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Ab initio structural study of the silicon/nickel disilicide interfaces

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Using our recently developed *ab initio* schemes for generating optimally smooth pseudopotentials, we have carried out the first fully relaxed structural study of a silicon/transition-metal-silicide interface, $NiSi_2$/Si(111), by allowing the atoms to be fully mobile in the direction perpendicular to the interface. We found that the contraction of the silicide triple layer immediately adjacent to the interface is responsible for most of the interface relaxation. This is in disagreement with the assumption that the relaxation occurs primarily at the interface Si-Si bond. Such an assumption has been used to interpret the experimental results as well as being used in most of the electronic-structure calculations and may be responsible for the disagreement between the calculated and measured results for the Schottky barrier heights. We also confirm that the type-*A* interface is more energetically favored than type *B*, while the type-*B* interface relaxes more than type *A*.

Epitaxial nickel disilicide on silicon has been studied extensively in recent years. The bulk lattice constant of the fluorite-type $NiSi_2$ is only 0.44% smaller than that of silicon, $a = 5.43$ Å at room temperature.[1] The interfaces are believed to be atomically flat and nearly perfect.[2] Such interfaces are important from a technological point of view[3] and serve as model Schottky barriers, providing the opportunity to directly correlate interface atomic structure with electrical properties.[4–7] In this work we have carried out a detailed study of the atomic structure of the $NiSi_2$/Si(111) interfaces.

Previous calculations by van den Hoek, Raveneck, and Baerends[8,9] and Hamann[10] have predicted that the sevenfold interface structures are energetically favored where seven is the number of nearest-neighbor Si atoms for each metal atom at the interface. Experiments using high-resolution transmission electron microscopy,[11] medium-energy ion scattering,[12,13] x-ray standing waves (XSW),[1,2] and surface x-ray diffraction[14] have verified the theoretical predictions. There are two possible interface structures referred to as *A* and *B* (Fig. 1). In *A*-type interface all the crystal axes of both Si and $NiSi_2$ are aligned, while in *B*-type interface, the epitaxial silicide is rotated around the (111) crystal axis by 180° with respect to the Si substrate. It is remarkable that the electronic properties of the *A*- and *B*-type interfaces are different with the latter typically having a higher Schottky barrier. Clearly, only the structural differences at the interface can be responsible for this behavior. Although most calculations of the Schottky barrier height predict the correct relative heights for the two different structures, there are large discrepancies with the measured values.[15] While these discrepancies are partly attributable to the use of the local-density approximation, they may also result from the use of inappropriate interface structure in the calculations. In most cases, the interface is taken to be simply an assembly of two bulk materials, with, at most, the interface Si-Si bond allowed to relax.

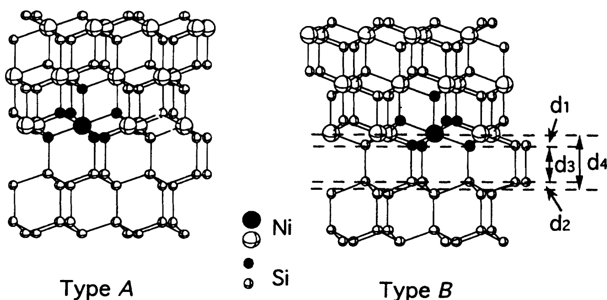

FIG. 1. Models for Si/$NiSi_2$ interfaces. d_1, d_2, d_3, and d_4 are the characteristic lengths used in the calculations.

There have been some experimental efforts to resolve these questions. However, different XSW measurements have furnished contradictory results. Vlieg *et al.*[2] have found that the interplanar separation at interface is reduced by 0.04 Å for type-*A* and by 0.1 Å for type-*B* interfaces, while Zegenhagen, Huang, and Gibson[1] give the values of 0.09 and 0.05 Å, respectively. Further uncertainty exists as to exactly where the relaxation takes place. This could occur either in the interface Si-Si bond or in Si and $NiSi_2$ layers immediately adjacent to the interface or a combination of all three.

We have carried out interface dynamics calculations for a model consisting of a supercell containing a silicon double layer and a disilicide triple layer (Fig. 2). Each cell consists of four silicon and one nickel atoms. The

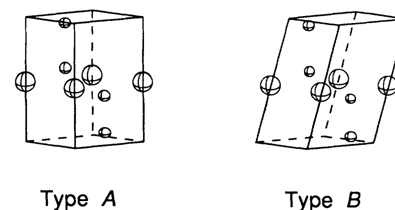

FIG. 2. Unit cells used for the type-*A* and -*B* interfaces.

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TABLE I. The relative interface energies per unit area for type-A and -B interfaces in eV/Å^3. The energy of the unrelaxed B interface is taken as reference.

Type A		Type B	
Unrelaxed	Relaxed	Unrelaxed	Relaxed
−0.03	−0.07	0.00	−0.04

lattice constants in the plane parallel to the interface are fixed during the dynamics process since there is no experimental evidence for lateral relaxation. The atoms are free to move in the direction normal to the interface. Total-energy calculations were first performed for bulk silicon and silicide at various lattice constants in order to obtain their equilibrium values. The average of these two values, 5.442 Å, is used as the fixed lateral lattice constant for the model. The total-energy calculations are carried out within the local-density approximation with the Hedin-Lundqvist[16] form of the exchange-correlation potential using *ab initio* norm-conserving pseudopotentials[17–19] with a plane-wave basis for the wave functions. The strong localized nature of the d electrons in Ni makes the use of traditional pseudopotentials prohibitively time consuming. Therefore we developed a scheme for generating optimally smooth Ni pseudopotentials,[19] resulting in rapid convergence of total energies with the number of plane waves. For Si it was sufficient to use pseudopotentials of the form introduced by Kerker.[18] Even so, the needed computational resources were the determining factor for the size of the unit cell chosen in our calculations. A kinetic-energy cutoff of 24.2 hartrees and three special k points[20] in the irreducible section of the Brillouin zone were used in the total-energy calculations. The coefficients in the plane-wave expansion of the electron wave functions are used as variables in a preconditioned conjugate-gradient procedure[21] to minimize the energy functional for the ground-state total energy of the system. Subsequently, a Broyden-Fletcher-Goldfarb-Shanno structural optimization procedure was carried out on the total energy for several values of the longitudinal (perpendicular to the interface) lattice constant and the atoms were allowed to fully relax to obtain minimum total energy for each value. The calculated points were then fitted to the Murnaghan equation of state.[22]

The resulting energies per unit area of the interface, relative to unrelaxed B-type structure, are given in Table I. It can be seen that the relaxation lowers the interface energies by 0.04 eV/Å^2. Energy of the relaxed type-A interface is lower by 0.03 eV/Å^2 than for B. This is opposite the results obtained by Matthai, Rees, and Shen,[23]

TABLE II. The unrelaxed and fully relaxed interface characteristic lengths for type-A and -B interfaces in Å

		d_1	d_2	d_3	d_4
Unrelaxed		0.781	0.392	2.343	3.516
Calculated	Type A	0.586	0.393	2.384	3.363
	Type B	0.568	0.391	2.387	3.345

TABLE III. Relaxations of the interface characteristic lengths in Å.

		Δd_1	Δd_2	Δd_3	Δd_4
Type A	Calculated	−0.195	+0.001	+0.041	−0.153
	Experiments				−0.09[a]
					−0.04[b]
Type B	Calculated	−0.213	−0.001	+0.044	−0.171
	Experiments				0.05[a]
					0.11[b]

[a]Reference 1.
[b]Reference 2.

who used a potential-energy function approach to determine the minimum-energy configuration. Table II gives the calculated results for the relaxed characteristic lengths d_1, d_2, d_3, and d_4 of the interface, as defined in Fig. 1, along with the unrelaxed values which were obtained from experimental results on bulk Si and $NiSi_2$. d_1 and d_2 represent the thickness of Si and $NiSi_2$ layers immediately adjacent to the interface, while d_3 denotes the Si-Si bond length at the interface. d_4, which is equal to $d_1+d_2+d_3$, represents the characteristic interface thickness and is the distance between the plane bisecting the silicon double layer immediately adjacent to the interface and the plane bisecting the silicide triple layer (Ni plane).

Table III gives the calculated changes (relaxation) of the different characteristic lengths along with the results of XSW measurements of the interfaces. Our results indicate that d_1 remains unchanged, d_2 contracts, and d_3 expands, resulting in a net decrease of d_4, in agreement with experiments which only provide information on the behavior of d_4. This demonstrates the confusion that can arise if the interface thickness is equated with the Si-Si

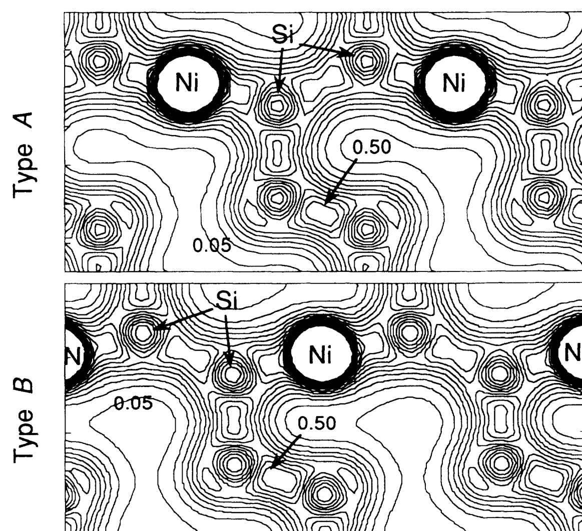

FIG. 3. Charge distribution in the plane perpendicular to the interface and containing the Si-Ni bond in nickel disilicide and the Si-Si bond in silicon. The value of the lowest contour and the step size are both 0.05 electrons/Å^3.

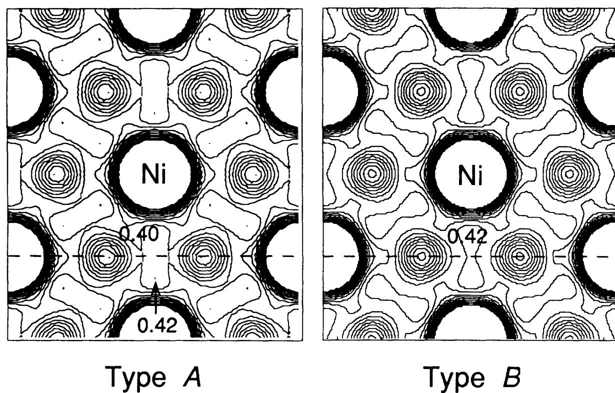

FIG. 4. Charge distribution in the Ni plane parallel to the interface. The value of the lowest contour and the step size are both 0.02 electrons/Å ^{3}.

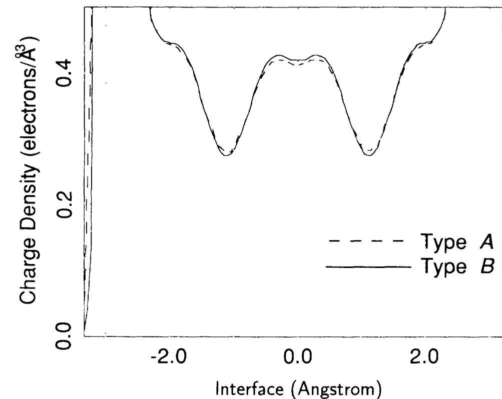

FIG. 5. The one-dimensional profiles of the charge distribution for type-*A* and -*B* interfaces along the dashed lines in Fig. 4.

bond length at the interface. The former decreases due to relaxation while the latter expands. The expanding of the interface Si-Si bonds results from the weaker bonding of the interface Si-Si atoms compared to that between the silicon atoms in the bulk. This can be seen from the contour plot of the charge distribution in Fig. 3, where the charge density for the interface Si-Si bond is seen to be slightly lower than that of the Si-Si bond in the silicon layer. The reason for the large contraction in the silicide triple layer could be due to the fact that the coordination number of the Ni atom at the interface is one less than that in the silicide bulk. The extra charge is transferred to the remaining bonds in the layer making the Ni-Si bond in the first silicide triple layer stronger than the interface Si-Si bond. As a result, the silicon layer in the silicide triple layer moves closer to the Ni layer, resulting in the contraction of d_1 and expansion of d_3. One can also see from Table III that the contraction of the silicide triple layer is 0.02 Å larger in the type-*B* interface than in type-*A*. This is due to the fact that there is more charge in the interatomic region inside the silicide triple layer in the type-*B* than in the type-*A* interface, which can be seen by comparing the charge distribution and the one-dimensional profiles (Figs. 4 and 5) for the two types of interface.

In conclusion, using our recently developed *ab initio* scheme for generating optimally smooth pseudopotentials, we have carried out the first dynamics calculations for the $NiSi_2$/Si(111) interface by allowing the atoms to fully relax in the direction perpendicular to the interface. Our results indicate that the contraction of the silicide triple layer adjacent to the interface is responsible for most of the interface relaxation. We have also found that the fully relaxed type-*A* interface has lower energy than type-*B* while the latter contracts more than the former. Such detailed structural information should allow for more accurate interpretation of the experimental results.

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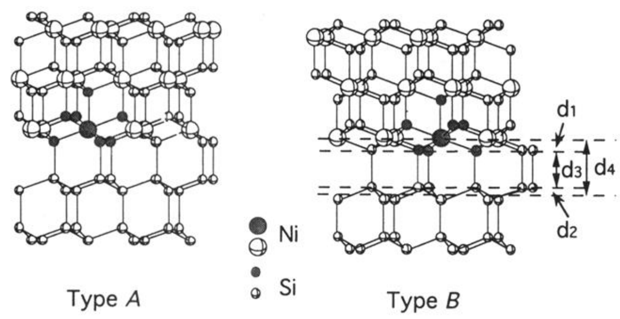

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