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Electronic structure of Si(111)-NiSi$_2$(111) *A*-type and *B*-type interfaces

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The self-consistent electronic properties of the epitaxial Si(111)-NiSi$_2$(111) interfaces are computed for the experimentally observed *A*- and *B*-type interface structures. The densities of states projected at the different atomic sites and the two-dimensional band structure provide a detailed analysis of the electronic properties of the silicon-silicide interface. The Schottky-barrier height turns out to be dependent not only on the interface structure, but also on the interface relaxation distance. A critical analysis of existing results is also presented.

I. INTRODUCTION

The metallic disilicides NiSi$_2$ and CoSi$_2$ are attracting much interest both from fundamental and technological points of view.[1] They have the CaF$_2$ crystal structure with lattice parameters very similar to that of silicon and are the only transition-metal silicides which have been demonstrated to grow as homogeneous, single-crystal, epitaxial interfaces on the low-Miller-index faces of Si. Moreover many x-ray and transmission electron microscopy (TEM) experiments have provided a detailed description of the interface atomic structure, such as the atomic coordination at the interface, the interface interplanar distances, and the directions of growth. Thus the study of these interfaces represents a good challenge to the theoretical analysis of silicon-metal interfaces.

In particular, when these silicides grow epitaxially on the (111) Si substrate, two different interface structures have been experimentally observed: the perfect epitaxial orientation (*A* type, where the silicide grows with the same orientation as the ideal substrate) and the 180° rotated structure (*B* type, where the lattice of the silicide is rotated around the normal to the silicon surface).

The Si(111)-NiSi$_2$(111) interface has been investigated intensively with special reference to the relation between epitaxial growth and Schottky-barrier formation. At present the *n*-type Schottky-barrier height (SBH) seems to be different in the two observed structures; following the results obtained by Tung,[2] the Schottky-barrier height for *B*-type-oriented NiSi$_2$ is higher (0.79 eV) than for *A*-type orientation (0.65 eV), while Ho *et al.*[3] find equal values for the two structures (0.78 eV). The results of Tung have been recently confirmed by Ospelt *et al.*[4] and by Werner.[5] The structures of these two interfaces are rather similar; they differ only for the locations of the third neighbors of the last layer Ni atoms. Therefore the Si(111)-NiSi$_2$(111) interface represents an ideal system to study the relation between structural and electronic properties. In this case every model based only on the knowledge of the bulk band structure cannot predict the difference in the Schottky barrier height. We need a self-consistent band-structure calculation which takes fully into account the rearrangement of the electron density at the interface to obtain a realistic interface result.

Recently LMTO-ASA (linear muffin-tin orbitals with atomic-sphere approximation) calculations have been performed for Si(111)-NiSi$_2$(111) (Si-NiSi$_2$ in the following) interfaces by different groups.[6–10]

Bisi and Ossicini[6] presented the first theoretical results for the electronic properties of this interface for the two different structures, using a 6 Si+5 NiSi$_2$ supercell. In Ref. 6, as in this paper, the two-dimensional (2D) lattice constant of the (111) planes is that of the Si substrate and the normal distance between the (111) planes (in the following: interplanar distance) is that of Si on the Si side and that of NiSi$_2$ on the other side. The interplanar distances at the interfaces were fixed for the two cases to values found by x-ray standing-wave experiments.[11] This choice, as we will see, is different from the simpler assumptions of other calculations.[7–10] In Ref. 6, a Schottky-barrier height of 0.8 eV has been estimated for the *B*-type rotated structure, lower than the value of 1.1 eV found in the *A*-type interface.

One year later Fujitani and Asano[7] performed a LMTO calculation for a very large supercell (24 silicon layers plus 11 silicide layers), with the same interplanar distance for both structures. This calculation neglects the lattice mismatch between Si and NiSi$_2$ and assumes *only one* lattice constant, that of NiSi$_2$, on both sides of the interface. The barrier height, obtained as the difference between the bottom of the conduction band and the Fermi energy E_F, turns out to be 0.24 and 0.30 eV for *A* type and *B* type, respectively. If one takes into account that the gap value is underestimated in a calculation performed in the local-density approximation (LDA), one can correct these values to the experimental gap, with the assumption that the Fermi energy is correctly positioned with respect to the top of the valence band E_v. In this way, the values for the *n*-type barrier are 0.78 eV for *A* type and 0.84 eV for *B* type.

Das *et al.*[8-10] presented recently a LMTO calculation in the tight-binding representation[12] for the case of a 12 Si+8 $NiSi_2$ supercell, where the interface interplanar relaxation between silicon and silicide was neglected. Like Fujitani and Asano,[7] they neglect the lattice mismatch between Si and $NiSi_2$ but now the *common* lattice constant is that of Si. These authors calculated an n-type Schottky-barrier height of 1.05 eV for the A-type and 1.18 eV for the B type,[8] a value in this case that is greater than the Si bulk band gap (1.17 eV).

The results of Refs. 7–10 do not reproduce the experimental Schottky-barrier values, even if they succeed in finding a higher Schottky-barrier height in the B-type interface, with a difference between B type and A type that in Refs. 8–10 is equal to the experimental one (0.14 eV). The rigid shift of ~0.4 eV between the measured and computed Schottky barrier is interpreted in terms of nonlocal correction to the LDA density-functional result.[10]

In these papers the discussion has been focused mainly on the difference in the electronic structure due to the different type of interface orientation. Here we will investigate more carefully the effect of another aspect of the interface structure: the relaxation of the Si—Si bond length at the interface.

Additionally we will discuss a careful self-consistent calculation of the band structure at the interface, of the density of states projected at the atomic sites, and of the Schottky barrier for both geometries.

II. METHOD OF CALCULATION

We performed LMTO calculations in the ASA approximation with the LDA parametrization of von Barth and Hedin[13] for exchange and correlation.

The **k**-point mesh is 55 **k** points in the 2D irreducible wedge of the Brillouin zone (IBZ), corresponding to a 9×9 **k** mesh. The energy bands have been computed and plotted on 28, 57, and 49 **k** points for the $\overline{M}-\overline{K}$, $\overline{K}-\overline{\Gamma}$, and $\overline{\Gamma}-\overline{M}$ directions, respectively. The self-consistent procedure is performed by Anderson's extrapolation scheme,[14] using a large (20–30) number of iterations (diagonalization at each **k** point). This procedure guarantees the convergence in eigenvalues and SBH up to 0.01 eV.

In order to overcome the loss of periodicity in the direction perpendicular to the interface, we treat the 2D surface problem as a bulk one using the supercell technique. The solid-solid interface is simulated by an infinite sequence of solid and solid films, which recover the third dimension. In this way the solid-solid interface can be studied directly by using the standard procedures of bulk compound.

In the LMTO-ASA procedure the muffin-tin interstitial region is *annihilated* through the expansion of the muffin-tin spheres and the neglect of the effect of the slight overlap between the spheres. As a consequence, this approximation, which greatly reduces the complexity of the computation, works well in close-packed solids.

Loosely packed solids can be investigated within LMTO-ASA by adding empty-sphere atoms. Empty spheres (ES) are fictitious atoms with zero atomic number to be placed on void sites in order to obtain a close packing. Since the empty spheres have $Z=0$, their net charge is always negative and the potential at the void sites is repulsive. In this way the real behavior of the electron potential in an open crystal, such as the diamond one, is well described.

In Si crystal the close packing is reached by adding one empty sphere to every Si atom. The empty-sphere lattice is equal to the Si one, with a simple shift of $(a/2,0,0)$, where a is the lattice constant of bulk Si. This procedure yields a close-packed solid that, neglecting the type of the atomic spheres, is bcc with lattice constant $a/2$.

In the case of $NiSi_2$, we have one empty sphere per molecular unit and the crystal can be viewed as composed by Si atoms forming a simple cubic lattice with Ni and empty spheres occupying alternatively the center of each cube. With abstraction of the atom types, the lattice of the $NiSi_2$ structure would be bcc with a small distortion due to the slight reduction of the lattice parameter along the normal axis.

When the interface (111) planes are located as ideal continuation of the Si underlaying lattice, we have an unrelaxed or ideal interface.

In our interface calculation we built up a Si-$NiSi_2$ superlattice by matching the two bcc slabs. Our supercell is then made by a slab of 21 atomic planes, which repeats itself periodically in the direction normal to the interface, as shown in Fig. 1 for A- and B-type orientations. In this approach the 21 atomic layers correspond to 6 Si (111) planes plus 5 $NiSi_2$(111) planes. This size guarantees a negligible interaction between contiguous interfaces; a 6-layer slab has often been used as a realistic simulation of the Si(111) surface.[15] Within this geometry we have a

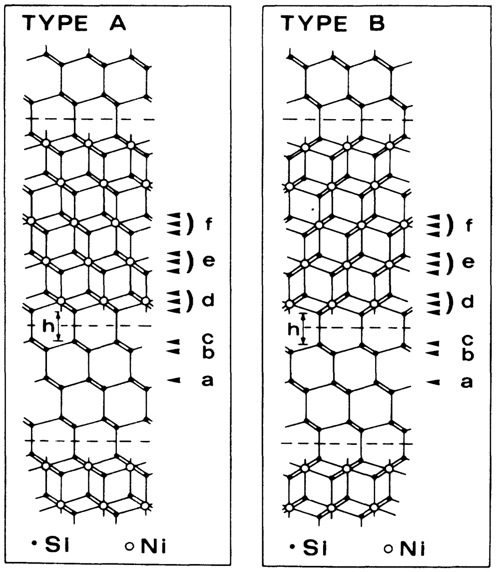

FIG. 1. Atomic arrangements in the structural models used in the computations for A-type (left panel) and B-type (right panel) structures of the Si(111)-$NiSi_2$(111) interface. The letters indicate the planes of Si and $NiSi_2$, whose local density of states is shown in Figs. 4 and 5. The unit cell contains 33 atoms: 16 Si+5 Ni +12 empty spheres (not shown here).

three-dimensional (3D) unit cell with one atom per (111) layer.

For both *A*- and *B*-type structures, the resulting sequence is

$$\cdots\mathrm{Ni{-}Si{-}ES{-}Si{-}Ni{-}Si{-}ES{-}ES{-}Si{-}Si{-}ES{-}ES{-}Si}\cdots .$$

With this configuration the number of spherical sites embedded in the muffin-tin region per unit cell is 33: 16 Si atoms + 12 ES + 5 Ni atoms.

On the Si side we have a couple of Si(111) planes alternating with a couple of (111) empty-sphere planes. The interplanar distance is $a/(4\sqrt{3})$, where $a=5.428$ Å, the Si lattice constant. On the NiSi$_2$ side we have an alternating sequence of Si,Ni,Si,ES (111) planes at an interplanar distance $a'/(4\sqrt{3})$, where $a'=5.406$ Å, the NiSi$_2$ lattice constant. The lattice constant of the two-dimensional hexagonal (111) planes is $a/\sqrt{2}$, fixed to the Si lattice value.

The choice of the sphere size is standard in LMTO-ASA. Firstly one build up a set of nonoverlapping spheres around each atom and each vacuum site. The maximum size of these touching spheres is S_i^0, where i is the index of the atom or ES. The volume associated to this set of spheres, Ω^0, is smaller than the cell volume Ω. The atomic-sphere approximation (ASA) is justified if the packing fraction $f=\Omega^0/\Omega$ is greater than or equal to $\frac{2}{3}$. In this case the ASA sphere size S_i is simply obtained by multiplying S_i^0 by the scaling factor $f^{-1/3}$. With the inclusion of 1 ES per Si atom and 1 ES per NiSi$_2$ molecule, both lattices become close packed. By taking equal-size spheres the packing fraction is the one of the bcc lattice: $f=0.680$ and the maximum overlap between the overlapping spheres is 13.7%.

By considering the slight difference between the lattice constant of Si and NiSi$_2$, we have nonoverlapping touching spheres if we choose their radii to be 1.176 Å in Si and 1.170 Å in NiSi$_2$. The packing fraction of our *A*-type supercell, in the ideal interface case, is 0.676 and the resulting size of the space filling ASA spheres is 1.339 Å (Si side) and 1.334 Å (NiSi$_2$ side). The interface region contains two voids, one filled by the last ES of the Si lattice and the second by the first ES of the silicide lattice. In the calculation of Ref. 6 only one empty sphere was located in the interface region; the packing fraction was smaller than the present one, even if already within the ASA packing requirement.

In the *B*-type interface the different stacking increases the void near the Si lattice and decreases the one near the NiSi$_2$ side. The resulting ASA sphere sizes, in the case of ideal interface distance, are 1.339 Å (Si side), 1.334 Å (NiSi$_2$ side), 1.563 Å (interface ES at Si side), and 0.989 Å (interface ES at NiSi$_2$ side). Relaxation of the interface interplanar distance decreases the sphere sizes up to 0.4%.

Similar sphere sizes have been used in Refs. 8–10, the only difference being the assumption of these authors of neglecting the lattice mismatch between Si and NiSi$_2$ and their use of the Si bulk lattice constant, not only in the interface plane, but also in the normal direction. The same choice of *only one* lattice constant has been made by Fujitani and Asano,[7] but they assumed that of NiSi$_2$ and different spheres for Si,Ni, and ES in NiSi$_2$. This choice produces a large overlap between the Si and ES spheres equal to 17.6%. We consider this choice questionable and at the origin of the disagreement with our result (see below).

We want to stress again that our geometry is different from the ones of Refs. 7–10: we chose a hexagonal 2D lattice fixed by the underlying Si lattice to simulate the epitaxy, but we allowed the interplanar distances of Si and NiSi$_2$ (111) planes to vary in order to reproduce the bulk values of Si and NiSi$_2$, respectively. The interplanar distance Si-NiSi$_2$ at the interface has been chosen to reproduce the experimental data.[11] For the perfect epitaxial *A*-type interface this distance is 2.31±0.05 Å; for the rotated *B* type it is slightly contracted, 2.24±0.03 Å. These values must be compared with the unrelaxed ideal 2.35 Å value; therefore we have a contraction of about 5% in the *B* type and 2% in the *A* type.

In the geometries investigated here the silicide is terminated by planes of silicon and the coordination of the Ni atom in the last Ni plane is seven. This value has to be compared with the eightfold coordination of Ni in bulk NiSi$_2$. If the silicide were terminated by a plane of Ni atoms, the coordination of these atoms would be five. The Ni atoms sevenfold coordination at the interface has been recently found for both *A*- and *B*-type orientations by x-ray standing wave measurements[11] and shows the lowest computed total energy.[16,17]

It is important to note that our approach to the interface problem, with no solid-vacuum region, simulate a thick silicon-silicide interface. Therefore the results will be appropriate to investigate the internal interface, when epitaxy is already established, not the early stages of metallic deposition, when the interface reaction is taking place.

III. ELECTRON STATES

In our calculation we assume the measured Si-Si distances at the interface: thus for the *B* type the interface distance is smaller (2.24 Å) than for the *A* type (2.31 Å). In the unrelaxed configuration the distance would be 2.35 Å. Before showing the results for the interface system it is interesting to consider the corresponding bulk results for Si and NiSi$_2$.

The result of our LMTO-ASA calculation of the electronic states of bulk Si (Ref. 18) is shown in Fig. 2. The energy gap between filled and empty states is ~0.57 eV, nearly half the experimental value. This discrepancy with the experimental value is not due to the LMTO-ASA method but, as it is well known, to the density-functional method itself and partially to the local-density approximation to the exchange and correlation potential. The site-projected density of states (PDOS) of Fig. 2 shows that within the empty spheres we have nonzero PDOS contribution. This effect, which is due to the tails of the wave functions centered on the Si atoms, is stronger in the conduction band, where the electron states are less localized.

Figure 3 shows our self-consistent density of states[19] of bulk NiSi$_2$. This result provides evidence of a relevant in-

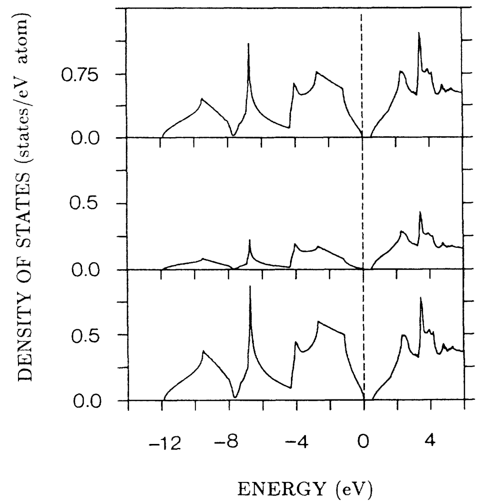

FIG. 2. Density of states (DOS) and site-projected density of states (PDOS) of bulk Si, obtained with the present LMTO-ASA calculation. Lower panel, PDOS at Si sites; central panel, PDOS at the empty spheres; upper panel, total DOS. Energies (in eV) are referred to the valence-band maximum.

teraction between Si *p* and Ni *d* orbitals, in agreement with the proposed picture of the chemical bond in Ni silicides.[1,20] In the occupied part of the PDOS two well-defined peaks are found: at higher binding energy the one related to the bonding interaction between Si *p* and Ni *d* states; nearer to the Fermi energy is the second structure derived from Ni *d* states with nonbonding character. The bulk band structure of silicon and $NiSi_2$ we obtained is in very good agreement with other existing calculations.[20,21]

The self-consistent local densities of states of the interface system, projected on the silicon and silicide sites, are shown in Figs. 4 and 5 for the *A*- and *B*-type orientation, respectively. The densities of states of Si include the empty-sphere contribution and those of $NiSi_2$ are built up with 2 Si, 1 Ni, and 1 empty sphere. The densities shown refer to the central Si atom [(a)], the interface Si atoms [(b) and (c)], and to the three $NiSi_2$ layers [(d)–(f)] of Fig. 1.

The perturbation caused by the presence of the interface is evident on both silicon and silicide sides. The densities of states of the central silicon atom and of the second and third $NiSi_2$ layers are already similar to that of bulk silicon and bulk silicides, showing that the 21 atomic planes slab is large enough to be considered a realistic interface; on the other hand those related to the interface layers show well-defined features.

From the densities of states relative to the silicide [Fig. 1(d)] layer we see that the characteristic double peak of $NiSi_2$ is narrower at the interface, the bonding structure

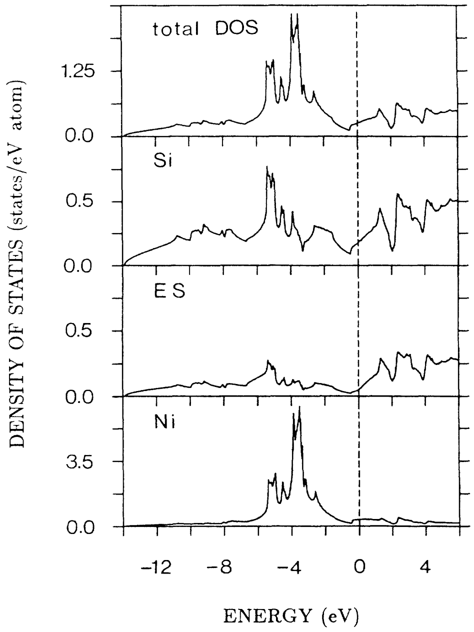

FIG. 3. Density of states and site-projected density of states of $NiSi_2$, according to this calculation. From the bottom to the top: PDOS at Ni sites; PDOS at the empty spheres; PDOS at Si sites; and total DOS. Energies (in eV) are referred to the Fermi level.

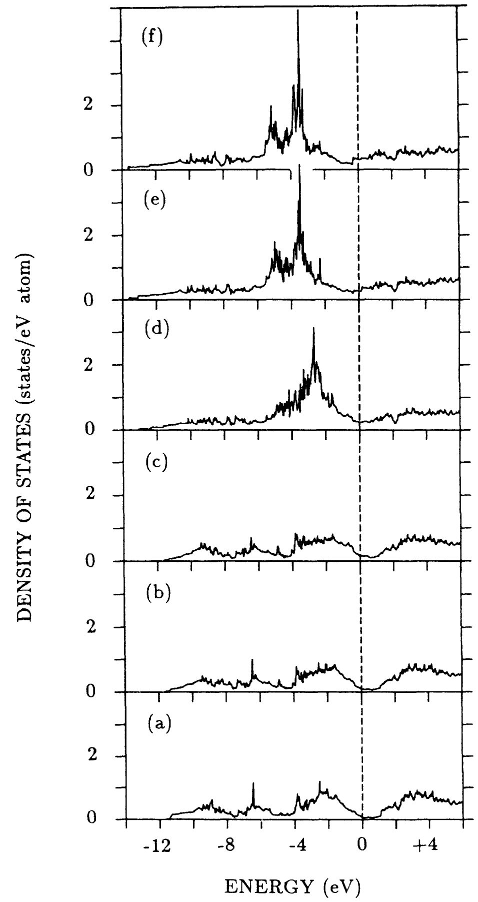

FIG. 4. Site-projected density of states for the Si(111)-$NiSi_2$(111) interface with *A*-type structure. The densities shown refer to (a) the central Si atom, (b),(c) the interface region Si atoms, and (d)–(f) to the three $NiSi_2$ layers as shown in Fig. 1.

having lost most of its weight in favor of the nonbonding one. This effect is due to the sevenfold coordination of the Ni atoms at the interface and to the presence of unpaired electrons which are not present in the eightfold bulk coordination.

Considering the silicon interface atoms, we observe that the presence of the interface gives rise to states inside the gap. These are responsible of the metallic character of these Si atoms. An interface feature is present in both *A*- and *B*-type densities of states at about 0.7–0.8 eV below the Fermi energy. This peak is clearly present also in the density of states of the silicide interface layer [panel (d)]; this is a true interface state and we will present a detailed discussion on this state later.

With reference to Figs. 3 and 4, we observe that the densities of states of Ref. 6 were incorrectly plotted.[22] They are different from those presented here; the mistake present in Ref. 6 only affected the graphical presentation and not the discussion on the Schottky-barrier height which was following in that paper.

We can compare our results with the ones of Ref. 7; we see an overall agreement for all the important features both for *A*- and *B*-type configurations; this is also true for the *A*-type PDOS shown in Refs. 8–10.

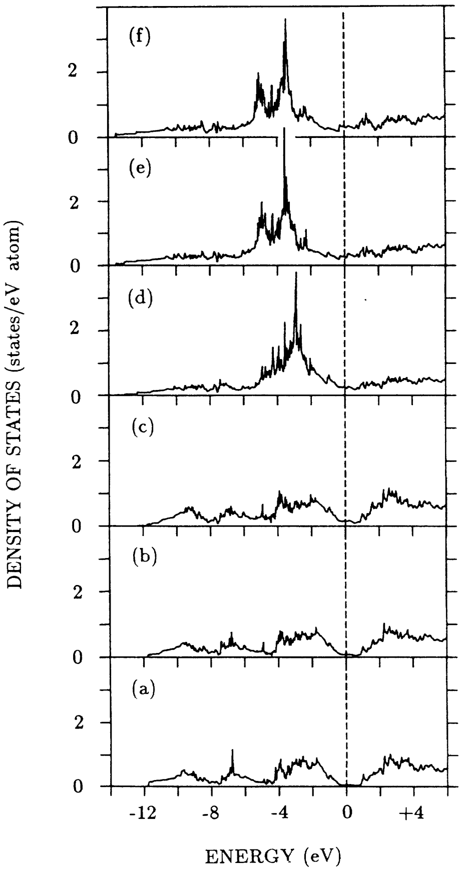

FIG. 5. Site-projected density of states for the Si(111)-NiSi$_2$(111) interface with *B*-type structure. The densities shown refer to (a) the central Si atom, (b),(c) the interface region Si atoms, and (d)–(f) to the three NiSi$_2$ layers as shown in Fig. 1.

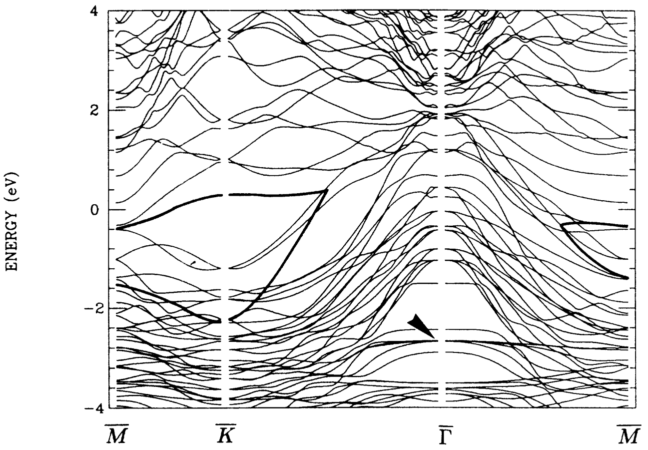

FIG. 6. Band structure along high symmetry directions of the two-dimensional Brillouin zone of the Si(111)-NiSi$_2$(111) interface with *A*-type structure. Energies are referred to the Fermi level. The arrow indicates the flat band formed by the Ni *d* states at the interface (see text). The gap common to the Si(111) and NiSi$_2$(111) projected bulk band structures is drawn by a thick line.

More-detailed information on the electron interface states can be obtained by looking at the two-dimensional band structure of the interface system for *A* type and *B* type (Figs. 6 and 7 show the band structures in the region near the Fermi level, which is relevant for our discussion). Near the center of the Brillouin zone we observe very flat bands located at -2.6 eV from E_F in the *A*-type and at -2.8 eV in the *B*-type interface. These states are marked by arrows in Figs. 6 and 7; their wave functions have more than 90% composition from *d* orbitals located at Ni atoms near the interface.

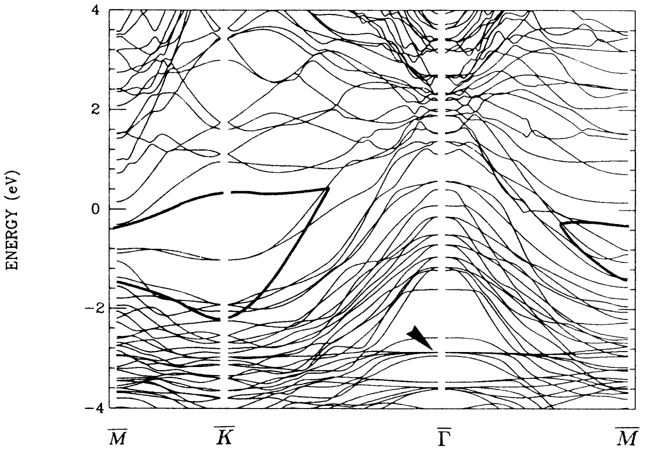

FIG. 7. Band structure along high symmetry directions of the two-dimensional Brillouin zone of the Si(111)-NiSi$_2$(111) interface with *B*-type structure. Energies are referred to the Fermi level. The arrow indicates the flat band formed by the Ni *d* states at the interface (see text). The gap common to the Si(111) and NiSi$_2$(111) projected bulk band structures is drawn by a thick line.

The band structure related to the B-type bands gives evidence of two nearly degenerate interface bands at the $\overline{M}$-$\overline{K}$ line. They are located 0.8 eV below the Fermi energy, showing a fair dispersion as a function of the surface wave vector. More-pronounced dispersion is found in the corresponding bands of the A-type case. These bands overlap regions where gaps are present in the projected bulk band structures of both Si and $NiSi_2$; thus they are true interface bands. These bands cross the Fermi-energy value which comes from the self-consistent calculation and therefore play an important role in the determination of the Schottky barrier.

We note that these interface states are mainly localized on the $NiSi_2$ interface layer, along the bond connecting the last Si plane of the silicide and the Ni atoms. Their character is mainly p on Si and p-d on Ni. Some interaction is also found with the orbitals (mainly for p character) of the Si atoms on the Si side. The fact that these states are mainly localized on the silicide side is the reason why their energy location and dispersion is not very different in A- and B-type structures. Similar dispersion curves have been obtained by Lin and Allen[23] with a semi-empirical tight-binding calculation for the A-type interface.

IV. SCHOTTKY-BARRIER HEIGHT

The Schottky-barrier height ϕ_B is given by the energy difference between the bottom of the semiconductor conduction band and the Fermi level of the metal. The minimum gap of Si and therefore the Schottky-barrier height ϕ_B are underestimated by LDA. This difficulty may be partially overcome by considering that in the density-functional theory (DFT) the energy of the highest occupied orbital of a metallic system equals the Fermi energy. It follows that we correctly estimate the energy difference Δ between the silicide Fermi level E_F and the Si valence-band maximum E_v; by adding the experimental Si gap value E_g (1.17 eV) we may compute the Schottky-barrier height by $\phi_B = E_g - \Delta$.

To do this correctly we use the potential alignment method developed by Christensen for the calculation of the band offsets at semiconductor interfaces.[24] The self-consistent potentials for the supercell geometry are calculated first, and then we extract the central layer potentials of silicon and silicide. These are used to perform two band calculations in the bulk geometries of both materials. Due to the 0.4% lattice mismatch between Si and silicide, the structure of $NiSi_2$ epitaxially grown on Si(111) is no more cubic, but hexagonal. The value of the computed Schottky-barrier height, within our uncertainty, is insensitive to the choice of the hexagonal or cubic cell: we checked that the difference in the two evaluations is of the order of 1.5 meV. From these band structures the Si valence-band maximum E_v and the silicide Fermi level E_F are computed in the same energy scale and Δ is determined. In this way we obtain for the experimental interplanar distances[11] $\phi_B = 1.16$ eV (A type) and $\phi_B = 0.89$ eV (B type). The Schottky barrier of the A-type interface is equal to the Si gap, while the different relaxation of the 180°-rotated B-type interface lowers the barrier by 0.27 eV. This is consistent with the results of the density of states for the supercell calculations, shown in Figs. 4 and 5, where all the PDOS structures are referred to the Fermi level of the interface system. From panels (a) of both figures it is evident that the position of the valence-band edges with respect to the Fermi level is shifted downwards in B-type case. It is interesting to note that a similar energy difference (~ 0.2 eV) occurs for the states marked by arrows in Figs. 6 and 7. These states are located at -2.6 eV (A type) and -2.8 eV (B type) and are mainly derived from the nonbonding region of the interface Ni d states. In both A- and B-type structures the interface Ni atoms sit at the center of a triangle formed by the Si(111) surface atoms. In the A-type interface the Ni atoms are above the fourth Si(111) layer [threefold hollow site (THS)], while in the B-type interface they are directly above the second Si(111) layer [threefold filled site (TFS)]. The void region below these Ni atoms is therefore different for the two interfaces, this difference being responsible of the different behavior upon interface interplanar relaxation. The wave functions of these states are localized in this void region below the interface Ni atoms. These states may be interpreted as dangling-bond d states of the sevenfold-coordinated interface Ni atoms (eight is the coordination of Ni in $NiSi_2$). The difference between A type and B type is primarily due to the difference in the Ni adsorption site (THS versus TFS) that corresponds to different void regions. The states we are discussing are located in this region, but not on the Si layer, and are sensitive to the variations of the potential at the interface.

The first conclusion of our Schottky-barrier height evaluation is that A- and B-type SBH can be different, in spite of the fact that the two interface geometries are very similar. In contrast with the experiment, we found that SBH is higher in the A-type interface than in the B-type structure. We feel that the disagreement between theory and experiment provides evidence of the complex nature of the Schottky-barrier formation in silicon-silicide interfaces. A possible mechanism, among others, which may modify the Schottky barrier height is the relaxation of the interplanar Si-$NiSi_2$ distance. A recent work[25] for the A-type structure finds a distance of 2.20 Å (a contraction of about 7% with respect to the unrelaxed distance), even smaller than the B-type value (2.24 Å), which we have used in our calculation. Moreover, very recently Rhees and Matthai,[26] using a tight-binding model, found that for the experimentally observed relaxations[11] the SBH for the A-type orientation was higher than for the B-type structure, as we found, and that a lowering of the interface planar distance by 0.07 Å in the B type produces a reduction of 0.14 eV for the SBH.

Therefore we have carefully investigated the dependence of the SBH on the interplanar Si-$NiSi_2$ distance. We have performed self-consistent calculations at different interface interplanar distances: the A-type structure with the unrelaxed distance and with the contraction found by Zegenhagen *et al.*[25] and the B-type structure with the unrelaxed distance. The results for the Schottky-barrier height, computed with the full self-consistent procedure previously described, are collected in Table I.

TABLE I. Our values of *n*-type Schottky-barrier height (in eV) for the Si(111)-NiSi$_2$(111) interface computed as $E_g-(E_F-E_v)$ with $E_g=1.17$ eV. In model 1 the interplanar distance in the silicide (silicon) side is that of NiSi$_2$(Si). In models 2 and 3, *only one* lattice constant is assumed: that of Si (model 2) or NiSi$_2$ (model 3).

Model	Interface relaxation	*A* type	*B* type
1	0.00 (ideal)	1.09	1.06
1	−0.04 Å (Ref. 11)	1.16	
1	−0.11 Å (Ref. 11)		0.89
1	−0.15 Å (Ref. 25)	1.06	
2	0.00 (ideal)	1.06	1.19
3	0.00 (ideal)	1.18	1.29

The difference between the values of the SBH in the *A*- and *B*-type structures is strongly related to the difference in the interplanar distances. At the unrelaxed ideal interplanar distance the difference between *A* and *B* type are indeed small. Furthermore we note that a contraction of the interplanar distance produces different behaviors in the SBH of *A*- and *B*-type structures. An effective lowering of the SBH is found in the *B*-type interface, while the SBH in the perfect epitaxial structure is practically insensitive to the change of the Si—Si bond length at the interface. The presence of an extended defect such as the stacking fault of the *B*-type structure makes the SBH more sensitive to the interface interplanar distance.

The different behavior of the *A*- and *B*-type interface upon interface interplanar distance is due to the difference in the THS and TFS structure. We consider this result to be quite important. With the exception of the tight-binding study of Ref. 26, this aspect has been, up to now, overlooked.

During the preparation of this work, Werner[5] published an experimental study on the dependence of the SBH from the hydrostatic pressure in the case of silicide-silicon interfaces. The results for the NiSi$_2$ *A*- and *B*-type interfaces and for polycrystalline silicides show that the perfect epitaxial interface has the lowest dependence of the SBH on the hydrostatic pressure. This is consistent with our results. The simple contraction of the interface distance is only a part of the effect of the hydrostatic pressure on the barrier, which also depends on the changes in the electronic structure of both bulk materials. However, these contributions are the same for both *A*- and *B*-type structures, thus it is possible to compare our outcome with the experimental findings obtained by Werner.[5]

Our results for the Si-NiSi$_2$ *A*- and *B*-type interfaces give evidence of quite a different dependence of the Schottky-barrier height on the interface interplanar distance: only for the *B*-type structure is the variation of the SBH significant. If the same unrelaxed interfacial distance is assumed, the values of the SBH are similar for both interfaces and for the *A*-type interface the SBH is larger (~ 1 eV) than the experimental value (0.65 eV). This disagreement cannot be eliminated by changing the interface interplanar distance. Therefore the SBH determination of the *A*-type structure is still an open problem. Local defects at the interface plane could be responsible for the SBH value in *A* type, which is known to be the less-probable structure at the beginning of the deposition process.[1] The behavior of the *A*-type interface is peculiar also considering the precusors structures, as shown in Ref. 27: the structures preceding *B*-type NiSi$_2$ on Si(111) are epitaxial with a well-defined habit plane, while those preceding *A*-type NiSi$_2$ are not.[27]

V. COMPARISON WITH PREVIOUS LMTO CALCULATIONS

We now investigate the differences between our calculations and those of others performed using the same method. We remember that in our paper we use for the planar lattice constant the one of Si and for the interplanar distances that of Si on the Si side and that of NiSi$_2$ on the other side: our choice is better than the ones of previous works, which have used *only one* lattice spacing. To have a deeper insight we have reproduced some of the calculations quoted below.

We will examine in detail the comparison with the results of the MPI-Suttgart group.[8-10] References 8 and 9 contain LMTO-ASA calculations, as do ours, but the ES *d*-LMTO orbitals were folded down.[28] It is shown that the SBH of the (NiSi$_2$)$_8$-(Si$_2$)$_6$ supercell is the same of our (NiSi$_2$)$_5$-(Si$_2$)$_3$ supercell (text and Fig. 6 of Ref. 9). The SBH computed in the *frozen-potential* approach as $E_g-(E_F-E_v)$ depends on the **k** mesh: for the (NiSi$_2$)$_8$-(Si$_2$)$_6$ supercell and for 8×8 divisions in the irreducible Brillouin Zone (IBZ) they obtain $\phi_B=1.13$ eV (*A* type) and $\phi_B=1.26$ eV (*B* type).[8] The extrapolation to zero mesh width is estimated to lower the SBH of 0.08 eV and the *corrected* estimates of 1.05 eV (*A* type) and 1.18 eV (*B* type) are presented. Similar results are presented in Ref. 9: $\phi_B=1.01$ eV (*A* type) and $\phi_B=1.17$ eV (*B* type).

Our SBH value is computed without the folding down of the ES *d* orbitals, for a finer mesh (9×9). In the case of the ideal interface distance it is 1.09 eV for *A* type and 1.06 for *B* type. We repeated the calculation by assuming *only one* lattice constant, that of Si: the result is $\phi_B=1.06$ eV (*A* type) and $\phi_B=1.19$ eV (*B* type), in excellent agreement with Ref. 8. It is evident that the approximation of taking *only one* lattice constant considerably modifies ϕ_B, in particular when the lattice constant is that of NiSi$_2$, smaller than that of Si (see below and Table I).

It is difficult to perform a detailed analysis of the paper by Fujitani and Asano,[7] since too many details are not given: in particular (i) the number of **k** points and (ii) the procedure to determine E_F-E_v. A suspicious aspect is the fact that they change the dimensions of the spheres in NiSi$_2$ up to 9%, in order to push the Γ_2' eigenvalue below E_F. In this way they obtain a large overlap (17.6%) between the Si and ES spheres. We have computed the SBH by neglecting the lattice relaxation and by using NiSi$_2$ lattice constant as in Ref. 7. As shown in Table I, we find $\phi_B=1.18$ eV (*A* type) and $\phi_B=1.29$ eV (*B* type). We believe that the disagreement with the data of Ref. 7, $\phi_B=0.78$ eV (*A* type) and $\phi_B=0.84$ eV (*B* type), is due to the questionable choice of the sphere sizes in Ref. 7.

By assuming *only one* lattice constant (models 2 and 3 in Table I) we always find the SBH higher in *B*-type than in *A*-type interface, as in the experiment. We have shown that this agreement is fortuitous, being due to the geometrical approximation.

VI. CONCLUSIONS

In this paper we have presented the results of a self-consistent calculation for the Si(111)-$NiSi_2$(111) interface. The electronic structure and the local density of states obtained for a repeated slab have been investigated by means of the LMTO-ASA method and compared with the corresponding bulk results. The role of the interface states in both *A*-type and *B*-type geometry has been discussed. The values of the Schottky-barrier height are determined not only by the different types of interface orientation, but also by the different relaxation of the interface distance.

The source of the apparent disagreement with other calculations has been identified. If a geometrical ordered interface is assumed, with the appropriate experimental interplanar separation on both sides of the interface, the *A*-type SBH is slightly larger than the one of *B* type. The difference becomes even larger if one assumes an interface distance slightly smaller than the ideal one, as indicated by the experiments.[11]

The dependence of SBH on the interface distance is much stronger in *B* type than in *A* type, in the range of the realistic values of the interfacial relaxation.

The only way to obtain SBH values lower in *A* type than in *B* type is to increase the interfacial distance or to assume in $NiSi_2$ slab an interplanar separation larger than the experimental one. The sign of the difference between the two cases can therefore be reproduced, but through a nonrealistic artifact, as also indicated by the two values of SBH, too large in both interfaces.

Our result for *B* type is close to the experimental determination, while the *A*-type value is overestimated. Hence we suggest that the ordered interface, with negative interfacial relaxation,[11] is a good model for *B* type, while the *A*-type growth can present some defects at the interface, which cannot be described in our framework, responsible for the reduction of the SBH. This is consistent with the observed higher stability of *B*-type interface at the early stages of deposition.

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[1] C. Calandra, O. Bisi, and G. Ottaviani, Surf. Sci. Rep. **4**, 271 (1985).

[2] R. T. Tung, Phys. Rev. Lett. **52**, 461 (1984).

[3] M. Liehr, P. E. Schmid, F. K. Legoues, and P. S. Ho, Phys. Rev. Lett. **54**, 2139 (1984).

[4] M. Ospelt, J. Henz, L. Flepp, and H. von Känel, Appl. Phys. Lett. **52**, 227 (1988).

[5] J. H. Werner, Appl. Phys. Lett. **54**, 1528 (1989).

[6] O. Bisi and S. Ossicini, Surf. Sci. B **189/190**, 285 (1987).

[7] H. Fujitani and S. Asano, J. Phys. Soc. Jpn. **57**, 2253 (1988).

[8] G. P. Das, P. Blöchl, N. E. Christensen and O. K. Andersen, unpublished.

[9] G. P. Das, P. Blöchl, N. E. Christensen, and O. K. Andersen, *Metallization and Metal-Semiconductor Interfaces*, edited by I. P. Batra (Plenum, New York, 1989), p. 215.

[10] G. P. Das, P. Blöchl, O. K. Andersen, N. E. Christensen, and O. Gunnarson, Phys. Rev. Lett. **63**, 1168 (1989).

[11] E. Vlieg, A. E. M. J. Fischer, J. F. van der Veen, B. N. Dev, and G. Materlik, Surf. Sci. **178**, 36 (1986).

[12] O. K. Andersen, K. Pawlowska, and O. Jepsen, Phys. Rev. B **34**, 5253 (1986).

[13] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1975).

[14] D. G. Anderson, J. Assoc. Comput. Mach. **12**, 547 (1965).

[15] J. I. Ihm, M. L. Cohen, and J. R. Chelikowsky, Phys. Rev. B **22**, 4610 (1980); S. Satpathy and R. Martin, *ibid.* **39**, 8494 (1989).

[16] D. R. Hamann, Phys. Rev. Lett. **60**, 313 (1988).

[17] P. J. van Hoek, W. Ravenek, and E. J. Baerends, Phys. Rev. Lett. **60**, 1743 (1988).

[18] S. Ossicini and O. Bisi, Surf. Sci. **211/212**, 572 (1989).

[19] O. Bisi and S. Ossicini, in *Photoemission and Absorption Spectroscopy of Solids and Interfaces with Synchrotron Radiation,* Proceedings of the International School of Physics "Enrico Fermi," Course CVIII, edited by M. Campagna and R. Rosei (North-Holland, Amsterdam, 1990).

[20] Xu Jian-hua and Xu Yong-nian, Solid State Commun. **55**, 891 (1985); W. R. L. Lambrecht, N. E. Christensen, and P. Blöchl, Phys. Rev. B **36**, 2493 (1987).

[21] D. Glötzel, B. Segall, and O. K. Andersen, Solid State Commun. **36**, 403 (1980).

[22] The error occurred in the standard LMTO program (variable dimension arrays version) when used for preparing the plots. It was due to an incorrect FORTRAN DIMENSION statement. All other results including the Schottky-barrier heights were correct.

[23] H. Lin and R. E. Allen, J. Vac. Sci. Technol. A **4**, 2328 (1986).
[24] N. E. Christensen, Phys. Rev. B **37**, 4528 (1988).
[25] J. Zegenhagen, K. G. Huang, W. M. Gibson, B. D. Hunt, and L. J. Schowalter, Phys. Rev. B **39**, 10 254 (1989).
[26] N. V. Rees and C. C. Matthai, Semicond. Sci. Technol. **4**, 412 (1989).
[27] P. A. Bennett, A. P. Johnson, and B. N. Halawith, Phys. Rev. B **37**, 4268 (1988).
[28] W. A. Lambrecht and O. K. Andersen, Phys. Rev. B **34**, 2439 (1986).