First-principles study of the stability of the $NiSi_2$/Si(111) interface

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(Received 15 October 1997)

The interface energies of two structures for the $NiSi_2$/Si(111) interface are explored using a full-potential linear augmented plane-wave method within the local density approximation. In supercell calculations, the type-*B* interface energy decreases as the $NiSi_2$ layer is made thicker from two to five molecular layers, while the type-*A* interface energy does not change. As a result, the interface structure with lowest energy changes from type *A* to type *B* as the thickness of the $NiSi_2$ layer is increased. Although epitaxial type-*A* and -*B* structures are very sensitive to experimental conditions, our result seems consistent with many experiments. [S0163-1829(98)01815-3]

Disilicides of Ni and Co are very important materials for LSI technology, and they also offer a unique opportunity to develop a detailed understanding at a microscopic level of the metal-semiconductor interface. As they have the fluorite (CaF_2) crystal structure with bulk lattice parameters close to those of Si, their epitaxially grown films on a Si(111) surface have atomically abrupt, structurally perfect interfaces, where the silicide overlayer has two orientations. The type-*A* structure has the same orientation as the Si substrate, while the type-*B* structure is rotated by 180° about the Si⟨111⟩ axis. At the $NiSi_2$/Si(111) interface, Tung *et al.* showed these structures can be selected by adjusting the thickness of the deposited Ni atoms. A thin Ni layer (about 5 Å) forms a type-*B* interface while a thick one (about 18 Å) forms a type-*A* interface after annealing at about 500 °C.[1] This discovery triggered a number of studies aimed at understanding this epitaxial metal-semiconductor interface.[2]

Hamann and Mattheiss first performed *ab initio* calculations for the energetics of these interfaces, using slab models with one $NiSi_2$ layer and one Si_2 layer. They found that the type *A* had lower interface energy than the type *B*. The difference between the interface energies was between 30 and 60 meV, depending on the boundary condition of the *H*-terminated or unterminated slab.[3] About the interface stability, there have been many discussions. From in situ studies of $NiSi_2$ growth, Gibson *et al.* found that a metastable phase θ-Ni_2Si was associated with the subsequent growth of type-*A* structure, while an as-deposited thin Ni film appeared to form the type-*B* structure. Therefore, they concluded that the type *B* has a lower interface energy than the type *A*.[4] However, this contradicts the *ab initio* calculation.

Two groups performed x-ray standing-wave measurements on the two types of $NiSi_2$/Si(111) interfaces. Vlieg *et al.* reported that the distance between the interfacial Ni plane and the Si(111) surface diffraction plane (*D* in Fig. 1) contracted by 0.04 Å for type *A* and by 0.11 Å for type *B*.[5] However, Zegenhagen *et al.* reported that this distance contracted by 0.16 Å for type *A* and by 0.07 Å for type *B*.[6] Although these results are conflicting, they suggest that the interfacial lattice relaxation differs between the two structures. Since Hamann and Mattheiss did not include the lattice relaxation, one might suspect that their calculation gave the wrong lowest-energy structure.

Using the norm-conserving pseudopotential method, Li and Rabii found that the interplaner separation at the interface was reduced mainly between the first Si and Ni layers on the $NiSi_2$ side (d_1 in Fig. 1), and not by the contraction of the interfacial Si-Si bonds (d_2 in Fig. 1).[7] By their calculation d_1 contracted by about 0.2 Å in both types. This seems excessive, so we performed calculations using the full-potential linear augmented plane-wave method (FLAPW).[8,9] Our results are that d_2 contracted by 0.005 Å and d_1 contracted by 0.055 Å in type *A*, and d_2 expanded by 0.023 Å and d_1 contracted by 0.073 Å in type *B*. Thus, the distance between the interfacial Ni plane and the Si(111) surface diffraction plane (*D*) contracted by 0.05 Å in both interface types. Even with these relaxation parameters, we also obtained that type *A* had a lower interface energy than type *B*.[10]

To investigate the energetics of the silicide/Si interface, we need a very accurate *ab initio* method, such as FLAPW. This requires a large amount of computer capacity. Therefore it is common to use small supercells that can represent the interface atomic structure.[11] However, our previous calculations suggested that the difference in the total energies between the two types of $NiSi_2$/Si(111) interfaces depends significantly on the supercell size.[10] In the usual experiments Ni films are deposited on a thick Si substrate, so that a large number of Si layers should be included. We also have to take account of the lattice relaxation at the $NiSi_2$/Si(111) interface.

To solve the mystery around the interface energy of the two types of $NiSi_2$/Si(111) interfaces, we performed more

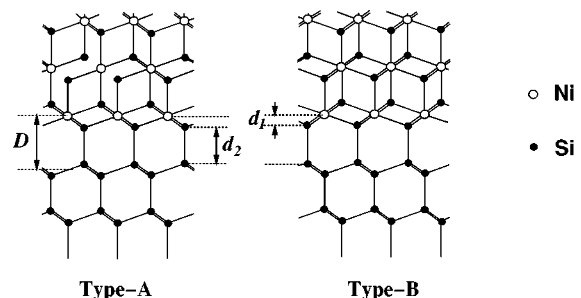

FIG. 1. The atomic structure of the two types of $NiSi_2$/Si(111) interface viewed in the $\langle 1\bar{1}1\rangle$ direction.

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TABLE I. The interface energies for the ideal and relaxed structures. The same relaxation parameters are used for both $NiSi_2$ thickness (see the text). The units are meV per interface area of the supercell (12.76 Å^2).

	$m(NiSi_2)/n(Si_2)$	2/6	5/6
Ideal	Type *A*	491	491
	Type *B*	500	479
Relaxed	Type *A*	474	478
	Type *B*	485	473

comprehensive FLAPW calculations. The calculation conditions were similar to the previous one. We used the scalar relativistic approximation and the local density approximation (LDA) parameters of Janak, Moruzzi, and Williams.[12] The muffin-tin sphere radii were 2.14 a.u. for Si and 2.18 a.u. for Ni. The plane-wave cutoff energy was 16 Ry, which gives around 120 plane waves per atom. The plane waves were expanded into spherical harmonics in each muffin-tin sphere up to $l=8$, and the electron distribution and potential were expanded up to $l=6$. We used hexagonal supercells with a space-group symmetry of $P\bar{3}m1$ (D_{3d}^3). Since there are two interfaces in one supercell, the interface energy is defined as half the supercell energy minus half the sum of total energies of a number of unit cells of each bulk material corresponding to the number of layers in the supercell. To calculate the reference total energies of bulk Si and $NiSi_2$, we used the same cutoff energy for the plane waves and 85 k points in the irreducible $\frac{1}{48}$ wedge in the first Brillouin zone.

Table I shows the interface energies for the ideal and relaxed structures. These values were calculated using the supercell with six Si_2 layers and 25 k points in the irreducible $\frac{1}{12}$ wedge in the hexagonal Brillouin zone. The ideal interface structure has Si-Si and Ni-Si bond lengths, which are determined from the bulk Si lattice constant of 5.429 Å. The relaxed structures are the previously mentioned structures, which were determined by FLAPW total energy calculations. With two layers of $NiSi_2$ type *A* has an interface energy that is lower than that of type *B* by 10 meV in both the ideal and relaxed structures. However, with five $NiSi_2$ layers type *B* has a lower interface energy than type *A*. This means the favorable interface structure changes from type *A* to type *B* according to the thickness of the $NiSi_2$ layer. The difference of the interface energies is so small that a careful and comprehensive check is necessary to confirm it.

First, we checked the convergence of the interface energy with respect to the number of **k** points. With 49 **k** points type *B* had an interface energy that is lower than that of type *A* by 14 meV for the ideal structures with five $NiSi_2$ and six Si_2 layers, while its difference is 12 meV with 25 **k** points. As these differ by only 2 meV, the 25 **k** points are enough for our objective. The cutoff energy for the plane waves is sufficiently large for both the supercell and bulk calculations, so that we are able to compare the interface energy very accurately between the supercells of different size.

The interface energies of the ideal structures in Table II were also calculated with 25 **k** points. Since Ni films are usually deposited on a thick Si substrate, the question is how many Si layers are needed to represent this experimental situation. Keeping the two $NiSi_2$ layers, we examined the

TABLE II. The interface energies for the ideal structures. The units are meV per interface area of the supercell (12.76 Å^2).

$m(NiSi_2)/n(Si_2)$	2/3	2/9	5/3
Type *A*	491	489	482
Type *B*	528	498	485

thickness dependence of the interface energy. With two layers of $NiSi_2$ the ideal type-*A* structure has almost the same interface energy for all the supercells with three, six, and nine Si_2 layers. In contrast, the type-*B* interface energy changes by 28 meV when the Si layer changes from three to six layers. Between the six and nine Si_2 layers, the interface energy changes by only 2 meV and the difference between the two types does not change. The type-*A* structure with five $NiSi_2$ and three Si_2 layers has an exceptionally low interface energy, about 8 meV below the other ideal type-*A* interfaces. This also demonstrates that three Si_2 layers are not enough to achieve convergence, as we see that convergence is only realized at six Si_2 layers.

A contour plot of the valence electron density gives more detailed information (Fig. 2). Figures on the left-hand side [(a) and (c)] show the total valence electron density near the interface, which are obtained from the supercells with five $NiSi_2$ and six Si_2 layers. On this scale, the electron density within the $NiSi_2$ and Si layers is very similar to the corresponding bulk densities. But, using a finer scale we could see the same charge transfer at the interface as is observed in our linear muffin-tin orbital in the atomic sphere approximation (LMTO-ASA) calculations.[13,14] It is because the sevenfold structure introduces a small additional volume at the inter-

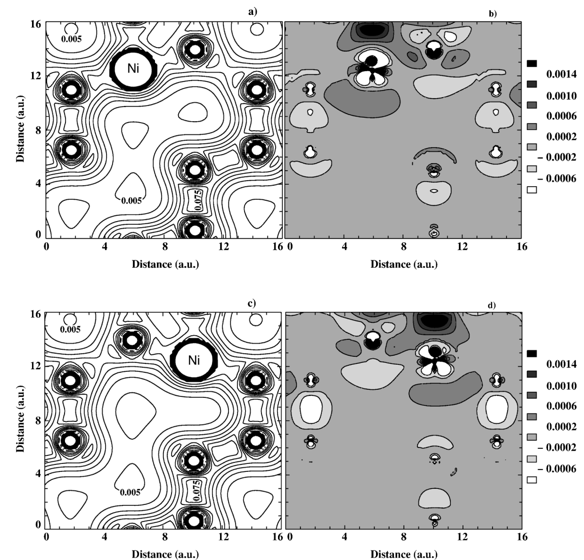

FIG. 2. Figures on the left-hand side are valence electron density maps in the $(1\bar{1}0)$ plane, (a) type *A* and (c) type *B*. The lowest contour level is $0.005a_{\mathrm{Bohr}}^{-3}$ and its step is $0.01a_{\mathrm{Bohr}}^{-3}$. Figures on the right-hand side are contour maps of the valence electron density difference between the two interfaces, one has five $NiSi_2$ layers and the other has two $NiSi_2$ layers, (b) type *A* and (d) type *B*. The contour step is $0.0004a_{\mathrm{Bohr}}^{-3}$. Two kinds of figures show the same area.

face that electrons move from the $NiSi_2$ and Si layers to fill the space.

The figures on the right-hand side [(b) and (d)] show the electron density of the supercell with five $NiSi_2$ and six Si_2 layers minus that of the supercell with two $NiSi_2$ and six Si_2 layers. As the areas are the same between the left- and right-hand figures, it is easy to identify how the electron density changes with the thickness of $NiSi_2$ layers. In the largest area of the right-hand figure, the electron density does not change, as the difference stays in the range from $-0.0002a_{\text{Bohr}}^{-3}$ to $0.0002a_{\text{Bohr}}^{-3}$. Dark tiles show the areas where the electron density increases and light tiles show the areas where it decreases, when the $NiSi_2$ layer thickens. These figures have common features. The density changes nonspherically within the interfacial Ni atoms, and it increases in the area just below the Ni atom, which has dangling *d* orbitals. Interfacial Si-Si bonds appear to be a little bit weaker and back bonds between the Ni atom and the third Si atom in the $NiSi_2$ layer (outside of the figures) appear to be stronger. As the peak density of the interfacial Si-Si bond is about $0.08a_{\text{Bohr}}^{-3}$ in the left-hand figures, it should be noted that its peak density changes by at most 1%. As the Ni-Si back bonds have a peak value of about $0.07a_{\text{Bohr}}^{-3}$, these change by at most 2%. The difference between the two types is tiny. The light area at the interfacial Si-Si bond is a little larger in type *B* than in type *A*, while the dark area of the Ni-Si back bond is a little larger in type *B* than in type *A*. The competition between these differences may be the origin of the thickness dependence of the interface energy.

With two layers of $NiSi_2$ the relaxed structures have an interface energy that is lower than that of the ideal structure by about 15 meV in both type *A* and *B* (Table I). With five layers of $NiSi_2$ this value decreases, especially in the type-*B* structure, although they still both have lower interface energies than the ideal structures. The interfacial Si-Si bond appears to be weaker owing to the $NiSi_2$ layer thickness and the relaxed structures were obtained using a supercell with two $NiSi_2$ layers.[10] It is probable that the interface with five $NiSi_2$ layers has slightly different parameters for lattice relaxation. If more accurate relaxation were included for the interface with five $NiSi_2$ layers, it should have a lower interface energy than the value in the Table I. This seems more likely for the type-*B* structure, because its adiabatic potential is a little flatter than that of type *A* (Fig. 3 in Ref. 10). Taking account of the lattice relaxation, we may conclude that the type-*B* interface with five $NiSi_2$ layers has a lower interface energy than the type-*A* interface with two $NiSi_2$ layers.

Since there are two interfaces in the supercell, the electronic structure of the interface is represented by half of the supercell. Although five $NiSi_2$ and six Si_2 layers are enough to screen charge transfer near the interface, two $NiSi_2$ layers is too small to do it.[13] Hamann and Mattheiss used the slab model with one $NiSi_2$ layer and one Si_2 layer as explained before. Their boundary condition differs with our supercell method. However, our interface energy difference between the two types obtained with two $NiSi_2$ and three Si_2 layers agrees well with theirs.

When a thick Ni layer of 18 Å forms the type-*A* interface by thermal annealing, Si atoms are supplied from the Si substrate to facilitate the $NiSi_2$ reaction or Ni atoms diffuse into the Si substrate. If a suitable amount of Si is deposited at room temperature following Ni deposition, subsequent annealing leads to the formation of uniform type-*B* interface.[15,16] The stability of the type-*B* interface was also demonstrated by a laser melting method. Prior to laser melting, $NiSi_2$ layers had both type-*A* and -*B* orientations, the recrystallized $NiSi_2$ phase from the melt has pure type-*B* orientations.[17] This agrees with our result that type *B* has lower interface energy than type *A* for a thick $NiSi_2$ layer.

When a thin Ni layer of 5 Å forms the type-*B* interface by thermal annealing, the type-*B* $NiSi_2$ layers are not uniform in thickness and, furthermore, they often contain a small fraction of type-*A* oriented grains.[2] As-deposited thin Ni film on a clean Si(111) forms the type-*B* structure at room temperature. But this is related with highly reconstructed 7×7 structure, because this does not happen on a 1×1 Si(111) surface.[18] The formation of the thin type-*B* $NiSi_2$ layer is controlled mainly by kinetics. Experimental evidence does not contradict the theoretical result that type *A* has lower interface energy than type *B* for one or two $NiSi_2$ layers.

In summary, we explored the interface energy of the type-*A* and type-*B* $NiSi_2$/Si(111) interfaces using a FLAPW supercell method. The type-*B* interface with five $NiSi_2$ layers has a lower interface energy than the type-*A* interface with two $NiSi_2$ layers. This should be connected with the fact that epitaxial type-*A* and -*B* structures are very sensitive to experimental conditions.

I would like to express thanks for the hospitality at the Material Modelling Laboratory in Oxford University. Large scale calculations were performed on VX-4 in the Fujitsu European Centre for Information Technology (FECIT).

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