Full-potential total-energy investigation on the lattice relaxation at the two types of $NiSi_2$/Si(111) interface

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We examined the lattice relaxation at the two types of the $NiSi_2$/Si(111) interface using total-energy calculations by the full-potential linear-augmented-plane wave method. Our calculations show that the distance of the interfacial Ni plane and the Si(111) surface diffraction plane contracts by 0.05 Å in both type interfaces. This is considerably less than the result obtained by Li and Rabii from their interface dynamics calculations with smooth pseudopotentials [Phys. Rev. B **49**, 2927 (1994)].

The main obstacle in understanding the formation of Schottky barriers is the obscurity of the atomic structure at the metal-semiconductor interface. A well-defined interface is needed to clarify the relationship between the Schottky barrier height (SBH) and other physical parameters. Metal silicide/silicon interfaces are good for this. $NiSi_2$ has a fluorite (CaF_2) structure with a lattice constant of 5.406 Å, which is 0.4% less than the 5.429-Å Si lattice constant. $NiSi_2$ epitaxially grown on a Si(111) surface forms an atomically abrupt, structurally perfect interface. This interface has two types of structure. Type-A $NiSi_2$ has the same orientation as the Si substrate, and type-B $NiSi_2$ is rotated 180° about the Si⟨111⟩ axis.[1] In 1984, Tung discovered that the SBH of the two types of interface differ by 0.14 eV. The n-type SBH (the conduction band minimum minus the Fermi level) is 0.65 eV for the type-A interface and 0.79 eV for the type-B interface.[2]

Using the linear muffin-tin orbitals in the atomic sphere approximation (LMTO-ASA),[3] we obtained different SBH's for the two types of $NiSi_2$/Si(111) interface, which is consistent with Tung's work.[4] Shortly after our work, Das *et al.* reported results that agreed qualitatively with ours, but differed quantitatively.[5] We performed further calculations under different conditions to resolve the discrepancy.[6] Since the interfacial relaxation was not yet clarified by experiments, we used the lattice constant of bulk Si and neglected the small lattice mismatch. Ossicini, Bisi, and Bertoni also performed LMTO-ASA calculations on the $NiSi_2$/Si(111) interfaces and argued that SBH depends not only on the interface structure, but also on the interface relaxation distance.[7]

Two groups reported x-ray standing wave measurements on the two types of $NiSi_2$/Si(111) interface. 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.[8] However, Zegenhagen *et al.* reported that this distance contracted by 0.16 Å for type-A and by 0.07 Å for type-B.[9] Experimental observations are conflicting. Moreover, since the detailed atomic structure of these interfaces has not been determined from experiments, the interfacial contraction was simply attributed to the Si-Si bond length just at the interface.[5,7]

Using a norm-conserving pseudopotential with plane wave basis for the wave functions, Li and Rabii carried out interface dynamics calculations at the two types of $NiSi_2$/Si(111) interface.[10] They fixed the lattice constant parallel to the interface and allowed the atoms to be fully mobile in the direction perpendicular to the interface. The important discovery was that the interplanar separation at the interface is 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). d_1 contracted by 0.195 Å for type-A and by 0.213 Å for type-B, and d_2 expanded by 0.04 Å at both interfaces. These values are too large to be neglected in the electronic structure calculation, since the 0.1-Å contraction of the interplanar separation at the YSi_2/Si(111) interface raised the SBH by 0.1 eV.[11] However, since the lattice mismatch is 0.4% between Si and $NiSi_2$, we suspected that their interfacial relaxation was excessive.

In this paper, we report total-energy calculations for the two types of $NiSi_2$/Si(111) interface using the full-potential linear-augmented-plane-wave (FLAPW) method,[12,13] which currently gives the most reliable to-

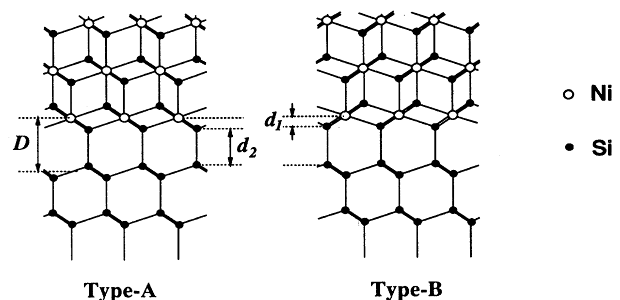

FIG. 1. Atomic structure at the two types of $NiSi_2$/Si(111) interface. d_1 and d_2 are the characteristic lengths used in the calculations as structural parameters.

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tal energy. Calculations used scalar relativistic approximation, neglecting spin-orbit interaction. The exchange and correlation were determined by the local-density approximation (LDA), using the parameters from Janak, Moruzzi, and Williams.[14] We used sphere radii of 2.14 a.u. for the Si sphere and 2.17 a.u. for the Ni sphere. Linear augmented plane waves (LAPW's) are expanded by spherical harmonics in each muffin-tin sphere through to $l = 8$, and the electron distribution and potential are expanded through to $l = 4$.

To examine the interfacial relaxation, we used supercells which contained two $NiSi_2$ layers and three Si_2 layers (2/3). According to Li and Rabii, the interfacial lattice relaxation is related to distances d_1 and d_2. We therefore chose these as structural parameters and performed total-energy calculations by FLAPW for different d_1 and d_2 values. We fixed other lattice parameters to those calculated from the bulk Si lattice constant. In the total-energy calculations, we included about 1500 LAPW's (the plane wave cutoff was $|\mathbf{K}|^2 = 12$ a.u.). We used four nonequivalent **k** points in the first Brillouin zone, while Li and Rabii used three special **k** points.

The FLAPW total energies of the supercell were interpolated by a fourth order Lagrange polynomial to obtain an adiabatic potential (Fig. 2). The vertical axis has a d_1 deviation from the unrelaxed value of 0.784 Å, and the horizontal axis has a d_2 deviation from the unrelaxed value of 2.351 Å. Minus means lattice contraction and plus means lattice extension. The contour step is 10 meV per supercell or 5 meV per interface, because there are two interfaces in the supercell. The relaxed atomic positions are a little different between the two types of $NiSi_2$/Si(111) interface. In type-A the interfacial Si-Si bond (d_2) contracts by 0.005 Å and the interplanar separation between the first Si and Ni planes (d_1) contracts by 0.055 Å. In type-B the former expands by 0.023 Å and the latter contracts by 0.073 Å. Therefore, the distance between the interfacial Ni plane and the Si(111) surface diffraction plane (D) contracts by 0.05 Å in both interface types.

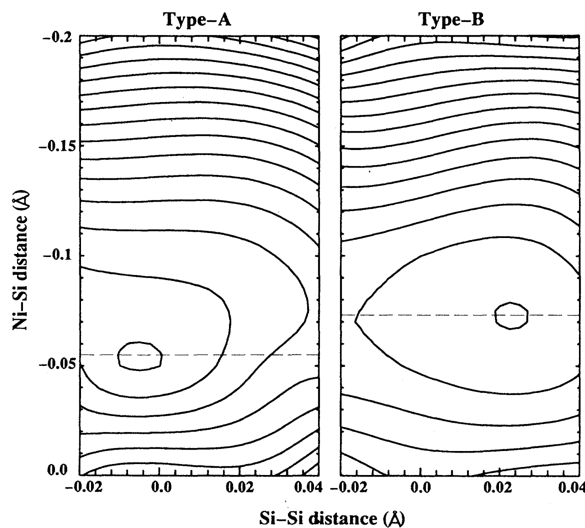

FIG. 2. The adiabatic potential at the two types of $NiSi_2$/Si(111) interface with respect to the lattice parameters of d_1 (vertical axis) and d_2 (horizontal axis). Contour step is 10 meV.

The adiabatic potentials of Si-Si bonds are taken along dashed lines in Fig. 2. The vertical axis of Fig. 3 is the supercell energy and the minimum energy of the type-A interface is set to zero. The type-A interface always has a lower total energy than the type-B interface. The adiabatic potential of bulk Si-Si bond was calculated using a supercell with six Si_2 layers to compare the curvature of the adiabatic potential. Its vertical absolute value is arbitrary. The adiabatic potentials of the interface have slightly sharper curves near the minimum energy positions than that of bulk Si. The Si-Si bond is slightly stiffer at the $NiSi_2$/Si(111) interface than in bulk Si.

Hamann and Mattheiss first examined the energetics of the $NiSi_2$/Si(111) interface using their LAPW method. They reported that the magnitude of the type-B minus type-A interface energies of the unrelaxed structure changed from 30 meV to 60 meV, depending on the boundary condition of the H-terminated or unterminated slab. The reason for this change was assumed to be a slab-thickness convergence error.[15] To check this, we performed total-energy calculations for the unrelaxed structure with different supercell sizes (Table I). The plane wave cutoff is the same as that of the 2/3 supercell; almost 2400 LAPW's for 5/3 supercells and 3300 LAPW's for 5/6 supercells. Hamann and Mattheiss used a 2/2 slab and ten **k** points. The magnitude of type-B minus type-A interface energies with the 2/3 supercells agrees well with theirs.

Since the two types of $NiSi_2$/Si(111) interface can be controlled by the initial Ni thickness,[1] the interface energy difference between the two types might be related to the interface formation mechanism. A thin Ni layer followed by thermal annealing or as-deposited Ni film at room temperature forms the type-B structure. One may

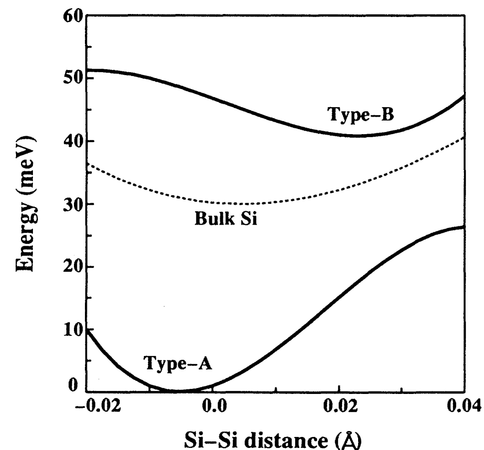

FIG. 3. Adiabatic potential of Si-Si bonds taken along dashed lines in Fig. 2. Dotted line is bulk Si potential, whose absolute value is arbitrary.

TABLE I. The magnitude of the type-B minus type-A interface energies in the unrelaxed structure for different supercell sizes with different numbers of nonequivalent **k** points. (Units are in meV.)

m ($NiSi_2$) / n(Si_2)		2/3			5/3		5/6
Number of **k** points	4	9	25	4	9	25	4
Type-B minus type-A	12	44	38	−15	−4	4	1

assume, therefore, that the type-B has a lower interface energy than the type-A.[16] However, the LDA calculation with small supercells indicates that the opposite is true.

In Table I, as the number of $NiSi_2$ layers increases from two to five, the magnitude of the type-B minus type-A reduces from 38 meV to 4 meV with 25 nonequivalent k points. The calculation with 5/6 supercells suggests further dependence of the cell size on the difference in the interface energies. In usual experiments, Ni films are deposited on a thick Si substrate, while it is difficult to include a large number of Si layers for accurate total-energy calculations. Furthermore, the lattice relaxation occurs at the interface. Since the difference in the interface energies of the two types of $NiSi_2$/Si(111) interface is very small, it may be premature to conclude that the LDA calculation gives a lower interface energy to the type-A structure than to the type-B interface.

Compared with our results, Li and Rabii reported a much larger lattice relaxation at the $NiSi_2$/Si(111) interface. We only mention two possible reasons for this discrepancy. One is pseudopotential versus FLAPW. In general, the pseudopotential method cannot accurately describe $3d$ electrons of Ni atoms. However, this is only speculative because the details of their optimally smooth Ni pseudopotential are not available. The other reason is the supercell size. Since the interface energy is significantly dependent on the supercell size, as mentioned above, we think their supercells with one $NiSi_2$ and one Si_2 layer are too small to determine accurate lattice relaxation at the $NiSi_2$/Si(111) interface.

In summary, we obtained adiabatic potentials from the total-energy calculation by FLAPW. Our results show that the lattice relaxation at the $NiSi_2$/Si(111) interface is very small, compared with Li and Rabbi's pseudopotential calculations, although the main lattice contraction similarly occurs between the interstitial Ni and Si planes. The difference in the interface energies between the two types is small and depends significantly on the number of $NiSi_2$ and Si_2 layers in the supercell.

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