First-principles calculations of the structural properties of $ScSi_2$ and the formation of $ScSi_{2-x}$ on the Si(111) surface

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(Received 18 January 2007; revised manuscript received 4 April 2007; published 26 July 2007)

Using first-principles total energy calculations, we have studied the structural properties of bulk $ScSi_2$, the two-dimensional arrangement of $ScSi_2$ on the Si(111) surface, and the formation of a few layers of $ScSi_{1.7}$ on the same surface. $ScSi_2$ crystallizes in the hexagonal Th_3Pd_5 structure that can be obtained from the AlB_2 structure after relaxation around the Si vacancies within the (0001) plane. Our calculated geometry is in excellent agreement with experimental values. One monolayer of $ScSi_2$ on Si(111) results in a two-dimensional phase with (1×1) periodicity that consists of a layer of Sc atoms on $T4$ sites and a Si bilayer on top. This double layer of Si atoms is very close to the ideal Si(111)-(1×1) surface, but rotated 180° with respect to the rest of the crystal. More layers of scandium silicide epitaxially grown on Si(111) result in a hexagonal structure similar to bulk $ScSi_2$: graphitelike Si planes (with vacancies) intercalated with scandium planes and forming a $(\sqrt{3}\times\sqrt{3})$ arrangement with a $ScSi_{1.7}$ stoichiometry. The top Si layer does not contain vacancies and it does not present a graphitelike structure, but forms a bilayer arrangement as in bulk Si.

DOI: 10.1103/PhysRevB.76.035333 PACS number(s): 68.35.−p, 68.43.Bc, 68.43.Fg

I. INTRODUCTION

There is a current interest in studying the properties of rare-earth (RE) silicides epitaxially grown on Si(111) surfaces,[1–24] since they can be used in the electronic industry. Their small lattice mismatch,[1] sharp interface, and low Schottky barrier height[2] make them ideal for applications in electronic devices, such as infrared detectors, and rectifying contacts. Although they are not rare-earth elements, Y and Sc share some of their properties, and YSi_2 and $ScSi_2$ have similar structural properties of the rare-earth silicides.[3] On the other hand, the chemical properties of Sc, a 3d transition metal, have strong similarities with group 13 metals such as Al and Ga. For example, combined with nitrogen scandium forms ScN, which is a semiconductor with a small indirect band gap. Although the ground state structure of ScN is rocksalt,[25,26] it has been shown that it also has a metastable hexagonal phase,[27,28] and therefore, it is possible to combine it with GaN to obtain a material with tailor-made optical and electronic properties.[29] Also, ScN is a promising buffer layer for the growth of GaN on Si(111), and since a few monolayers of $ScSi_2$ can be formed when growing ScN on Si(111), it is important to know the details of the atomic structure of the $ScSi_2$/Si(111) interface. The control of such interface could be crucial for the quality of the GaN films.

Recent scanning tunneling microscope (STM), atomic force microscope, and electron diffraction studies have found that it is possible to grow hexagonal $ScSi_2$ on Si(111) at a temperature of 900–920 °C.[4] Although no structural analysis of the $ScSi_2$/Si(111) surface has been known, there are many reports about the interfaces of some rare-earth disilicides with Si(111). For RE coverage of around 1 ML, the silicides present a two-dimensional structure with (1×1) periodicity.[5] At higher coverage, a three-dimensional (3D) silicide is formed with $(\sqrt{3}\times\sqrt{3})$ periodicity.[6–12] Two different models, based on STM images with atomic resolution, have been proposed for $YSi_{1.7}$.[13–16]

Although the structural properties[13–16] of bulk YSi_2 and its surface have been studied in the past, it is not obvious *a priori* that scandium and yttrium silicides have the same structural properties. For example, it is found experimentally that $LaSi_2$ (La in the same row as Sc and Y) has a different α-$ThSi_2$ atomic structure. Therefore, as a check, we have first studied scandium silicide in bulk and compared our results with those of yttrium silicide. In this way, we can also test our computational variables such as pseudopotentials, plane wave energy cutoff, and exchange correlation approximations. We have then studied the energetics and atomic configuration of a few $ScSi_2$ layers on the (111) surface of silicon. To our knowledge, there is only one previous theoretical work in a similar system YSi_2 on Si(111). However, in that work, the authors have assumed the so-called $BT4$ atomic geometry and optimized it. In this paper, we considered several possible sites for the Sc atom on top of the Si(111) surface and under a Si bilayer (rotated and nonrotated). We have then studied the atomic structure of a few $ScSi_{1.7}$ layers on the same surface. We are not aware of any calculation on Sc silicides or any similar system. Only cal-

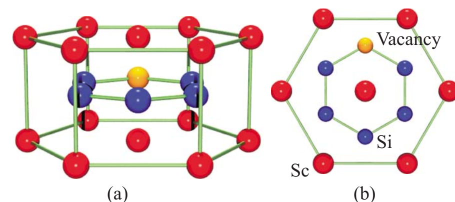

FIG. 1. (Color online) (a) AlB_2 structure with a vacancy in the Si plane. (b) Projection on a (0001) plane.

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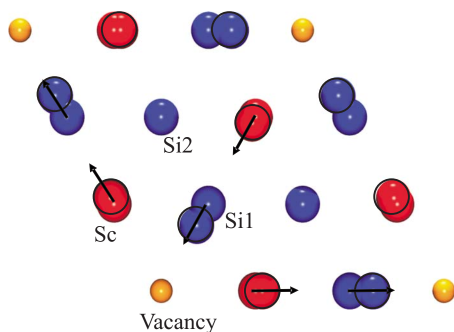

FIG. 2. (Color online) Relaxation of Sc and Si atoms in the (0001) plane; arrows indicate displacements from the AlB_2 to the Th_3Pd_5 structure.

culations of the YSi_2 surface have been reported,[23] and as is shown in this paper, some differences exist between the two systems. The paper is organized as follows: Sec. II describes the method, Sec. III is dedicated to the description of the results, and Sec. IV is for the conclusions.

II. METHOD

Periodic density functional theory calculations have been performed using the PWSCF code,[30] with the gradient corrected Perdew-Burke-Enzerholf[31] functional. Electron-ion interactions are described using ultrasoft pseudopotentials.[32] The electronic states are expanded in plane waves with kinetic energy cutoffs of 25 and 200 Ry for the wave function and charge density, respectively. Different supercells and corresponding number of k points were used, as detailed in the following. For bulk $ScSi_2$, we use a $(\sqrt{3}\times\sqrt{3})$ $R30$ cell with a Si vacancy as shown in Fig. 1. The structural parameters c/a and a have been fully optimized, relaxing the atomic positions at each calculation.

For the surface calculations, we have used a periodic supercell approach. For the two-dimensional phase with 1 ML of $ScSi_2$ on Si(111) and (1×1) periodicity, the surface was modeled as a substrate of four bilayers (eight layers) of silicon and one layer of $ScSi_2$. On the bottom surface of the slab, the Si dangling bonds (DB's) were saturated by H atoms. The six topmost Si layers of the slab as well as the $ScSi_2$ layer were fully relaxed, whereas the two lowest Si layers and the saturating H atoms were fixed at the ideal positions in order to simulate a bulklike environment (the Si-H distance was previously optimized). No vacancies were present in these calculations. The system consisting of a few layers of scandium silicide epitaxially grown on Si(111) was also modeled by a supercell geometry with $(\sqrt{3}\times\sqrt{3})$ periodicity and consisting of four bilayers of Si, two graphitelike Si planes (with vacancies), and three layers of Sc. On the bottom surface of the slab, the Si DB's were also saturated by H atoms. The two lowest Si layers and the saturating H atoms were fixed at the ideal positions in order to simulate a bulklike environment. All other atoms were fully relaxed.

III. RESULTS

A. Bulk $ScSi_2$

We have optimized the structural parameters a, c/a, and the atomic positions of the structure shown in Fig. 1.

It is an AlB_2 structure with one Si vacancy out of six atoms, resulting in a $(\sqrt{3}\times\sqrt{3})$ $R30$ supercell. As shown in the figure, the vacancy divides silicon atoms into two types, first (Si1) and second (Si2) neighbors. The vacancy induces relaxations of the other atoms, resulting in the hexagonal Th_3Pd_5 structure. Si1 and Sc atoms move toward and away from the vacancies, respectively. Si2 atom do not move due to the symmetry (Fig. 2). The atomic positions can be expressed with two parameters x and x'. The Sc atom is located at $(x,0,0)$, the Si1 at $(x',0,1/2)$, and the Si2 atom at $(1/3,2/3,1/2)$. We show in Table I the calculated structural parameters compared with the experimental values, and with results of a previous calculation of YSi_2. We can observed that our calculated a and c/a are in excellent agreement with experiments,[1] and our x and x' are similar to those of YSi_2.[23]

B. Si(111)+$p(1\times1)$-$ScSi_2$ system

Many RE silicides present a two-dimensional (2D) phase with (1×1) periodicity close to the monolayer coverage. Different from the bulk, this phase does not contain Si vacancies and has a $RESi_2$ stoichiometry. The atomic structure of this phase consists of a monolayer of RE atoms on $T4$ sites and a Si bilayer on top. This double layer of Si atoms is very close to the ideal Si(111)-(1×1) surface, but rotated 180° with respect to the rest of the crystal. This model has been proposed for Er, Y, Dy, and Ho silicides.[17–22]

We have first considered geometries in which the Si atoms of $ScSi_2$ bond directly with the Si(111) surface, resulting in

TABLE I. Lattice parameters, volume, and atomic displacements with respect to the AlB_2 structure.

System	a (Å)	c/a	V (Å^3)	x	x'
$ScSi_2$	3.66	1.057	44.90	0.357	0.749
$ScSi_2$ (Experiment)[a]	3.66	1.057	44.90		
YSi_2[b]	3.759	1.082	49.73	0.354	0.733
YSi_2 (Experiment)[c]	3.842	1.0786	52.974		

[a]Reference 4.
[b]Reference 23.
[c]Reference 1.

TABLE II. Energetics of different configurations of a monolayer of $ScSi_2$ on Si(111).

Sc layer on top			Si bilayer rotated 180° on top			Si bilayer on top
*T*4	*H*3	Top	*T*4	*H*3	Top	*T*4
0	0.1 eV	1.1 eV	−1.1 eV	−0.5 eV	0.2 eV	−0.9 eV

an additional Si bilayer and the Sc atoms on top. This is equivalent to studying the adsorption of Sc atoms into the unreconstructed Si(111)-(1×1) surface. We have optimized atomic configurations with Sc atoms on top of high symmetry sites as shown in Fig. 3. It is found that as in other adatom systems, the most stable geometry corresponds to the *T*4 site on top of a second layer Si atom. The relative energies of the different configurations are summarized in Table II. The energy reference corresponds to the *T*4 site.

We have then studied configurations similar to those of other RE silicides, with a double layer of Si atoms (rotated 180° with respect to the rest of the crystal) on top of the Sc layer. As shown in Table II, this configuration is more favorable for all structures, with the *T*4 being the most stable. In the last column of Table II, we show the energy of a configuration in which the top of the Si bilayer is not rotated, resulting in a slightly less stable configuration. Rogero *et al.* have found a similar difference in the case of YSi_2.[22] A schematic representation of the most stable structure is shown in Fig. 4, and the distances between atomic planes along the (111) direction are summarized in Table III together with theoretical and experimental results for YSi_2.[22]

The relaxed atomic positions follow similar trends to those of YSi_2. The largest difference corresponds to the Sc-Si2 and Sc-Si3 interlayer spacings and it is due to the smaller size of the Sc atom. Si atoms in the first bilayer are in positions similar to those of the bulk: their nearest neighbor distances are 2.39 Å, slightly larger than the calculated bulk Si-Si distance of 2.37 Å, while their bond angles are 108°, close to the ideal bulk angle of 109°. All other Si-Si nearest neighbor distances are also close to the bulk, with the exception of the second bilayer. An expansion from the ideal 0.79 Å to the 0.94 Å, results in a slightly elongated Si-Si bond length of 2.43 Å. The Sc atoms form bonds with atoms of the second and third layers, and their respective bond lengths are 280 and 2.89 Å.

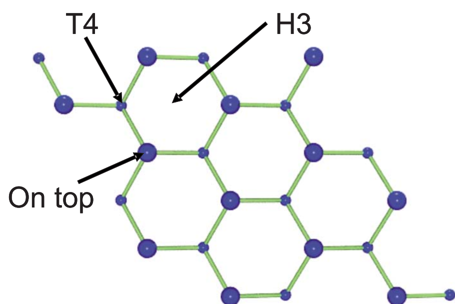

FIG. 3. (Color online) Schematic atomic structure of ideally terminated Si(111) showing some high symmetry sites.

C. Few layers of scandium silicide grown on Si(111)

At coverage larger than 1 ML, rare-earth silicides form a 3D phase with $(\sqrt{3}\times\sqrt{3})$ periodicity. The atomic structure of the inner silicide planes is similar to the bulk (Fig. 1) and it consists of a hexagonal structure with graphitelike Si planes intercalated with RE planes. The Si planes contain vacancies resulting in a $RESi_{1.7}$ stoichiometry. As in the 2D phase, the presence of a Si bilayer termination was found by x-ray photoelectron diffraction.[8] However, two different models were proposed for the $ErSi_{1.7}$ epitaxially grown on Si(111). In the first one, proposed by Roge *et al.*,[13,14] a Si atom of the first layer (Si_{up}) is on top of the vacancy, and it relaxes inward as shown schematically in Fig. 5(a). As a consequence, this atom is at a lower vertical position with respect to the other first layer atoms. In the second model, proposed by Martín-Gago *et al.*,[15,16] one of the second Si layer atom (Si_{down}) is on top of the vacancy [see Fig. 5(b)]. In this configuration, instead of moving vertically, the three first layer atoms are displaced (by the same amount) toward the Si_{down} atom situated on top of the vacancy. This second model was favored by first-principles total energy calculations of the YSi_2 surface,[23] and by low-energy electron diffraction (LEED) experiments on $YSi_{1.7}$/Si(111)-$(\sqrt{3}\times\sqrt{3})$.[24]

We have, therefore, fully optimized the atomic positions of the two different models, finding that the structure pro-

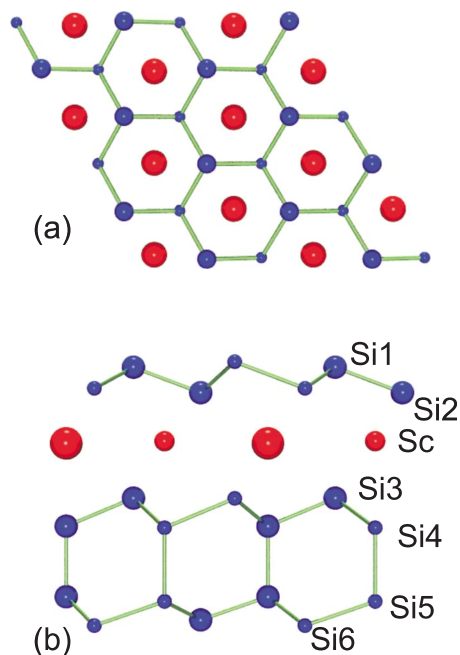

FIG. 4. (Color online) Schematic representation of the Si(111)-(1×1) $ScSi_2$ system: (a) top view and (b) side view.

TABLE III. Interlayer distances between atomic planes along the (111) direction for the Si(111)-(1×1) $ScSi_2$ system compared with results for YSi_2 (Ref. 22).

Layers	$ScSi_2$	YSi_2 (Theory)	YSi_2 (Expt.)
Si1-Si2 (Å)	0.85	0.84	0.79
Si2-Sc (Å)	1.69	1.83	1.83
Sc-Si3 (Å)	1.83	1.99	2.08
Si3-Si4 (Å)	0.94	0.92	0.90
Si4-Si5 (Å)	2.35	2.35	2.35
Si5-Si6 (Å)	0.77	0.77	0.78

posed by Martín-Gago *et al.* is more stable by 0.22 eV. This difference is much larger than the 23 meV reported in Ref. 23. However, we have to point out that this later result was obtained for the YSi_2 surface. In our case, there is a lattice mismatch between the $ScSi_2$ layers and the Si substrate of more than 4%. We have also investigated the influence of the variation of the stacking of the vacancies in the graphitelike planes. Three different configurations are possible: a vacancy on top of the other (0° rotation) and a 60° or 120° rotation of the vacancy from one plane to the other. Within the accuracy of our calculations, all three configurations have the same total energy. As shown in Table IV, structural parameters change little with the different vacancy configurations. In the following, we will describe in detail the structure with the vacancies piled up.

As suggested by Martín-Gago *et al.*, atoms in the topmost Si atomic layer (Si_{up}) are slightly laterally shifted by 0.03 (0.06) Å. Contrary to the calculations of Ref. 23, we found no atomic buckling in this layer. Again, we have to mention that Ref. [23] is related to the surface of $YSi_{1.7}$, while our calculations correspond to a few layers of $ScSi_2$ on the Si(111) surface, with a difference of 0.17 Å between the two lattice constants. However, this result is in good agreement

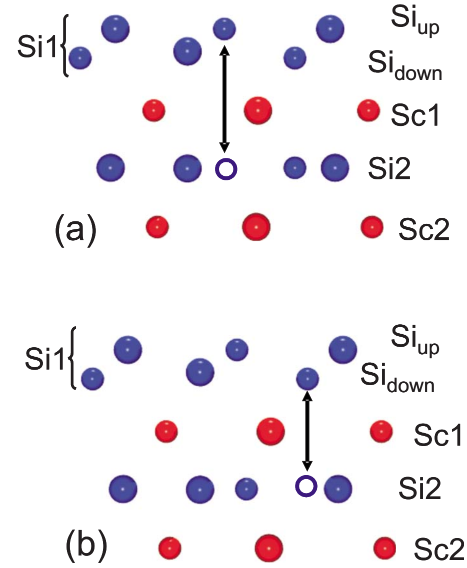

FIG. 5. (Color online) (a) Surface model proposed by Roge *et al.*, in which the vacancies are located below the Si_{up} atoms, (b) Surface model proposed by Martín-Gago *et al.*, in which the vacancies are below the Si_{down} atoms.

with the LEED results of Rogero *et al.*[24] for the $YSi_{1.7}$/Si(111) system. We do find a difference in the vertical positions of 0.21 Å between the Si down atom on top of a vacancy with respect to the other down atoms (a similar result was found in Ref. [23] for the $YSi_{1.7}$ system). These atoms do not move laterally, and the buckling distances between the up and down atoms are 0.91 and 0.70 Å, respectively. Si up atoms are 2.56 Å over the first Sc layer that do not present vertical distortions. Vertical distances between down Si and Sc atoms are 1.86 and 1.65 Å. There is a very small vertical distortion in the Si2 layer of 0.02 Å. However, this value is slightly larger for the 60° and 120° configurations (0.13 Å). As in the case of bulk $ScSi_2$, Sc atoms move away from the

TABLE IV. Structural parameters of $ScSi_{1.7}$ on Si(111). All distances are in Å.

Configuration	0°	60°	120°
	Vertical distances		
Si_{up}-Si_{down}	0.70	0.70	0.70
Si_{up}-Si_{down} (vacancy)	0.91	0.90	0.90
ΔSi_{down}	0.21	0.21	0.19
Sc1-Si_{up}	2.56	2.55	2.55
Sc1-Si_{down}	1.86	1.85	1.85
Sc1-Si_{down} (vacancy)	1.65	1.65	1.64
Sc1-Si2 (highest)	1.79	1.77	1.77
ΔSi2	0.02	0.13	0.13
	Lateral displacements		
Si_{up}	0.06, 0.03, 0.0	0.03, 0.03, 0.04	0.03, 0.05, 0.03
Si_{down}	0.00	0.00	0.00
Sc1	0.07, 0.07, 0.11	0.07, 0.15, 0.09	0.15, 0.09, 0.09
Si2 (close to vacancy)	0.57, 0.33, 0.33	0.31, 0.31, 0.54	0.31, 0.54, 0.37
Si3 (away from vacancy)	0.00	0.00	0.00

vacancies; as seen in Table IV, the displacement is smallest for the 0° configuration. Sc1 atoms form bonds with three Si_{down} atoms of lengths 2.89 Å (2) and 2.83 Å (1), while it forms four bonds with Si2 atoms: two bonds of length 2.86 Å and two of 2.79 Å. Respective bulk values are 2.81 and 2.79 Å, and differences can be attributed to the different lattice constant of Si with respect to $ScSi_2$. The vertical distance between the topmost Sc layer (Sc1) and the Si_{down} plane is 1.86 Å, slightly shorter than the Sc-Si bulk distance of 1.93 Å. with respect to the last graphite Si plane, Si2, the Si atoms surrounding the vacancies are laterally displaced by 0.33 (0.57) Å toward the vacancy. In this way, the hexagonal structure is distorted, forming a "more pentagonal" configuration with four bond lengths of 2.42 Å and one of 3.30 Å. These values are to be compared with 2.42 and 2.76 Å in bulk $ScSi_2$.

IV. CONCLUSIONS

We have performed first-principles total energy calculations to investigate the structural properties of $ScSi_2$ in bulk and grown on Si(111). The ground state configuration of bulk $ScSi_2$ is a hexagonal Th_3Pd_5 structure that can be obtained from the AlB_2 structure after relaxation around the Si vacancies within the (0001) plane. Our calculated geometry is in excellent agreement with experimental values. One monolayer of $ScSi_2$ on Si(111) results in a two-dimensional phase with (1×1) periodicity that consists of a layer of Sc atoms on *T*4 sites and a Si bilayer on top. The strain in the topmost Si layer is released by a buckling of the Si atoms, forming a bilayer structure similar to the ideal Si(111)-(1×1) surface but rotated 180° with respect to the rest of the crystal. Different from bulk $ScSi_2$, there are no Si vacancies in the structure. A few layers of scandium silicide epitaxially grown on Si(111) consist of a hexagonal structure similar to bulk $ScSi_2$: graphitelike Si planes (with vacancies) intercalated with scandium planes and forming a $(\sqrt{3}\times\sqrt{3})$ arrangement with a $ScSi_{1.7}$ stoichiometry. The top Si layer does not contain vacancies and it is similar to the 2D phase. In the most stable configuration, one of the Si_{down} atoms is on top of the vacancy. Within the accuracy of our calculations, Si vacancies in the different graphitelike planes are not arranged in a special order.

ACKNOWLEDGMENTS

This work was partially supported by Conacyt under Grant No. 48549, DGAPA Project No. IN109007, and by VIEP-BUAP Project No. 31/EXC/06–G.

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