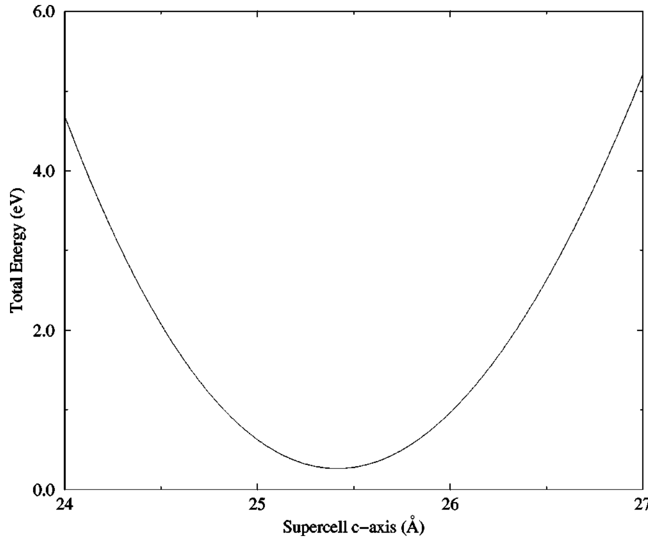

FIG. 3. The dependence of the total energy of the heterojunction system on the c axis of the β-$FeSi_2[010]||Si\langle 110\rangle$ supercell is shown. The minumum energy gives the relaxed supercell lattice parameter.

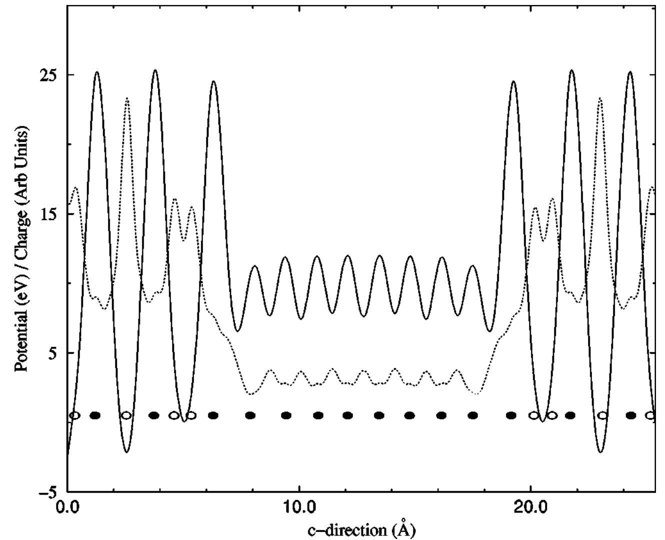

FIG. 4. The planar averages of the charge density (dotted line) and of the total potential (solid line) along the c axis, which is perpendicular to the interfacial plane of the supercell. To aid the interpretation of the diagram we also show the positions of planes of atoms. The filled symbols indicate the positions of planes of silicon atoms and the open symbols indicate the positions of planes of iron atoms.

able lattice parameters. The valence electronic wave functions were expanded in a plane wave basis set up to a kinetic energy cutoff of 560 eV. This was large enough to converge the total energy of the unit cell to better than 1 meV/atom. The Brillouin zone integrations were performed by sampling on regular Monkhorst-Pack meshes at a density of 0.05 Å^{-1} for the Si, β-$FeSi_2$, and supercell structures, which we also found converges the total energy to approximately 1 meV/atom. The total energy was minimized using a preconditioned conjugate gradient algorithm and a charge density mixing scheme. The forces on the atoms were calculated using the Hellmann-Feynman theorem and a conjugate gradient scheme was used to relax the geometric structure of the material.

For the band structure calculations (for the two materials forming the supercell, i.e., Si and β-$FeSi_2$) that were carried out following the geometrical optimization, we used the self-consistent charge density obtained from the relaxed calculations to construct the Hamiltonian of the system. This was then diagonalized at various points in the Brillouin zone to obtain the energy eigenvalues.

III. RESULTS AND DISCUSSIONS

We first optimized the structure of the Si/β-$FeSi_2$ interface by calculating the energy of the cell for different values of the supercell c lattice parameter, optimizing the positions of the atoms within the supercell each time. The a lattice parameter was fixed at the relaxed value of bulk silicon as this is the substrate material. The results of total energy against c lattice parameter are shown in Fig. 3, where it was found that the energy has a minimum value at $c=25.4$ Å.

It was found that the relaxed atomic positions in the heterojunction interface show a substantial deformation from the bulk structure geometry in both materials. At the center of each material within the supercell (furthest from the interface) there is no significant difference in structure between that and the individual bulk structures, which was our criterion for convergence of the calculation with respect to the size of the supercell. In the silicon part of the supercell, we find that the bond lengths at the interface (closest monolayer to the junction) are 2.506 Å compared to the natural Si bond length of 2.345 Å. In the next layer below the interface the Si bond lengths are 2.332 Å, followed by 2.354 Å and 2.339 Å, finally relaxing to 2.345 Å at the center of the silicon part of the simulation cell. At the interface, the silicon bond angles are also deformed away from the natural tetrahedral angle (109.5°) varying from 105.8° to 114.7°. In the silicon layer below the interface the bond angles range from 107.5° to 111.8°. In the third layer from the interface, the perfect tetrahedral angle is obtained to within 0.2°.

On the $FeSi_2$ side of the interface, we also observe small deviations from the bulk values which occur as slightly strained bonds are formed between the two materials. An inspection of the valence electronic charge density at the interface shows that the material is covalently bonded between silicon atoms at the interface.

To examine the electronic structure of the material across the interface, the total potential and the electronic charge density have been microscopically averaged (in a manner analogous to obtaining the average potential described above) in the directions parallel to the interface. These results for the planar averaged charge density $\bar{n}$ and the averaged total potential $\bar{V}_{tot}$, are shown in Fig. 4. It is seen that both $\bar{V}_{tot}$ and the charge density $\bar{n}$ (calculated in a manner analogous to $\bar{V}_{tot}$) rapidly recover their bulk behavior in each of the two materials comprising the junction as one moves away from the interface. However, the positions of

the macroscopic averages of the potentials in the bulklike regions are shifted with respect to one another, providing the potential line-up $\Delta\bar{\bar{V}}_{tot}$, which is found to be about 0.64 eV, with Si being lower.

We have also carried out the necessary *ab initio* calculations on the bulk Si and β-$FeSi_2$ unit cells, to obtain information about the top of the valence-bands in the two materials and the macroscopically averaged potential with respect to which the band structure energies are measured. We obtain 6.464 eV and 5.43 eV for the Si and β-$FeSi_2$ respectively. Using Eq. (3), the maximum of the valence-band on the β-$FeSi_2$ side was found to be lower by about 0.39 eV than that on the Si side of the supercell. This is much higher than the value of the experimentally measured valence-band offset of 0.05 eV for the β-$FeSi_2$/Si(111) interface, which was obtained from the diode properties.[17] However, this is not unexpected as the interface was made using a different silicon surface. This difference is because the origin of the band offset is primarily the absolute relation of the band structure of the materials concerned and the surface dipole,[18,19] which in turn is determined by the interface structure. Obviously, the structure of the Si(001) and Si(111) interfaces with β-$FeSi_2$ will differ greatly, and hence the band offset will also differ.

IV. CONCLUSIONS

In summary, the band offset in the lattice-matched $FeSi_2[010]||Si\langle 110\rangle$ heterostructure has been calculated by *ab initio* density functional techniques. A supercell method was employed so that an unbiased plane wave basis set could be used, but required careful checking of convergence criteria with respect to interactions between periodically repeating interfaces. These calculations are necessary due to the experimental difficulties in obtaining electronic properties such as band offsets in complicated heterojunctions. In the present case we find that the band potential is 0.39 eV higher in Si than in $FeSi_2$. The results of such calculations will be extremely useful for integrated β-$FeSi_2$ optoelectronic devices used within standard silicon technology.

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