ATOMIC STRUCTURE OF $CaSi_2$/Si INTERFACES

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ABSTRACT

The $CaSi_2$/Si interface is studied with state-of-the-art first-principles calculations. Various models for the interfacial structure are examined, in which the Ca atoms at the interface exhibit 5-, 6-, 7-, or 8-fold coordination. The structures with sevenfold coordination (as in bulk $CaSi_2$) have the lowest energy. However, the sixfold- and eightfold-coordinated structures are only ~0.1 eV higher in energy. Schottky barrier heights are briefly discussed.

INTRODUCTION

Epitaxial silicide/silicon interfaces may have great technological impact, because of their potential use in Schottky barriers, Ohmic contacts, or metal-base transistors. The $CaSi_2$/Si interface, recently proposed by Morar and Wittmer[1], is of particular interest because the absence of d-electrons in Ca makes this system qualitatively different from transition-metal silicides such as $NiSi_2$ and $CoSi_2$. Morar and Wittmer[1], using transmission-electron microscopy (TEM), showed that $CaSi_2$, when grown epitaxially on Si(111), assumes the trigonal-rhombohedral phase[2] (a=3.855 Å, c=30.6 Å), which is nearly lattice matched to Si (a_{Si} = 5.43 Å, $\sqrt{2} \times a_{Si} \approx 2a$). The interfaces were atomically abrupt and step-free. In this paper I examine the properties of bulk $CaSi_2$ and the atomic and electronic structure of the $CaSi_2$/Si interface with state-of-the-art theoretical techniques, based on pseudopotential-density-functional theory in a superlattice geometry. These methods are eminently suited for such an investigation, based on their established reliability both in studies of semiconductor interfaces[3] and of metals.[4] The hexagonal unit cell of $CaSi_2$, space group D^5_{3d}-$R\bar{3}m$, contains six $CaSi_2$ molecules and has a 30.6 Å repeat distance along the c axis. As illustrated in Fig.1, the structure can be pictured as a stacking in the [111] direction of double layers of Si atoms, which are shifted and rotated by 180°, with Ca atoms in between.[2] For stacking in the [111] direction, there are three possible positions for each (Si or Ca) atom, which can be labeled by A, B, C. If we label each triple layer, which consists of one $CaSi_2$ formula unit, with one letter (corresponding to the position of the Ca atom in the triple layer), the overall stacking sequence can be described as AABBCC.

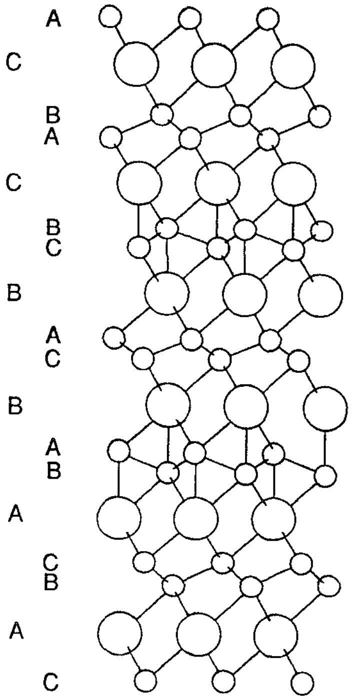

Figure 1: *Schematic representation of the trigonal-rhombohedral $CaSi_2$ structure in a projected view. Large spheres represent Ca atoms, small spheres Si. Two planes of atoms are shown; projected "short" bonds connect atoms in the plane of the figure to those in a plane below.*

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Each Ca atom sits between two Si double layers, and has a different coordination with respect to each of these two. With respect to one Si double layer, the Ca sits in a so-called T_4 site (a threefold site on top of a second-layer Si atom), at a distance of 3.03 Å from three Si atoms in the first layer, and 3.06 Å from the Si atom in the second layer. With respect to the other Si double layer, the Ca sits in a so-called H_3 (threefold hollow) site, at a distance of 3.03 Å from its three Si neighbors in the first layer. In total, the Ca is therefore sevenfold-coordinated. The Si atoms have three Si neighbors at 2.45 Å and three Ca neighbors at 3.03 Å. In addition, some Si atoms have another Ca neighbor at 3.06 Å.

METHODS

The calculations are based on local-density-functional theory[5] and *ab initio* nonlocal normconserving pseudopotentials.[6] A supercell geometry is used,[3] in which layers of Si and $CaSi_2$ are periodically repeated, forming a superlattice $(CaSi_2)_m(Si_2)_n$. In principle, the full $CaSi_2$ bulk unit cell can only be represented if $m \geq 6$. However, it can be expected (and was verified) that the details of the stacking sequence in the bulk which involve changes more than six atoms (or 10 Å) away from the interface have no effect on the interfacial structure. The small lattice mismatch (0.4%) between $CaSi_2$ and Si is neglected; all calculations are carried out using the Si lattice constant. Results for an isolated interface can be obtained provided the interfaces are sufficiently well separated. The interface energy can be determined by taking the supercell energy and subtracting the energies of the corresponding slabs of bulk material. The latter are calculated in the same geometry and using the same convergence parameters as the supercell, to minimize systematic errors.

In order to be able to investigate a large number of different interface structures, most calculations were carried out with a 6 Ry energy cutoff (determining the size of the plane-wave basis set), a supercell with $m=2$ and $n=2$ or 3, and 39 special points[7] in the irreducible part of the Brillouin zone. Tests were performed to check the convergence with respect to all parameters. The total error bar on interface energies is estimated to be ±0.1 eV. However, some cancellation of systematic errors is expected when taking *differences* of interface energies, so that the accuracy is higher when making a direct comparison between different interface structures. Finally, calculations of Hellmann-Feynman forces[8] were carried out for selected interfaces to investigate atomic relaxation near the interface.

RESULTS

Bulk $CaSi_2$

First, the structure of bulk $CaSi_2$ itself was investigated. Using the stacking illustrated in Fig. 1 and a fixed c/a ratio, the energy was calculated as a function of a, leading to a lattice constant which was within 1% of its experimental value. Insight into the electronic structure can be obtained from inspection of the charge distribution in the system. Fig. 2 shows a contour plot of the valence charge density in a plane perpendicular to a $CaSi_2$/Si interface. The upper part of the figure provides information about the bonding in $CaSi_2$ itself. Fig. 2 shows that the charge density in the Si double layers is very similar to bulk Si, as evidenced by examination of the Si-Si bonds in the plane of the contour plot. The Ca atoms are characterized by a very low charge density (only valence electrons are shown), which should not be surprising, since Ca easily gives up its two electrons. These electrons go into dangling-bond-like states on each of the Si atoms. The "dangling bonds" arise as follows: the Si atoms are arranged in corrugated layers, in which they are threefold coordinated. Each Si therefore has an orbital sticking out perpendicular to the layer, in a direction in which no atoms are present for bonding. One Si electron is present in

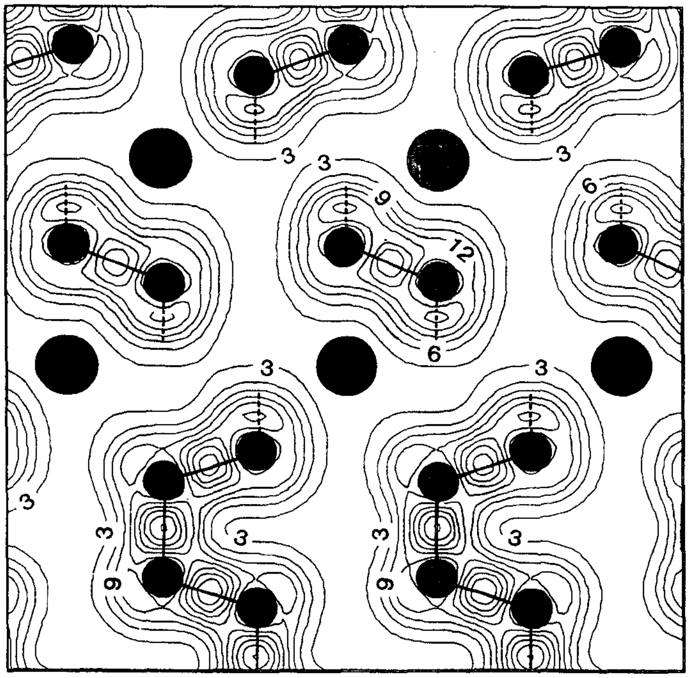

Figure 2: *Contour plot of the valence charge density in a plane perpendicular to the $CaSi_2$/Si interface with the 7B structure. The contour spacing is 3; units are electrons per unit cell, scaled to a unit cell containing 2 Si atoms (8 electrons). Small spheres represent Si atoms, large spheres Ca. Si-Si bonds are drawn in solid lines; dangling-bond states are indicated by dotted lines. Note the stacking fault on the Si side.*

this orbital, while the Ca contributes a second, making this "dangling bond" negatively charged. The electrostatic interaction between the negative charges on the Si layers and the positively charged Ca holds the layers together. One can therefore consider $CaSi_2$ to be a compound with mixed covalent (in the Si layers) and ionic (between Si and Ca) bonding.

It can be concluded that the electronic structure of $CaSi_2$ is very different from the transition-metal silicides $CoSi_2$ and $NiSi_2$. The latter are characterized by strong covalent interactions between the metal d states and the Si sp^3 hybrids.[9] In contrast, little covalent bonding is evident between Ca and Si atoms.

Structure of the interface

Many different possibilities for the atomic arrangements at the interface were investigated. They can be classified according to the coordination of the Ca atoms at the interface, which can be 5-, 6-, 7-, or 8-fold, and according to the relative orientation of the $CaSi_2$ and the Si crystals. In a type-A structure the relative orientation is the same, while in a type-B structure the $CaSi_2$ is rotated by 180° with respect to the Si. Some of the structures that were examined in this study are illustrated in Fig. 3.

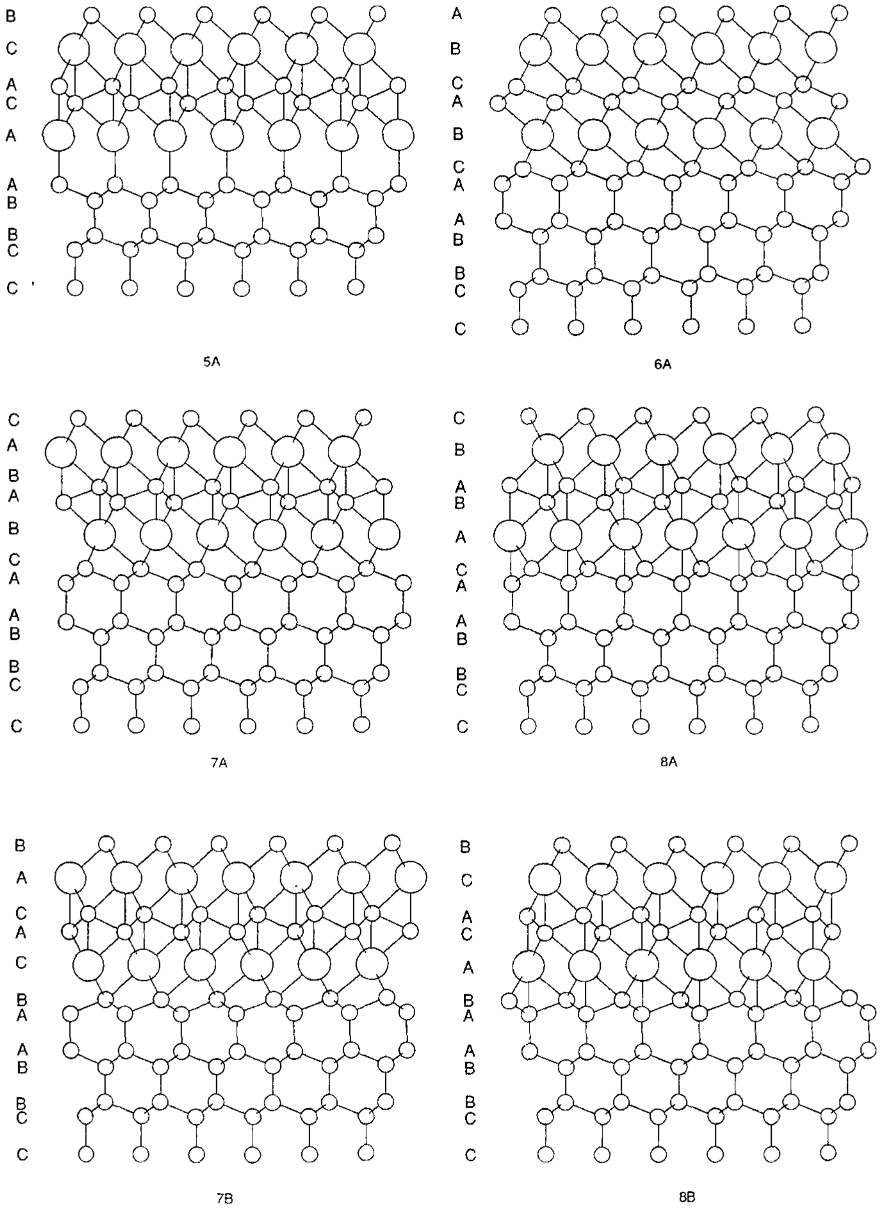

Figure 3: *Schematic representation of various $CaSi_2/Si$ interfaces. Small spheres represent Si atoms, large spheres Ca. The 5B and 6B interfaces, which were also examined in the calculations, are not shown here.*

In principle, there is a choice between terminating the $CaSi_2$ with a Ca layer which is threefold coordinated to the bulk $CaSi_2$ (i.e. Ca in an H_3 site), or fourfold (in a T_4 site). This corresponds to having either a full period at the interface (i.e. AABB...) vs. only one-half period (i.e. ABB...). The first possibility occurs in the 6A and 6B structures, while the second case occurs for all five-, seven- and eightfold coordinated systems studied here. In the sevenfold-coordinated structure, Ca sits in an H_3 site with respect to the Si substrate, while in the eightfold structure it sits in a T_4 site. In a fivefold-coordinated structure, the $CaSi_2$ has a half period at the interface, with the Ca atoms sitting on top of first-layer Si atoms. Note that all the shown structures have a double layer of Si at the interface. Having only a single Si layer at the interface is energetically extremely unfavorable. Also note that for the six- and higher-fold structures, the "B" orientation (in which $CaSi_2$ is rotated by 180° with respect to the Si substrate) implies that the double layer of Si at the interface exhibits a stacking fault when viewed with respect to the Si substrate.

The interface energy of the various models is given in Table 1. The values in this Table were calculated assuming that all structures are "ideal", i.e. no relaxations were included. The atomic positions on the $CaSi_2$ side were taken to be those in the bulk up to the last Ca atom (but at a lattice constant a=5.43 Å/$\sqrt{2}$). The bond lengths in the double layer of Si at the interface were taken to be those of bulk Si. This actually corresponds to the optimum geometry for the sevenfold structures. For the fivefold structures, the Ca-Si distance at the interface was taken to be equal to the smaller one of those in bulk $CaSi_2$. The effect of relaxations was examined for selected interfaces, using calculated Hellmann-Feynman forces. Relaxations are only important for the 8-fold interfaces, where the outer Si-Si double layer has to expand in order to generate an acceptable distance between Ca and the second-layer Si atoms. Even there, the results indicate that the bond lengths are changed by less than 2%, shifting the energy by less than 0.05 eV.

Table 1: *Interface energies for various $CaSi_2$/Si interfaces, characterized by the coordination of interfacial Ca (5-, 6-, 7-, or 8-fold) and the relative orientation of $CaSi_2$ with respect to Si (A or B). All values in eV per interface unit cell.*

	5	6	7	8
A	0.94	0.05	-0.03	0.08
B	0.88	0.05	-0.03	0.09

From Table 1, we conclude that the fivefold structures are high in energy. Among the others, the sevenfold interfaces are lowest, but the sixfold and eightfold structures are only slightly higher. The energy difference between A and B orientations is very small.

Schottky barrier

The (p-type) Schottky barrier height is defined as $\Phi = E_F - E_v$ where E_F is the metal Fermi level and E_v is the valence-band maximum of the semiconductor. The self-consistent interface calculations allow the derivation of this quantity in a manner analogous to the technique used for semiconductor heterojunctions, as described in Ref. 3. However, there are numerical complications which make the calculation of Schottky barrier heights much harder than that of heterojunction band offsets. In addition, LDA errors may be significant, as discussed by Das *et al.*[10] I therefore put an error bar of 0.5 eV on the calculated values of Φ; however, the trends between different interface structures are much more reliable. The following values were obtained for Φ: 1.02 eV for the 7A and 7B interfaces, and 0.95

eV for the 8A and 8B interfaces. The metal Fermi level is thus located in the upper part of the Si band gap. No experimental values are available to date. I also examined whether the Schottky barrier would be sensitive to the specific atomic positions near the interface. Increasing the Si-Si distance in the Si double layer at the interface by 4% leads to an increase in Φ of less than 0.1 eV.

DISCUSSION

The sevenfold-coordinated structure which I find to be lowest in energy is also the one that was observed in the experiments of Morar and Wittmer.[1] Their TEM results showed that the break in the bulk $CaSi_2$ structure falls between Ca layers of the same type. They also found that the relative orientation of the epitaxial $CaSi_2$ and bulk Si in their sample was of type-B. The Si double layer at the interface can be regarded as a continuation of the bulk $CaSi_2$ structure; considered with respect to the bulk Si lattice, it can be viewed as a stacking fault characterized by rotation of 180° about the c axis. In the present calculations, no energy difference is found between the 7A and 7B orientations.

It should actually come as no great surprise that the sevenfold structure is most stable, since it exhibits the same coordination for the interfacial Ca as in the bulk. More intriguing is the question why the sixfold and eightfold structures are only slightly higher in energy. The answer can be found in the nature of the bonding between Ca and Si atoms, as discussed above. No covalent bond is formed, and the cohesion results from electrostatic attraction between Ca^{++} and negative Si "dangling bonds". For all structures with sixfold or higher coordination, the stacking is such that Ca is surrounded by a "cage" of six of these dangling bonds. The interaction with a seventh or eighth Si atoms occurs via the charge density in the backbond region of a Si atom directly above or below the Ca, at a slightly larger distance than the other Si (see Fig. 2). The change in energy due to this additional interaction is quite minor, on the order of 0.1 eV. This was also found from a comparison of the energy of different stacking sequences in bulk $CaSi_2$. Various interface structures are therefore expected to have competing interface energies, as seen in Table 1. It should therefore be anticipated that experimentally more than one of these structures can be obtained, making this a challenging system for growth studies.

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