Atomic and electronic structure of $CaSi_2$/Si interfaces

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The atomic and electronic structure of $CaSi_2$/Si (111) interfaces is studied with the pseudopotential-density-functional technique. Various models for the interfacial structure are examined, in which the Ca atoms at the interface exhibit fivefold, sixfold, sevenfold, or eightfold coordination. Relaxation is included based on calculated Hellman-Feynman forces. Fivefold coordination is found to be energetically unfavorable. Structures with sevenfold coordination (as in bulk $CaSi_2$) have the lowest energy. However, other structures with sixfold and higher coordination are very close in energy. Schottky-barrier heights are discussed.

I. INTRODUCTION

Silicides on silicon have been extensively investigated in recent years, mainly because of the potential technological impact of an epitaxial metal-semiconductor interface. Applications include ballistic transport in metal-base transistors, and the possibility of three-dimensional circuit integration. Ideal metal-semiconductor interfaces also provide an opportunity to examine the mechanisms of Schottky-barrier formation and electron transport, in an environment which allows a direct link between theory and experiment.

Most of the attention so far has been focused on $NiSi_2$ and $CoSi_2$.[1,2] Recently, Morar and Wittmer[3] showed that epitaxial $CaSi_2$/Si interfaces can be obtained. $CaSi_2$ as an epitaxial silicide is interesting from various points of view. First of all, it is close to lattice matched to Si, minimizing problems with strain and/or misfit dislocations. Second, Ca does not contain d electrons, making $CaSi_2$ qualitatively different from transition-metal silicides such as $NiSi_2$ and $CoSi_2$.

Bulk $CaSi_2$ occurs in three different forms.[4] Two are trigonal rhombohedral (the so-called TR3 and TR6 modifications of $CaSi_2$-I), and one is tetragonal ($CaSi_2$-II). Among these, the TR6 modification of the trigonal-rhombohedral phase is the one that naturally occurs and which was experimentally found to grow epitaxially on Si(111).[3] In this paper, I will therefore focus on this structure. It can be visualized 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 (see Fig. 1). 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 each triple layer, which consists of one $CaSi_2$ formula unit, is labeled with one letter (corresponding to the position of the Ca atom in the triple layer), the overall stacking sequence can be described as $AABBCC$. The hexagonal unit cell, space group D_{3d}^5-$R\bar{3}m$, contains six $CaSi_2$ molecules and has a 30.6-Å repeat distance along the c axis. Each Ca atom is surrounded by seven Si nearest neighbors. The bonding in this compound is expected to be quite different from that occurring in other metal silicides, in which d electrons play an important role. Investigations of the charge density will show that in $CaSi_2$ the double layers of Si are bonded covalently, much like in bulk Si, while bonding between the Ca and the Si layers occurs through interactions between charge in Si dangling bonds and Ca atoms.

When an epitaxial layer of $CaSi_2$ on Si is formed, the

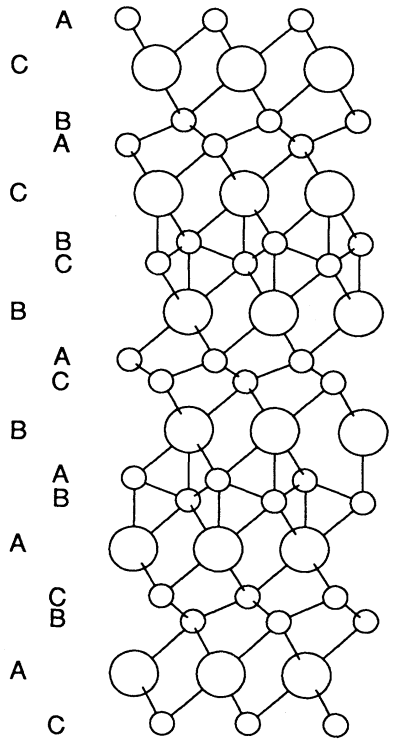

FIG. 1. Schematic representation of the TR6 modification of the trigonal-rhombohedral phase of $CaSi_2$, in a projected view. Large spheres represent Ca atoms, small spheres Si. Two planes of atoms are shown; projected "short" bonds connect atoms in the plane of the figure to those in a plane below.

following questions can be asked.

(a) What is the orientation of the overlayer with respect to the substrate? The overlayer can have the same orientation (type A), or can be rotated 180° about the [111] axis (type B).

(b) What is the coordination of the atoms near the interface? Does Ca maintain its sevenfold coordination or assume a different one?

(c) Are there any relaxations in the neighborhood of the interface, i.e., do the atoms assume positions which differ from what could be expected based upon the Si and $CaSi_2$ bulk bond lengths?

In this paper, I will address these questions with the aid of pseudopotential-density-functional calculations. These techniques have previously successfully been applied to studies of semiconductor interfaces,[5] and of metals.[6] Apart from issues relating to the atomic structure, it is important to also investigate the electronic properties of these junctions. At this point in time, the reliability of local-density-functional theory for the prediction of Schottky-barrier heights has not been established.[7] A full calculation of barrier heights is also beyond the scope of the present work. I will limit myself to discussing a number of qualitative results.

Section II will briefly outline the methods. Before addressing the details of the $CaSi_2$/Si interface structure, it is important to examine some of the bulk properties of $CaSi_2$ (Sec. III). This will aid in understanding some of the features of interface formation. Sections IV contains results on atomic structure, and Sec. V discusses electronic structure. Section VI concludes the paper with a discussion and comparison with experiment. A brief account of some of the initial results of this study was presented elsewhere.[8]

II. METHODS

The calculations are based on local-density-functional theory[9] and *ab initio* nonlocal normconserving pseudopotentials.[10] A supercell geometry is used,[5] in which layers of Si and $CaSi_2$ are periodically repeated, forming a superlattice $(CaSi_2)_m(Si_2)_n$. This approach is similar to the one followed in previous studies of semiconductor interfaces.[5] All the supercells are constructed with the third translation vector perpendicular to the interface. In principle, the full $CaSi_2$ bulk unit cell can then only be represented if $m \geq 6$. However, it was found that the details of the stacking sequence in the bulk which involve changes more than a triple layer (Si-Ca-Si, or ~ 5 Å) away from the interface have no effect on the interfacial structure. This is consistent with Hamann's findings for $NiSi_2$/Si and $CoSi_2$/Si interfaces.[2] The lattice mismatch (0.4%) between $CaSi_2$ and Si is neglected; all calculations are carried out using the experimental Si lattice constant. Atomic relaxations near the interface were investigated using calculated Hellmann-Feynman forces.[11]

Results for an isolated interface can be obtained provided the interfaces are sufficiently well separated, which was checked by testing convergence as a function of superlattice layer thickness. 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. Not all the supercells used to model the various interface structures contain the same number of atoms. In order to investigate whether this might lead to systematic errors, I have carried out calculations for supercells containing extra layers of Si and/or $CaSi_2$ in all relevant cases. Calculations were performed with m varying from 2 to 4, and n from 2 to 6. It was found that the interface energies were affected by less than 0.05 eV, confirming the convergence with respect to supercell size.

Most calculations are carried out with a 6-Ry energy cutoff (determining the size of the plane-wave basis set), a supercell with $m=2$ and $n=3$, and 39 **k** points[12] in the irreducible part of the Brillouin zone. [Note that 39 **k** points correspond to the Monkhorst-Pack[12] (MP) q values (8,8,2).] Tests were performed to ensure that the results are converged with respect to the number of **k** points in the integration over the Brillouin zone.[12] Increasing the number of **k** points in the irreducible part of the Brillouin zone from 39 [MP (8,8,2)] to 78 (8,8,4) or 84 (12,12,2) changed the interface energy by less than 0.025 eV. Finally, I tested the size of the basis set, which is expressed as a cutoff for the kinetic energy of the plane waves included in the expansions of wave functions and potentials. It was found that the interface energy is essentially converged at 12 Ry, and is within 0.05 eV of its final value already at 6 Ry. The total error bar on interface energies is estimated to be ± 0.05 eV.

III. BULK

Morar and Wittmer,[3] using transmission-electron microscopy (TEM), showed that $CaSi_2$, when grown epitaxially on Si(111), assumes the TR6 modification of the trigonal-rhombohedral phase.[4] The TR6 structure has experimental lattice constants of $a=3.855$ Å and $c=30.6$ Å. In a {111} plane in bulk Si, the distance between two Si atoms is $a_{Si}/\sqrt{2}=3.84$ Å, which is very close to the lattice constant $a=3.855$ Å of $CaSi_2$.

The TR6 structure is illustrated in Fig. 1. 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 2.44 Å and three Ca neighbors at 3.03 Å. In addition, some Si atoms have another Ca neighbor at 3.06 Å. Note that the coordination of the Ca is determined by the arrangement of the second-layer Si atoms. Indeed, Ca is always surrounded by six Si atoms in the first layers (three above, three below). The presence of an additional Si atom in an "on-top" position [i.e., in the same (A, B, or C) location as the Ca] adds one to the coordination. Depending on the

stacking, the coordination of the Ca could therefore be sixfold (no additional Si), sevenfold (one additional Si), or eightfold (two additional Si). In the TR6 structure, the coordination is sevenfold.

Fahy and Hamann have recently independently carried out a detailed theoretical investigation of this structure of $CaSi_2$, as well as others in which the Ca exhibits different coordinations.[13] Their results, obtained with the linear augmented-plane-wave method (LAPW), are very similar to the ones presented here.

The primitive unit cell for the TR6 structure is rhombohedral and contains two $CaSi_2$ formula units. Calculations for this structure were carried out for a fixed c/a ratio, equal to the experimental value. The energy was calculated as a function of a, leading to a lattice constant which was $a=3.82$ Å at a 6-Ry cutoff; calculations with a 9- and 12-Ry plane-wave cutoff both gave the value 3.79 Å. These values are within 2% of the experimental value.

Insight into the electronic structure can be obtained from inspection of the charge distribution in the system. Figure 2 shows a contour plot of the valence charge density in a (110) plane perpendicular to the $CaSi_2$/Si interface. From comparison with bulk calculations it was established that the charge density becomes very similar to its bulk value at a distance of a few atomic planes, so that Fig. 2 can be used to study the bonding in $CaSi_2$ itself. 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 charge density around the Ca atoms is lower than in the free atom, indicating that part of the Ca charge is transferred to 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. The interaction between the Si dangling bonds and the Ca atoms holds the layers together.

The energy bands and density of states (DOS) of $CaSi_2$ were investigated based on a self-consistent calculation at 9 Ry with 10 **k** points in the irreducible part of the Brillouin zone. The Fermi level crosses several bands, indicating the metallic character. The band structure (not shown here) is very similar to that obtained by Fahy and Hamann using the LAPW method (Fig. 6 in Ref. 13): most band positions (with only a few exceptions) coincide to better than ±0.1 eV. I refer to Ref. 13 for a discussion of the nature of various bands. In Fig. 3 the density of states (DOS) is shown, obtained with the tetrahedron-integration method,[14] using a total of 86 points in the irreducible part of the Brillouin zone. The curves were smoothed using a Gaussian with a full width at half maximum of 0.1 eV. Note the occurrence near the Fermi level of a quasigap in the DOS. A three-peak structure can be seen in the DOS curve, similar to bulk Si, although the $CaSi_2$ DOS has more structure within the peaks. This similarity suggests that the electronic structure is heavily influenced by covalent bonds between Si atoms. My results are overall quite similar to those obtained by Bisi *et al.*,[15] using the linear muffin-tin orbital (LMTO) method in the atomic-sphere approximation.

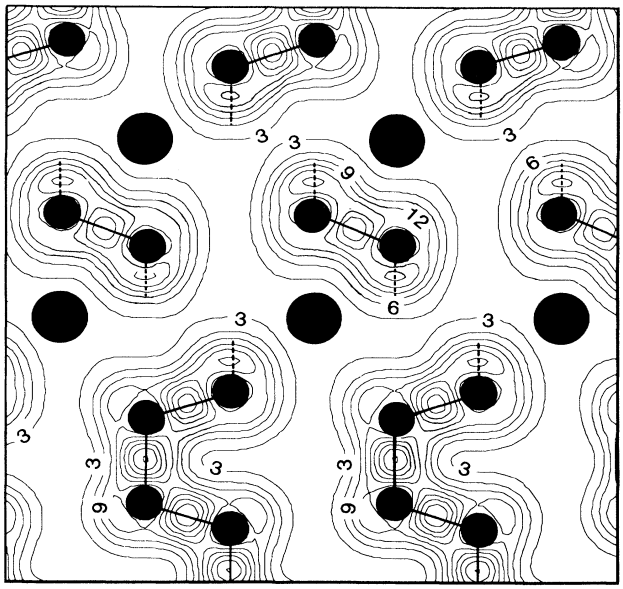

FIG. 2. Contour plot of the valence charge density in a plane perpendicular to the $CaSi_2$/Si interface with the $7B$ structure. The contour spacing is 3; units are electrons per unit cell, scaled to a unit cell containing two Si atoms (eight electrons). Small spheres represent Si atoms, large spheres 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.

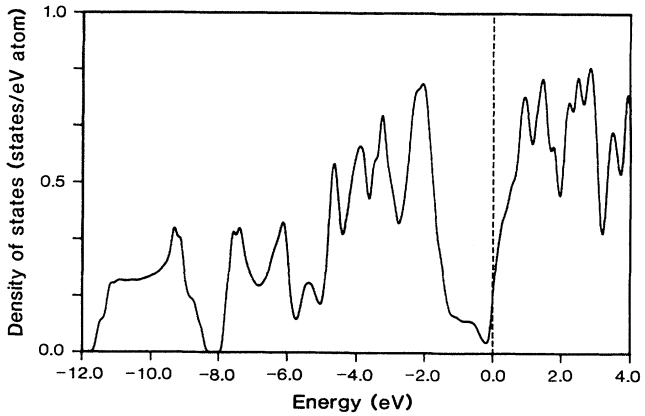

FIG. 3. Density of states of $CaSi_2$ in the TR6 structure. Units are states per eV and per atom. The Fermi level is chosen as the zero of the energy scale, and indicated by the dashed line.

IV. ATOMIC STRUCTURE OF THE INTERFACE

Many different possible structures for the $CaSi_2$/Si(111) interface were investigated in this study. They can be classified according to two criteria: the coordination of the Ca atoms at the interface, and the relative orientation of the $CaSi_2$ and Si crystals. The coordination can be fourfold, fivefold, sixfold, sevenfold, or eightfold. 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 schematically represented in Fig. 4. Note that the atomic arrangements shown in Fig. 4 do not necessarily represent a complete period of the superlattices used in the calculations.

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 a H_3 site), or fourfold (in a T_4 site). This corresponds to having either a full period at the interface (i.e., *AABBCC*...) versus only one-half period (i.e., *ABBCC*...). The first possibility occurs in the 6*A*-6*B* and in the 7*A*′-7*B*′ structures, while the second case occurs in the 5*A*-5*B*, 7*A*-7*B*, and 8*A*-8*B* systems. The distinction between 7*A*-7*B* and 7*A*′-7*B*′ arises from the choice between having Ca fourfold coordinated to $CaSi_2$ and threefold to Si, or vice versa. In the 7*A*-7*B* structures, Ca sits in a H_3 site with respect to the Si substrate, while in the 7*A*′-7*B*′ structures 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. In principle, one could also explore structures with fourfold coordination of the Ca at the interface. They would be analogous to the fivefold structures, but the $CaSi_2$ would be terminated with a full period. Given the high energy of the fivefold structures, however (see below), such fourfold structures are certain to be energetically very unfavorable.

Note that all the shown structures have a double layer of Si at the interface. I have found that having only a single Si layer at the interface is energetically extremely unfavorable. Also note that for the sixfold and higher-fold structures, the difference between *A* and *B* orientations is related to the presence of a stacking fault in the double layer of Si at the interface, when viewed with respect to the Si substrate.[3,16]

These choices, together with the requirement of perfect

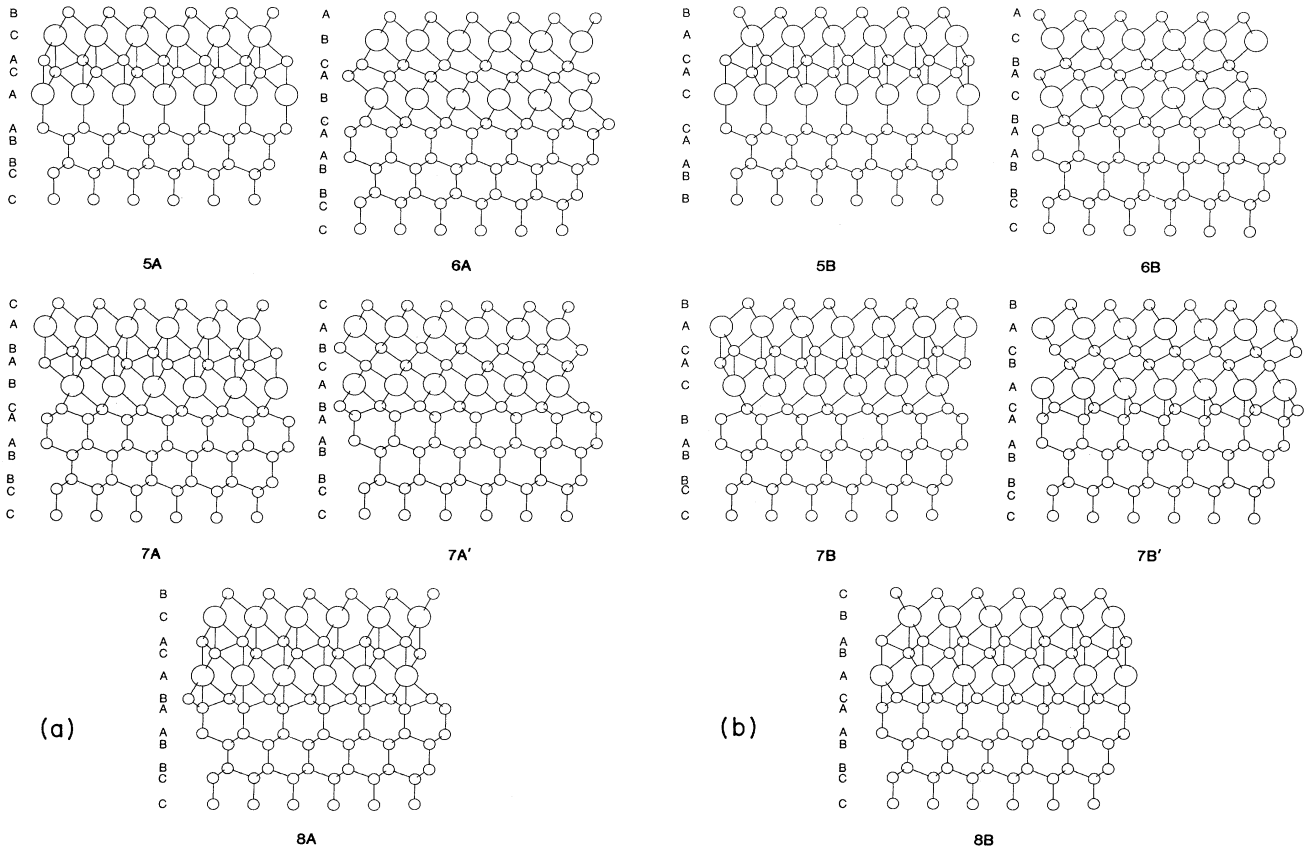

FIG. 4. Schematic representation of the $CaSi_2$/Si interfaces examined in this study. Small spheres represent Si atoms, large spheres Ca. The labels 5, 6, 7, or 8 represent the coordination of the Ca atoms at the interface (see text). (a) Type-*A* structures, in which the relative orientation of the $CaSi_2$ and Si crystals is the same. (b) Type-*B* structures, in which the $CaSi_2$ is rotated by 180° with respect to the Si.

TABLE I. Interface energies, including relaxation, for various $CaSi_2$/Si (111) interfaces, characterized by the coordination of interfacial Ca (see text) and the relative orientation of $CaSi_2$ with respect to Si (A or B). Values are in eV per interface unit cell, with an estimated uncertainty of ±0.05 eV.

	5	6	7	7′	8
A	0.94	0.05	−0.03	0.09	0.03
B	0.88	0.04	−0.03	0.09	0.03

pseudomorphic matching, determine the coordinates of all atoms in the plane of the interface. The atomic positions perpendicular to the interface are not fixed, however, and may exhibit relaxations. Hellmann-Feynman forces[11] were calculated, and the atoms moved in the direction of these forces until the forces were smaller than 0.1 mdyne; I found that atomic positions were then within 0.02 Å of the equilibrium positions. The results can, *a posteriori,* be interpreted as follows. The atomic positions on the $CaSi_2$ side correspond to those in the bulk up to the last atom (but at a lattice constant $a = a_{Si}/\sqrt{2}$). For the fivefold structures, the Ca-Si distance at the interface is 2.94 Å, which is 4% smaller than the larger of the Ca-Si distances in bulk $CaSi_2$ (3.06 Å). For the sixfold, sevenfold, and eightfold interfaces, the distance between Ca and first-layer Si is the same as in bulk $CaSi_2$. For the $6A$-$6B$ and $7A$-$7B$ interfaces, the bond lengths in the double layer of Si at the interface are close to those of bulk Si (2.35 Å). (Note that the Si—Si bond length in bulk $CaSi_2$ is 2.44 Å, i.e., 4% larger than in bulk Si.) At the $7A'$-$7B'$ and $8A$-$8B$ interfaces, however, this Si-Si double layer has to expand in order to generate an acceptable distance between Ca and the second-layer Si atoms. The Si-Si interlayer distance expands by 13% (from 0.78 Å in bulk Si to 0.88 Å; the corresponding value in bulk $CaSi_2$ is 1.02 Å), making the relevant Si—Ca bond length equal to 2.92 Å.

The interface energy of the various models is given in Table I. We immediately note that the fivefold structures are so high in energy that they can be excluded as viable candidates for the interfacial structure. Among the others, the $7A$-$7B$ interfaces are lowest. The other structures are only slightly higher, however. The energy difference between A and B orientations is very small or zero. These results will be discussed in Sec. VI.

V. ELECTRONIC STRUCTURE OF THE INTERFACE

A typical charge density contour plot in a plane cutting through the $CaSi_2$/Si $7B$ interface was given in Fig. 2. Note that there is little perturbation of the bulk charge densities in the neighborhood of the interface.

One of the most important quantities characterizing the electronic properties of a metal-semiconductor interface is the Schottky-barrier height. 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 in principle allow the derivation of this quantity in a manner analogous to the technique used for semiconductor heterojunctions, as described in Ref. 5: the superlattice calculations yield the shift in average potentials between the metal and the semiconductor layers. Separate bulk calculations provide values for the energy difference between Fermi level and average potential in the metal, and between valence-band maximum and average potential in the semiconductor. However, there are numerical complications which make the calculation of Schottky-barrier heights much harder than that of heterojunction band offsets. The accurate determination of the electronic structure of a metal requires a large number of sampling points to be used in the Brillouin-zone integrations. The position of the Fermi level is much more sensitive to this integration than the total energy is. In contrast, in the case of a semiconductor both total energy and band positions can be obtained with great accuracy using a small number of special points in the self-consistent calculations.[5,12] Derivation of the $CaSi_2$/Si Schottky-barrier height also requires larger supercells than needed for heterojunction band lineups, as will be shown below. Furthermore, the use of density-functional theory in the local-density approximation[9] may lead to deviations in the calculated Schottky-barrier height from its true value, as observed in the case of $NiSi_2$/Si interfaces by Das *et al.*[7] Those authors also showed, however, that even though the absolute value of the barrier height may be unreliable, relative changes as a function of interfacial structure are produced quite accurately.

Because of these difficulties, the error bars on the values of Φ calculated in this work are quite large. Nonetheless, the information obtained here may be valuable as a basis for further investigations. In addition, it is possible to discuss some trends which are likely to be reliable, even though the absolute values of the barrier heights are not.

In Table II I report values for Φ obtained for the 6-, 7-, 7′-, and 8-fold interfaces, in the relaxed structures for which interface energies were reported in Table I. The fivefold-coordinated structures were not considered here since they are high in energy and therefore not of practical interest. The energy cutoff was 6 Ry, and 39 **k** points[12] in the irreducible part of the Brillouin zone were used. The supercells contained $m = 2$ layers of $CaSi_2$ and $n = 3$ or 5 double layers of Si. The bulk calculations for Si were carried out with an energy cutoff of 24 Ry and ten

TABLE II. p-type Schottky-barrier heights, in eV, for various $CaSi_2$/Si (111) interfaces, characterized by the coordination of interfacial Ca (see text) and the relative orientation of $CaSi_2$ with respect to Si (A or B). The error bar on the absolute values is large (±0.5 eV), due to the LDA uncertainty and supercell-size convergence (see text). *Differences* are expected to be more accurate.

	6	7	7′	8
A	0.63	0.90	0.52	0.85
B	0.67	0.91	0.53	0.86

special points. For bulk $CaSi_2$, the Fermi-level position was found to be quite sensitive to the plane-wave cutoff. Calculations were carried out at various energy cutoffs, and extrapolated to estimate the converged value (the 15-Ry result was within 0.05 eV of the extrapolated value). 86 points in the irreducible part of the zone were used in the integration to obtain the Fermi level (26 points gave the same result to within 0.02 eV). Convergence as a function of iteration in the self-consistent calculations was checked, and found to be entirely adequate at the level required for convergence of the total energy (to better than 0.01 eV per cell) (usually less than ten iterations).

The superlattice calculations that yielded values for the average potential were checked for convergence as a function of energy cutoff by increasing the cutoff from 6 to 9 Ry; Φ changed by less than 0.05 eV. Convergence as a function of **k**-point sample was investigated by increasing the number of points in the irreducible wedge for the superlattice from 13 [MP (4,4,2)] to 39 (8,8,2), 78 (8,8,4), and 84 (12,12,2). It should be pointed out that even with the densest mesh the energy sampling in the neighborhood of the gap is still rather sparse. Nonetheless, it was very encouraging that the variations in Φ observed between the various **k**-point grids are less than 0.01 eV.

Convergence as a function of supercell size turned out to be the most problematic. Tests were carried out (for the $7B$ and the $8A$ interfaces) in which the semiconductor layer thickness was increased up to $n=6$ (12 Si atoms), and the metal layer thickness up to $m=4$ (four Ca and eight Si atoms) or $m=6$ (six Ca and 12 Si atoms). It was found that increasing the thickness of the Si layer has minor effects (less than 0.05 eV). This trend is similar to that observed for semiconductor heterojunctions.[5] However, increasing the thickness of the $CaSi_2$ layer can cause significant changes in the barrier height (on the order of several 0.1 eV). Even the largest supercells (with $m=6$) could not be confidently considered large enough to obtain converged results. Extensive computations on larger cells were beyond the scope of the present study. I conclude that supercells which are entirely adequate for calculations of the total energy can still be too small for derivations of Schottky-barrier heights. The observation that the results are more sensitive to the thickness of the metal layer was unexpected. However, the described dependence on layer thickness emerged very clearly from the present calculations, and has also been observed in the $NiSi_2$/Si system.[17] Simple arguments about screening being more effective in the metal do not seem to be applicable here. One reason may be that for $CaSi_2$ (and also $NiSi_2$) the density of states in the neighborhood of the Fermi level is quite low. More work is needed, however, to obtain a better understanding of these effects.

The difficulties associated with supercell-size convergence, combined with LDA uncertainties, lead to the large error bar on the values quoted in Table II. Nonetheless, one might expect *differences* in Schottky-barrier heights to be more reliable, since systematic errors are more likely to cancel; this is the reason why the results in Table II are quoted to two decimal places. A comparison of calculations for similar-size supercells allows us to identify the following trends. Probably the most reliable result is that there is virtually no difference between A and B orientations (unlike the case of $NiSi_2$/Si, see Ref. 7). I also examined whether the Schottky barrier would be sensitive to the specific atomic positions near the interface. At the $8A$ interface, increasing the Si-Si distance in the Si double layer at the interface by 4% (corresponding to changing the interlayer distance from its value in bulk Si to its value in bulk $CaSi_2$) leads to an increase in Φ of 0.04 eV, i.e., only a minor change. Finally, the values in Table II seem to indicate that the $7A$-$7B$ and $8A$-$8B$ structures (all of which are terminated with a half period of $CaSi_2$) yield quite similar barriers. The value of Φ for the $6A$-$6B$ and $7A'$-$7B'$ structures (which are terminated with a full period of $CaSi_2$) is significantly lower (by several tenths of an eV).

VI. DISCUSSION

A. Comparison with experiment

The experiments of Morar and Wittmer[3] produced an interfacial structure which corresponds to the $7B$ interface. Their TEM results showed that the break in the bulk $CaSi_2$ structure falls between Ca layers of the same type, i.e., the $CaSi_2$ terminates with a half-period. The interfaces were atomically abrupt and step-free. 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, the sevenfold structures are found to be lowest in energy. However, the energy difference with other structures is very small, and on the order of the estimated error bar. No energy difference is found between the $7A$ and $7B$ orientations.

It is actually not surprising that the sevenfold structure would be 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 so close in energy. The answer can be found in the nature of the bonding between Ca and Si atoms. Cohesion between the Ca and the Si layers results mainly from interaction between Ca atoms and 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 atom 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 atoms (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 $CaSi_2$, in my own calculations as well as in those of Fahy and Hamann.[13] Various interface structures are therefore expected to have competing interface energies, as seen in Table I. It should therefore be anticipated that experimentally more than one of these structures might be ob-

tained, making this a challenging system for growth studies.

Schottky-barrier heights have not been measured to date. If it turns out to be experimentally possible to grow interfaces with different structures, it would be very interesting to study whether these differences lead to changes in the Schottky-barrier heights.

B. Comparison with other interfaces

Among other silicides, $CoSi_2$ and $NiSi_2$ have been most intensively investigated. Hamann[2] has investigated the structure of their interfaces with Si, and compared the results with experiment. He found that, in analogy with the present results, the fivefold coordinated interfaces are prohibitively high in energy. Clear energy differences were found between sevenfold- and eightfold-coordinated structures. Hamann explained the differences in bonding between the $CoSi_2$/Si and $NiSi_2$/Si interfaces in terms of the different position of the Fermi level with respect to the "quasigap" separating bonding and antibonding states. In contrast, for the case of $CaSi_2$ the energy difference between sevenfold and eightfold structures is found to be very small.

For reasons similar to the interest in $CaSi_2$, CaF_2 has received a great deal of attention lately: it is an insulator which is closely lattice matched to Si, and can be used to create epitaxial insulator-semiconductor interfaces. Tromp and Reuter,[18] in their ion-scattering experiments on this interface, have found that the interface between CaF_2 and (111) Si has a structure in which the Ca atom is bonded to the Si substrate in a T_4 configuration; they pointed out the similarity to the bonding in bulk $CaSi_2$. In their first-principles calculations for this interface, Satpathy and Martin[19] found this interface structure to be a possible candidate, but also included a model in which Ca is bonded to only one Si atom in the substrate. This structure is similar to the fivefold-coordinated interface studied above for $CaSi_2$, which I found to he high in energy. Furthermore, the insight in Ca—Si bonding obtained from the present study seems to make it unlikely that Ca would sit on top of a first-layer Si atom. On the basis of such arguments I would suggest that a CaF_2/Si structure with fivefold-coordinated Ca is extremely unlikely.

In conclusion, I have carried out first-principles calculations for a large number of interface structures for the $CaSi_2$/Si(111) interface. Structures with sevenfold orientation for the interfacial Ca are lowest in energy (see Fig. 4 and Table I). However, other structures with sixfold or higher coordination have interface energies which are only slightly higher. It seems therefore likely that these structures may be obtained by varying the growth conditions.

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