

## A Green function theory of the electronic structure of metal disilicide surfaces and their interfaces with silicon

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 7607

(<http://iopscience.iop.org/0953-8984/3/39/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 23:48

Please note that [terms and conditions apply](#).

# A Green function theory of the electronic structure of metal disilicide surfaces and their interfaces with silicon

K W Sulston† and S M Bose

Department of Physics and Atmospheric Science, Drexel University, Philadelphia, PA 19104, USA

Received 20 March 1991, in final form 3 June 1991

**Abstract.** A theoretical study of the electronic structure of the (111) surfaces of  $\text{CoSi}_2$  and  $\text{NiSi}_2$  and their interfaces with Si has been carried out with particular attention paid to the existence of localized states. A Green function method has been used within the empirical tight-binding approximation to calculate the bulk, surface and interface densities of states of these samples. The (111) surface electronic structures of both the Si-terminated disilicides are qualitatively similar, each possessing a pair of localized states. One of these states is associated with the dangling bond at the surface (Si) layer and the other with that at the first subsurface (Co or Ni) layer. Formation of an interface with Si(111) gives rise to two localized resonance states below the Fermi level in both Si/ $\text{CoSi}_2$  and Si/ $\text{NiSi}_2$ , even though their origins are quite different because of the different atomic geometries at the interfaces.

## 1. Introduction

The electronic properties of the interfaces of  $\text{NiSi}_2$  and  $\text{CoSi}_2$  with Si have been the subject of significant experimental and theoretical research over the past decade [1–9]. When these disilicides are grown epitaxially on the (111) face of silicon, because of the small lattice mismatch (0.4% for  $\text{NiSi}_2$ , and 1.2% for  $\text{CoSi}_2$ ), virtually perfect interfaces are formed [1]. In our theoretical study, we have also ignored any complications that may arise owing to lattice mismatch at the interface. A number of groups have studied the interface electronic structure of these samples, using a variety of theoretical techniques (such as linear muffin-tin orbitals [4, 5], local-density approximation clusters [6], and several tight-binding schemes [7–9]) usually on a finite-sized system.

In this paper we investigate the electronic structure of the interface of semi-infinite Si(111) with semi-infinite  $\text{NiSi}_2$  and  $\text{CoSi}_2$ , with particular emphasis on the existence of localized states. We have adopted the Slater–Koster (SK) [10] tight-binding method to model the infinite solids, and have then used the Green function (GF) method of Kalkstein and Soven (KS) [11] to study the electronic structure of the clean surfaces and the interfaces. This approach has been widely used for a number of systems and has the major advantage that it allows one to see the origin of localized states, i.e. whether they are modified surface states or true interface states. This method also allows calculation of the densities of states (DOS), both extended and localized, at an arbitrary layer of the

† Present address: Department of Mathematics and Computer Science, University of Prince Edward Island, Charlottetown, PEI, C1A 4P3, Canada.

solid, from which one can study the decay of the localized states as one recedes into the bulk. Furthermore, we believe that by working with infinite and semi-infinite three-dimensional solids, we avoid certain problems that may arise when only a finite-sized cluster or supercell is used.

## 2. Bulk electronic structure

The bulk band structure of NiSi<sub>2</sub> has been studied theoretically by a number of methods [7, 12–16], but investigations of CoSi<sub>2</sub> are relatively scarce [15–17]. Experimentally, enough work has been done using photoemission spectroscopy [13, 18–20], to identify the major features in the DOS, thus providing a check for the theoretical results. Here we calculate the bulk electronic structure of NiSi<sub>2</sub> and CoSi<sub>2</sub>, using the SK tight-binding method, which has not been used previously for these systems, even though it has been widely used for a variety of other solids. This calculation serves as corroboration for the previous work and provides a basis for our study of the surface and interface properties of these compounds using the KS method.

NiSi<sub>2</sub> and CoSi<sub>2</sub> both possess the CaF<sub>2</sub> crystal structure, with lattice constants of 5.406 Å and 5.363 Å, respectively. This structure can be characterized as a face-centred cubic lattice of M ( $\equiv$  Ni, Co) atoms, with each tetrahedral site occupied by a Si atom. Thus, a unit cell consists of an M atom at (0, 0, 0), connected to two Si atoms located at  $\pm a(1, 1, 1)/4$ . The most relevant orbitals are the 3d and 4s on M, and 3s and 3p on Si, giving a total of 14 orbitals per unit cell.

In order to construct the tight-binding Hamiltonian, we first define  $\phi_n(\mathbf{r} - \mathbf{R}_i)$  to be an orthogonalized atomic orbital, with quantum numbers symbolized by  $n$ , located on an atom at vector position  $\mathbf{R}_i$ . Then, orthonormal Bloch functions  $N^{-1/2} \sum_{\mathbf{R}_i} \exp(i\mathbf{k} \cdot \mathbf{R}_i) \phi_n(\mathbf{r} - \mathbf{R}_i)$  can be formed, so that it becomes possible to calculate the matrix elements of the Hamiltonian between various atomic orbitals in the same unit cell, for Bloch sums of the same  $\mathbf{k}$ -value. We write these as

$$n/m = \sum_{\mathbf{R}_j} \exp[i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)] E_{n,m}(t, u, v) \quad (1)$$

where

$$E_{n,m}(t, u, v) = \int \phi_n^*(\mathbf{r}) \mathbf{H} \phi_m(\mathbf{r} - t\mathbf{i} - u\mathbf{j} - v\mathbf{k}) d\mathbf{r} \quad (2)$$

with

$$\mathbf{R}_j - \mathbf{R}_i = t\mathbf{i} + u\mathbf{j} + v\mathbf{k} \quad (3)$$

$i, j$  and  $k$  being unit vectors along the  $x, y$  and  $z$  axes. In principle, the summation in (1) should be taken over all neighbours of the atom at  $\mathbf{R}$ , but, in practice, it must be truncated to a finite number of neighbouring atoms. Here, we shall consider only interactions up to nearest neighbours for metal atoms and next-nearest neighbours for silicon atoms, which is found to be sufficient to produce the main features of the band structure. According to the SK procedure, the integrals in (2) are treated as disposable constants. Some of these integrals can be taken to be zero, because they represent distant interactions and some are related to other integrals by symmetry, leaving a relatively small number of independent parameters.

Table 1. Tight-binding parameters.

Parameter	Value (eV)	
	NiSi <sub>2</sub>	CoSi <sub>2</sub>
$E_{4s,4s}(000)$	1.035	3.291
$E_{xy,xy}(000)$	-4.925	-3.761
$E_{z2,z2}(000)$	-4.94	-3.96
$E_{2s,2s}(000)$	-7.442 5	-7.169 5
$E_{x,x}(000)$	-0.137 5	0.191 5
$E_{4s,2s}(\frac{111}{111})$	-0.965 5	-0.978
$E_{4s,x}(\frac{111}{111})$	0.210 75	0.126 75
$E_{xy,2s}(\frac{111}{111})$	-0.609 5	-0.712 75
$E_{xy,x}(\frac{111}{111})$	0.187 5	0.382 25
$E_{xy,z}(\frac{111}{111})$	0.530 5	0.641 25
$E_{x2-y2,x}(\frac{111}{111})$	-0.254 75	-0.354 75
$E_{z2,x}(\frac{111}{111})$	0.110 25	0.153 5
$E_{x2,z}(\frac{111}{111})$	-0.3	-0.45
$E_{2s,2s}(100)$	-0.973 75	-1.075 25
$E_{2s,x}(100)$	1.485	1.655
$E_{x,x}(100)$	2.911 25	2.885 75
$E_{x,x}(001)$	-1.163 75	-1.228 25

Determination of the explicit form of the matrix elements (1) of the Hamiltonian  $\mathbf{H}(k)$ , using the above prescription, is a lengthy but straightforward task. Once accomplished, however, it is a simple matter to diagonalize numerically the resulting  $14 \times 14$  Hamiltonian matrix  $\mathbf{H}(k)$  for any particular wavevector  $k$ , to obtain the corresponding eigenvalues  $E_b(k)$  and eigenvectors  $\psi_b(k)$ . It must also be mentioned that, at the Brillouin zone (BZ) centre  $\Gamma = (0, 0, 0)$  and face centre  $X = 2\pi(1, 0, 0)/a$ , most of the matrix elements of  $H(k)$  become zero, so that with a little effort, the eigenvalues of  $H(k)$  can be found analytically, in terms of the parameters (2). This point is very important, as it allows all but two of the parameters (2) to be selected so that most of the eigenvalues at  $\Gamma$  and  $X$  match those of other calculations [14, 16] or experiment [18, 20]. Specifically, assigning calculated values of the lower eigenvalues to the corresponding analytic expressions leads to small sets of algebraic equations which are easily solved for the parameters. The two remaining parameters are chosen empirically so as to give a fairly reasonable reproduction of the eigenenergies at  $L = \pi(1, 1, 1)/a$ . This is the usual method for generating the Hamiltonian in the empirical tight-binding approximation [21]. The sets of parameter values for NiSi<sub>2</sub> and CoSi<sub>2</sub>, evaluated by this procedure, are given in table 1, and the corresponding band structures are shown in figure 1. (Note that the diagonal parameter values have been uniformly shifted so that the Fermi level is the energy zero.)

Comparison of the band structures in figure 1 with those obtained by other methods, especially linear combinations of Gaussian orbitals [14] and linear muffin-tin orbitals [16], shows a very good overall agreement. The valence bands tend to match up very well (especially along  $\Gamma - X$ ), as would be expected, while the upper conduction bands are reproduced less satisfactorily, although this is quite common with tight-binding methods.

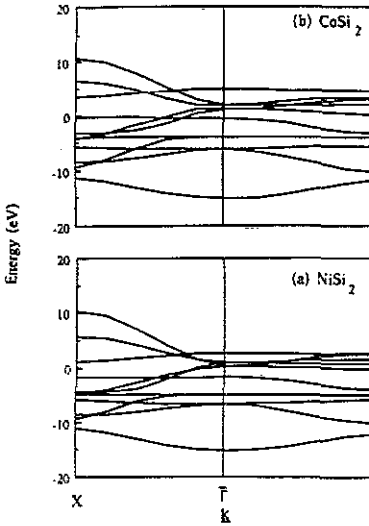


Figure 1. Calculated band structure  $E(k)$  for (a)  $\text{NiSi}_2$  and (b)  $\text{CoSi}_2$ .

It is now a matter of applying standard techniques to calculate the bulk DOS by means of the GF, which can be written as

$$\mathbf{G}(E, k) = \sum_b \frac{|\psi_b(k)\rangle\langle\psi_b(k)|}{E + i\lambda - E_b(k)} \quad \lambda = 0^+ \quad (4)$$

The matrix elements of (4) can be evaluated for any value of  $E$  and  $k$  by diagonalizing the  $14 \times 14$  Hamiltonian matrix  $\mathbf{H}(k)$  whose elements are given by (1), thus yielding a set of eigenvalues  $E_b$  and eigenvector coefficients  $\langle\phi_n|\psi_b\rangle$  (for  $b = 1, \dots, 14$ ).

The total DOS  $\rho(E)$  is then found by integrating (4) over the entire BZ, so that

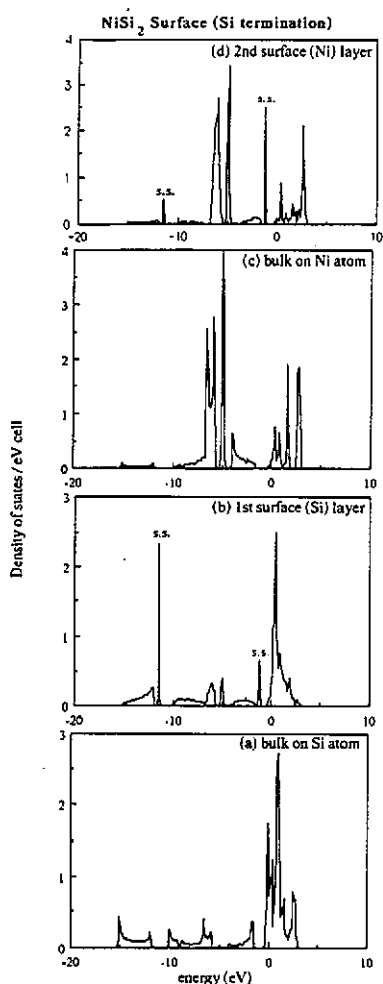
$$\rho(E) = -\frac{1}{\pi} \text{Im} \left[ \text{Tr} \left( \int_{\text{BZ}} dk \mathbf{G}(E, k) \right) \right] \quad (5)$$

where  $\text{Tr}$  denotes the trace and the BZ is like that for a FCC lattice. The BZ integration in (5) is done numerically as a summation of values of  $\mathbf{G}(E, k)$  at particular  $k$ -points, with enough points being used to ensure convergence of the results. The calculated bulk DOSs for  $\text{NiSi}_2$  and  $\text{CoSi}_2$  are in general agreement with those calculated by other methods and with the available experimental information. The calculated bulk DOSs at the  $\Gamma$  point are shown in figures 2 and 3.

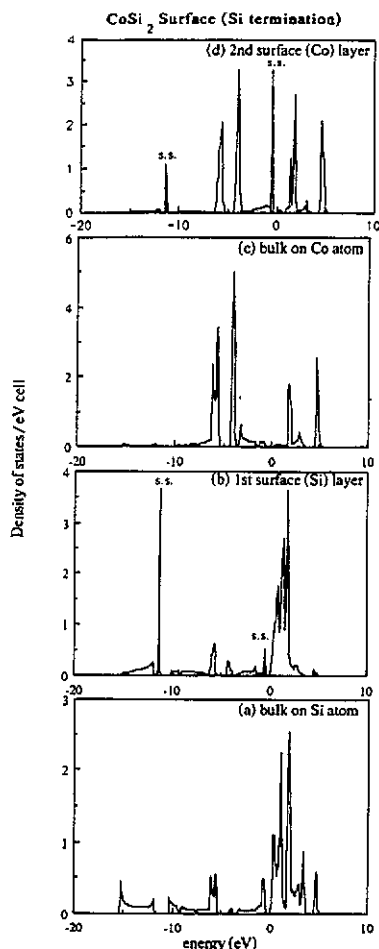
For application to surface and interface study, it is useful to construct the bulk GF  $\mathbf{G}(E, n, n', k_{\parallel})$  in the mixed Wannier–Bloch representation following the method of [22], where the wavefunctions are given by  $|n, k_{\parallel}\rangle$ ,  $n$  being the index representing the layer number, and  $k_{\parallel}$  the wavevector parallel to the surface.

### 3. Surface electronic structure

The general procedure for calculating the surface GF is to use a cleavage plane to slice the infinite crystal in half [22]. In order to compute the surface GF  $\mathbf{g}$ , we adopt the Dyson



**Figure 2.** Bulk and surface DOS of  $\text{NiSi}_2(111)$  at  $\Gamma$  for (a) a Si layer in the bulk, (b) the first surface (Si) layer (c) a Ni layer in the bulk and (d) the second surface (Ni) layer. The bulk results are shown for easy comparison. The two new localized surface states are indicated by *s.s.*



**Figure 3.** Bulk and surface DOS of  $\text{CoSi}_2(111)$  at  $\Gamma$  for (a) Si layer in the bulk, (b) the first surface (Si) layer, (c) a Co layer in the bulk and (d) the second surface (Co) layer. The bulk results are shown for easy comparison. The two new localized surface states are indicated by *s.s.*

equation approach of KS, wherein  $\mathbf{g}$  is related to the bulk GF  $\mathbf{G}$  by

$$\mathbf{g} = \mathbf{G} + \mathbf{G}\mathbf{V}\mathbf{g} \quad (6)$$

where the scattering potential  $\mathbf{V}$  is

$$\mathbf{V} = \mathbf{h} - \mathbf{H} \quad (7)$$

with  $\mathbf{H}$  and  $\mathbf{h}$  the corresponding Hamiltonians for the bulk and semi-infinite systems, respectively. In the current model,  $\mathbf{V}$  is assumed to incorporate only the breaking of the bonds across the cleavage plane (i.e. between layers  $n = 0$  and  $n = -1$ ). This feature can be represented mathematically by writing

$$\mathbf{h}(0, -1) = \mathbf{h}(-1, 0) = 0 \quad (8)$$

i.e.

$$\mathbf{V}(0, -1) = -\mathbf{H}(0, -1) \quad \mathbf{V}(-1, 0) = -\mathbf{H}(-1, 0). \quad (9)$$

In a more general model,  $\mathbf{V}$  would also include the perturbation of the atoms in the surface layer ( $n = 0$ ), owing to the formation of the surface. It is a straightforward but tedious procedure to calculate, in mixed-basis representation, the matrix elements of  $\mathbf{V}$  required in (9). With these in hand, it is possible to calculate the surface GF  $\mathbf{g}$  from the Dyson equation (6). For the scattering potential used here, (6) leads to the matrix equation

$$\mathbf{g}(n, n') = \mathbf{G}(n, n') + \mathbf{G}(n, -1)\mathbf{V}(-1, 0)[\mathbf{I} - \mathbf{G}(0, -1)\mathbf{V}(-1, 0)]^{-1} \mathbf{G}(0, n') \quad (n, n' \geq 0) \quad (10)$$

which is  $14 \times 14$  for the disilicides.

Once the relevant matrix elements of the bulk GF  $\mathbf{G}$  and potential  $\mathbf{V}$  have been calculated, it is a simple matter of matrix algebra to calculate the GF  $\mathbf{g}$  for the cleaved crystal at any desired layer  $n$ , and the corresponding DOS for that layer and for a particular  $k_{\parallel}$  is then given by

$$\rho_n(E, k_{\parallel}) = -1/\pi \operatorname{Im} \{ \operatorname{Tr} [\mathbf{g}(E, n, n, k_{\parallel})] \}. \quad (11)$$

The (111) surface of  $\text{MSi}_2$  ( $M \equiv \text{Ni, Co}$ ) exhibits the hexagonal pattern of atoms typical of the (111) surface of a cubic crystal. Each plane parallel to the surface plane consists entirely of one type of atom, with each third layer composed of the metal constituent. Consequently, there are three possible terminations for the surface:

- (i) a layer of metal atoms,
- (ii) a single layer of Si, with a metal layer underneath, or
- (iii) a layer of Si with another layer of Si underneath.

In order to create the known interface structures (see section 4), the termination that we must adopt is the second, so that the disilicide surface goes as  $\text{Si-M-Si-Si-M} \dots$ . Formation of this surface requires that a cleavage plane be passed between two adjacent silicon layers, which means the cutting of nearest-neighbour bonds between a surface-layer Si atom and an M atom across the cleavage plane, and between a second-layer M atom and a Si atom across the cleavage plane. Next-nearest-neighbour bonds between Si atoms in adjacent layers at the cleavage plane must also be cut.

As the formation of the surface cuts two nearest-neighbour ( $M\text{-Si}$ ) bonds per unit cell, we expect to see two bands of dangling-bond (surface) states appear in the DOS. For the other two possible terminations, four  $M\text{-Si}$  bonds per unit cell must be removed, so that four surface states should exist. We have calculated the surface DOSs for  $\text{NiSi}_2$  and  $\text{CoSi}_2$  and have found that these expectations are indeed borne out. In this paper, we have restricted ourselves to the  $\Gamma$  point ( $k_{\parallel} = 0$ ), which suffices to show the main qualitative features of the surface. Graphs of these DOSs, for both the bulk samples at the Si and M layers, and for the first two surface layers of the semi-infinite samples, are shown in figures 2 and 3.

For  $\text{NiSi}_2$ , the bands show a total width of about 18 eV. The lowest-lying structures, from  $-15$  to  $-7$  eV are basically the Si s and p orbitals, which are quite strongly hybridized. From  $-7$  eV to around the Fermi level is primarily the domain of the Ni d bands, while above the Fermi level is an area of strong coupling between Si p states and Ni d states. Note that introduction of the surface substantially modifies the bulk DOS. More importantly, two localized dangling-bond surface states appear in the band gaps.

One surface state is observed at  $-11.4$  eV (relative to the Fermi level), with greatest localization on the first Si layer, and this state is primarily Si-like in nature. The second state occurring at  $-1.2$  eV is localized on the second Ni layer and has its origins principally in the Ni d states. The surface electronic structure of  $\text{CoSi}_2$  is fundamentally the same as for  $\text{NiSi}_2$ , and the surface states are of similar nature, but at different energies. The lower state, originating from Si orbitals, is seen at  $-11.35$  eV, while the higher state, of Co d character is at  $-0.49$  eV. Note that in both cases the lower surface state localized on the surface Si layer loses its strength on the neighbouring M layer, whereas the upper surface state localized on the M layer is greatly reduced on the Si layer.

A similar calculation for the surface electronic structure of Si(111), using the  $\text{SK}$  parameters of Chadi and Cohen [23], has also been performed and the results will be presented in a separate publication [24]. We use this surface GF (with the Chadi–Cohen parameters) for Si, in conjunction with that for  $\text{MSi}_2$  introduced above, as our basis for the calculation of the interface GF for Si/ $\text{MSi}_2$ .

#### 4. Interface electronic structure

We must now turn to the question of the atomic geometry at the silicon–disilicide (111) interface, which has been the subject of much discussion in the literature [2, 3, 5–7, 9, 25–27]. This problem can be thought of in terms of the coordination of the metal atoms nearest the interface, i.e. the number of nearest-neighbour silicon atoms possessed by one of these metal atoms. Three different models have been proposed, giving the metal atom fivefold, sevenfold and eightfold coordination. (Atoms in the bulk are eightfold coordinated.) For Si/ $\text{NiSi}_2$ , the structure with sevenfold coordination (figure 4(a)) now seems to be generally accepted while, for Si/ $\text{CoSi}_2$ , eightfold coordination (figure 4(b)) currently has the strongest support. Indeed, recent independent calculations by Hamann [25] and by van den Hoek *et al* [6], using different methods, have both shown that the sevenfold and eightfold models are the energetically favourable ones for Si/ $\text{NiSi}_2$  and Si/ $\text{CoSi}_2$ , respectively. Thus, we adopt these models in this work. For each coordination, two orientations of  $\text{MSi}_2$  relative to Si are possible: the so-called type A where the orientation of  $\text{MSi}_2$  is identical with that of Si, and type B, where there is a  $180^\circ$  rotation about the axis normal to the Si surface. In the current work, we have examined the electronic structure only at  $k_{\parallel} = \mathbf{0}$  ( $\Gamma$  point), where types A and B have the same structure; so no distinctions can be made. The type A orientation is shown in figure 4. Because the lattice constants of the disilicides and Si are so close, they have been taken as equal.

The GF  $\mathcal{G}$  for the interfacial system can be found via the Dyson equation

$$\mathcal{G} = \mathbf{g} + \mathbf{g}\mathcal{V}\mathcal{G} \quad (12)$$

where  $\mathbf{g}$  embodies the surface GFs for Si(111) and  $\text{MSi}_2$ (111), with the energy levels shifted so as to align the calculated Fermi levels of the two crystals. Also in (12),  $\mathcal{V}$  is the potential creating nearest-neighbour couplings between M and Si atoms on opposite sides of the interface. Calculation of the matrix elements of  $\mathcal{V}$  and the subsequent solution for  $\mathcal{G}$  are straightforward, and hence one can compute the DOS at any layer of the system. Indeed, for  $k_{\parallel} = \mathbf{0}$ , it turns out that the matrix elements of  $\mathcal{V}$  can be assumed equal to the corresponding bulk ones between Si–Si and Si–M, for the sevenfold and eightfold coordinations, respectively (see figure 4). Our numerical calculations have used an analytic continuation procedure [28] which computes the GF for real energies from that for complex energies, so that the densities of both extended and localized



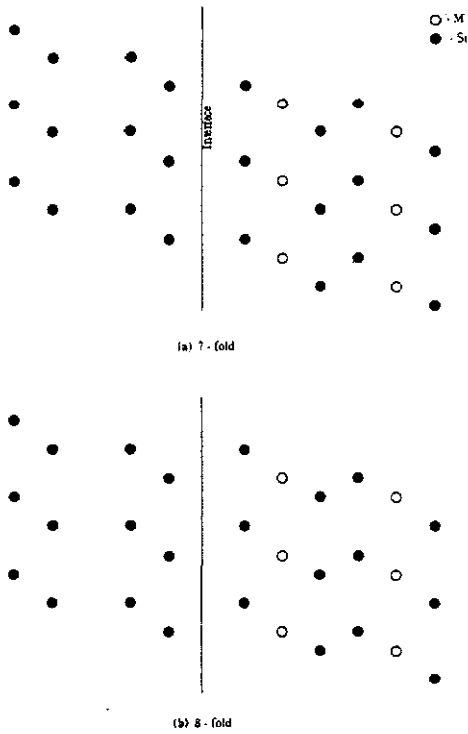
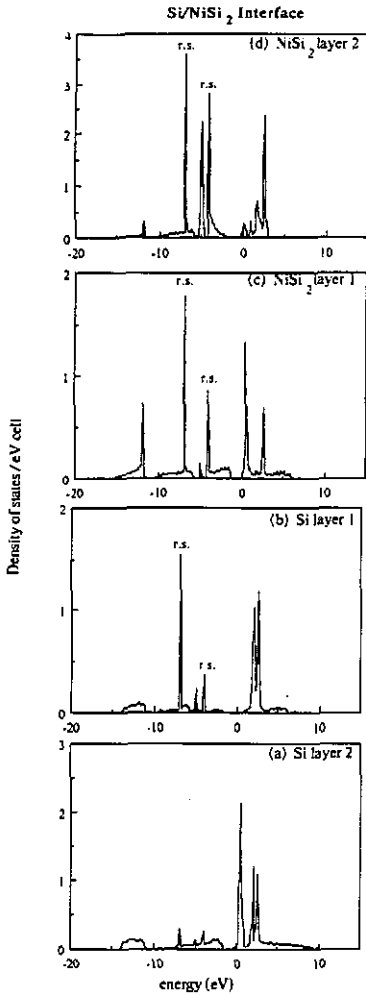


Figure 4. (a) A planar view of the Si(111)-NiSi<sub>2</sub>(111) interface atomic distribution with sevenfold coordination of the metal atom. (b) A planar view of the Si(111)-CoSi<sub>2</sub>(111) interface atomic distribution with eightfold atomic coordination.

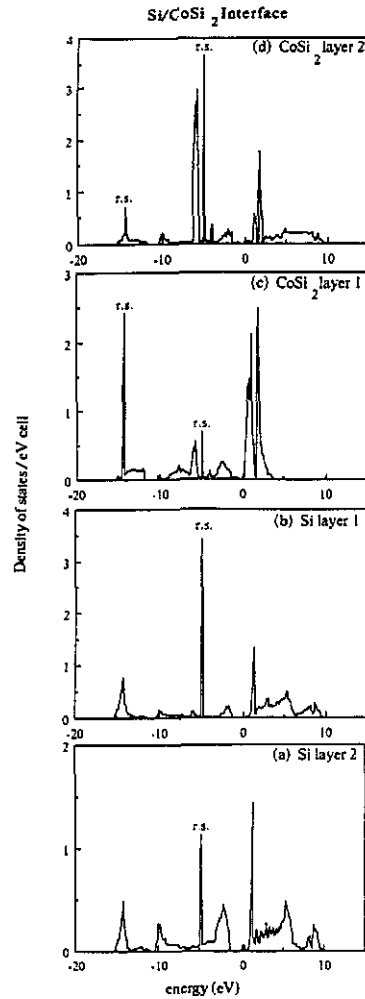
states are determined with less difficulty than by other methods. This approach allows us to examine the origins of any localized states; as we are 'creating' bonds between the two surfaces, we expect to see their dangling-bond states play a major role in the bonding across the interface. Thus, at any layer in the lattice, we can calculate the local DOS for the infinite system and then study to what extent it differs from the DOS of the bulk material. Any problems that may arise owing to the finite size of the sample are therefore avoided.

The DOS of Si/NiSi<sub>2</sub>, for layers near the interface, are shown in figure 5 (with the Fermi level taken as the energy zero). A major feature in the DOS is the appearance of an interface resonance state at  $-6.94$  eV, with localization primarily on the first layer of the silicon (figure 5(b)) and the first two layers of NiSi<sub>2</sub> (figures 5(c) and 5(d)). This state is formed from the combination of the Si-like surface state (at  $-11.4$  eV) and the surface state of clean Si, so that the main coupling across the interface is of a p-p nature. The Ni-like surface state, previously at  $-1.2$  eV, is shifted downwards to become a resonance state at  $-4.1$  eV, and plays a lesser role in the bonding across the interface. The tall peak at  $-4.9$  eV prominent in figures 5(c) and 5(d), is a Ni bulk d state, chiefly of  $x^2 - y^2$  symmetry, and does not participate in the interfacial couplings as it appears unchanged from figure 2(d). Other workers [5, 6] calculate the total DOS for finite supercells and report a single interface state near  $-2$  eV. It is hard to determine whether the two resonance states that we report here at the  $\bar{\Gamma}$  point are present in other calculations, because the integration of the DOS over the surface BZ may obliterate the resonance peaks.

The DOS of Si/CoSi<sub>2</sub>, for layers near the interface, are shown in figure 6 (again with the energy zero at the Fermi level). As before, an interface resonance is seen, at energy



**Figure 5.** Interface DOS for Si/NiSi<sub>2</sub> in (a), (b) the first two layers of silicon, and (c), (d) the first two layers of NiSi<sub>2</sub>. The localized resonance interface states are represented by *r.s.*



**Figure 6.** Interface DOS for Si/CoSi<sub>2</sub> in (a), (b) the first two layers of silicon and (c), (d) the first two layers of CoSi<sub>2</sub>. The localized resonance interface states are represented by *r.s.*

$-4.91$  eV, but in this case its origin is completely different. This state is formed from the disilicide surface state (of Co  $d$  nature), formerly at  $-0.49$  eV, and the dangling-bond state of Si, to create a bond across the interface. There is also a strong contribution from a bulk Co  $x^2 - y^2$  state at  $-4.0$  eV, so that there is a very strong Si  $p$ -Co  $d$  coupling at the interface. The localization of the interface state is greatest on the first layer of Si, and the second layer of CoSi<sub>2</sub>, corresponding to Co (see figures 6(b) and (c)). The Si-like surface state of the disilicide, originally found at  $-11.35$  eV, is shifted downwards to become a resonance state at  $-14.3$  eV, localized at the first layer of CoSi<sub>2</sub> (figure 6(c)), which is comprised of Si. The two resonance states reported here would appear to correspond to the two interface states calculated by Fujitani and Asano [4], one close to the Fermi surface and the other just below the valence band minimum. The difference

in the locations of these states may be due to the different natures of the approximations used in the two calculations.

## 5. Summary

In this paper, we have first calculated the band structures of NiSi<sub>2</sub> and CoSi<sub>2</sub> using the tight-binding SK method; the band structures are in substantial agreement with calculations using other methods. We have then performed calculations of the electronic structures of the (111) surfaces of semi-infinite NiSi<sub>2</sub> and CoSi<sub>2</sub> and their interfaces with semi-infinite Si(111), using the KS technique to find the surface and interface GFs from that for the bulk. This approach allowed us to find localized surface states of the disilicides, and to see how they are modified by the formation of the interface. For both disilicides, the relevant surface termination was found to give rise to a pair of dangling-bond surface states at the  $\bar{\Gamma}$  point: one associated with the metal constituent, and the other with Si. This is a new finding since most other workers deal with the interface problem directly and do not calculate the surface DOS separately.

Upon formation of the interface, the surface states seem to play very different roles in each system. In Si/NiSi<sub>2</sub>, the interface resonance is formed from surface states associated with Si on both sides of the interface, so that the dominant coupling is p-p in nature. In contrast, for Si/CoSi<sub>2</sub>, the Co-like surface state of the disilicide plays the major role in interface formation, so that p-d bonding is the most important. This difference in the bondings can be traced back to the different atomic geometries at the interface for the two systems (sevenfold versus eightfold coordination of the metal atoms). The Ni-like surface state of NiSi<sub>2</sub> appears as a resonance state at a lower energy in Si/NiSi<sub>2</sub>. The Si-like surface state of CoSi<sub>2</sub> also appears as a resonance state at a lower energy in Si/CoSi<sub>2</sub>. The interface states reported by other workers occur at somewhat different energies. This discrepancy may be due to the difference in the natures of the approximations used.

## Acknowledgments

We thank M M Sokoloski, N J DiNardo and J T Schick for helpful discussions. The work reported here was supported by NASA-JPL contract 958144.

## References

- [1] Tung R T, Poate J M, Bean J C, Gibson J M and Jacobson D C 1982 *Thin Solid Films* **93** 77
- [2] Tung R T 1984 *Phys. Rev. Lett.* **52** 461
- [3] Tung R T and Gibson J M 1985 *J. Vac. Sci. Technol.* **A3** 987
- [4] Fujitani H and Asano S 1988 *J. Phys. Soc. Japan* **57** 2253; 1989 *Appl. Surf. Sci.* **41-42** 164; 1990 *Phys. Rev. B* **42** 1696
- [5] Das G P, Blöchl P, Andersen O K, Christensen N E and Gunnarsson O 1989 *Phys. Rev. Lett.* **63** 1168
- [6] van den Hoek P J, Ravenek W and Baerends E J 1988 *Phys. Rev. Lett.* **60** 1743; 1988 *Surf. Sci.* **205** 549
- [7] Robertson J 1985 *J. Phys. C: Solid State Phys.* **18** 947
- [8] Xu Y-N, Zhang K-M and Xie X 1986 *Phys. Rev. B* **33** 8602
- [9] Rees N V and Matthai C C 1988 *J. Phys. C: Solid State Phys.* **21** L981; 1989 *Semicond. Sci. Technol.* **4** 412
- [10] Slater J C and Koster G F 1954 *Phys. Rev.* **94** 1498

- [11] Kalkstein D and Soven P 1971 *Surf. Sci.* **26** 85
- [12] Bisi O and Calandra C 1981 *J. Phys. C: Solid State Phys.* **14** 5479
- [13] Chabal Y J, Hamann D R, Rowe J E and Schluter M 1982 *Phys. Rev. B* **25** 7598
- [14] Bylander D M, Kleinman L, Mednick K and Grise W R 1982 *Phys. Rev. B* **26** 6379
- [15] Tersoff J and Hamann D R 1983 *Phys. Rev. B* **28** 1168
- [16] Lambrecht W R L, Christensen N E and Blochl P 1987 *Phys. Rev. B* **36** 2493
- [17] Sen Gupta R and Chatterjee S 1986 *J. Phys. F: Met. Phys.* **16** 733
- [18] Chang Y-J and Erskine J L 1982 *Phys. Rev. B* **26** 7031
- [19] Weaver J H, Franciosi A and Moruzzi V L 1984 *Phys. Rev. B* **29** 3293
- [20] Gewinner G, Pirri C, Peruchetti J C, Bolmont D, Derrien J and Thiry P 1988 *Phys. Rev. B* **38** 1879
- [21] Hass K C, Ehrenreich H and Velicky B 1983 *Phys. Rev. B* **27** 1088
- [22] Schick J T, Bose S M and Chen A-B 1989 *Phys. Rev. B* **40** 7825
- [23] Chadi D J and Cohen M L 1975 *Phys. Status. Solidi. B* **68** 405
- [24] Engle W P, Sulston K W and Bose S M 1991 unpublished
- [25] Hamann D R 1988 *Phys. Rev. Lett.* **60** 313
- [26] Catana A, Schmid P E, Rieubland S, Levy F and Stadelmann P 1989 *J. Phys.: Condens. Matter* **1** 3999
- [27] Cherns D, Anstis G R, Hutchison J L and Spence J C H 1982 *Phil. Mag. A* **46** 849
- [28] Hass K C, Velicky B and Ehrenreich H 1984 *Phys. Rev. B* **29** 3697