

Electronic Structure and Schottky-Barrier Heights of (111) NiSi₂/Si *A*- and *B*-Type Interfaces

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The electronic structures of NiSi₂/Si(111) *A*- and *B*-type interfaces are calculated within the local-density approximation (LDA) using large supercells and the linear-muffin-tin-approximation (LMTO) full-potential and atomic-spheres approximation (ASA) methods. The Schottky-barrier heights for the two interfaces differ by 0.14 eV, in agreement with experiment. The difference is caused by a partly filled interface band present in both structures. The LDA barrier heights $E_F - E_v$ are both 0.4 eV too low, and insensitive to interface relaxations and to external potentials. The correct density-functional expression for the barrier height is $E_F - E_v + \Delta v_{xc}$, where Δv_{xc} is a nonlocal correction.

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The properties of metal-semiconductor interfaces are not quantitatively understood at the microscopic level. Recent advances were the epitaxial preparation of atomically abrupt and structurally perfect interfaces of NiSi₂ and CoSi₂ on (111) Si,¹ and subsequent qualitative explanations of their interface bonding.^{2,3} It is now a challenge for theory to account *a priori* for the single most important property of metal-semiconductor interfaces, the (*p*-type) Schottky-barrier height, $\epsilon_F - \epsilon_v$, which is the position of the Fermi level above the top of the valence band. Two distinct interface structures of NiSi₂/Si(111), the *A* and *B* types, have been observed and reported to have different Schottky-barrier heights: 0.52 and 0.38 eV.⁴ With the gap in Si being 1.17 eV, this means that the Fermi levels lie well inside the gap.

We have performed density-functional calculations of the Schottky barrier. This is a valid procedure because $\epsilon_F - \epsilon_v$ is a functional of the electronic density, as the following argument shows: Consider a metal-semiconductor bicrystal forming a thick slab. In the vacuum outside the metal the density decays asymptotically as $\exp[2z\sqrt{W}]$ and thus provides the value of the work function $W \equiv \phi(-\infty) - \epsilon_F$, where ϕ is the electrostatic potential.⁵ Similarly, the decay of the density in the vacuum outside the semiconductor provides the photothreshold $P \equiv \phi(\infty) - \epsilon_v$. The moment of the charge density provides the dipole shift $D \equiv \phi(\infty) - \phi(-\infty)$. Therefore, since P , W , and D are functionals of the density, so is $P - W - D = \epsilon_F - \epsilon_v$. The standard way of obtaining the density is through a Kohn-Sham self-consistent calculation.⁶ It is then convenient to obtain $\epsilon_F - \epsilon_v$ in terms of the Kohn-Sham one-electron energies E_F and E_v , which are related to the density via $W = v_{xc}(-\infty) + \phi(-\infty) - E_F$ and $P = v_{xc}(\infty) + \phi(\infty) - E_v$. Hence,

$$\epsilon_F - \epsilon_v = E_F - E_v + \Delta v_{xc}, \quad (1)$$

with $\Delta v_{xc} \equiv v_{xc}(\infty) - v_{xc}(-\infty)$, and the exchange-correlation potential v_{xc} being a functional of the density. In the local-density approximation (LDA),⁷ v_{xc} vanishes where the density vanishes, e.g., at $-\infty$ and at ∞ , so

that $\epsilon_F - \epsilon_v = E_F - E_v$. This is the approximation which we have used. Calculated⁸ LDA valence-band offsets at semiconductor interfaces tend to agree with experiments within 0.1 eV.

NiSi₂ has the fluorite structure in which Ni is eight-fold coordinated with Si. At the (111) interface Ni loses one Si neighbor, and the outermost Si atoms bind along the [111] direction to the atoms at the Si surface (Fig. 1). The *A* and *B* types are related by a 180° rotation about this Si-Si bond. We have considered both struc-

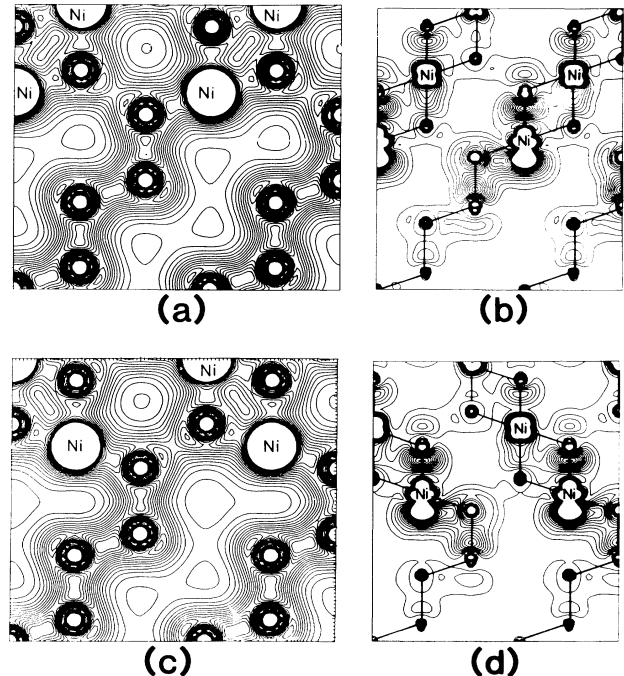


FIG. 1. Valence-electron density in the (110) plane for (a) *A* interface, (b) occupied interface states in *A* type, (c) *B* interface, and (d) occupied interface states in *B* type. The lowest contour value as well as the contour step is $0.005e/a_0^3$ in (a) and (c) and $0.0005e/a_0^3$ in (b) and (d). See text for details.

tures and shall discuss our findings for the chemical binding, interface states, and Schottky-barrier heights. Reference 9 gives a detailed preliminary account.

We used the LDA parametrization of Barth and Hedin⁷ and the linear-muffin-tin-orbital (LMTO) method¹⁰ either in the atomic-spheres approximation (ASA), or with a new full-potential scheme.¹¹ The 0.4% lattice mismatch between Si and NiSi₂ was neglected. Except in three cases, there was no interface relaxation.¹ For the LMTO's and for the ASA we used equal-sized atomic and interstitial (*E*) spheres ($s=2.526$ a.u.), so that the sphere packing in the bulks are bcc.¹² This also holds at the unrelaxed *A* interface where the stacking of the (111) layers of spheres is . . . *ESiNiSiEESiSi*. . . (see Fig. 1). At the *B* interface we used one double layer with a large and small sphere . . . *ESiNiSi(E < E >)SiSi*. . . The basis set included the *s*-, *p*-, and *d*-LMTO's on all spheres. We used supercells with two identical interfaces per formula unit, (*ESiNiSi*)_{*n*}(*EESiSi*)_{*m*}*E*, and calculations were performed for different cell sizes (*n+m*) to assure size convergence. Further, the width of the *k* mesh was watched in order to include properly the contributions of the Fermi-surface states to the interface dipole. We used the full-Brillouin-zone tetrahedron method¹³ and quote results obtained with ten irreducible *k* points. Extrapolation to zero mesh width⁹ would add 0.03–0.05 eV to $E_F - E_v$.

In the left-hand part of Fig. 1 we show the valence-electron densities calculated for the *A* and *B* interfaces. We clearly see the sp^3 - sp^3 bonds on the Si side and the $d(t_{2g})$ - sp^3 bonds on the NiSi₂ side. For Ni at the interface the Si coordination is reduced from 8 to 7, and we shall see that this gives rise to an interface band with semidangling bond character. Figure 2 gives the LDA

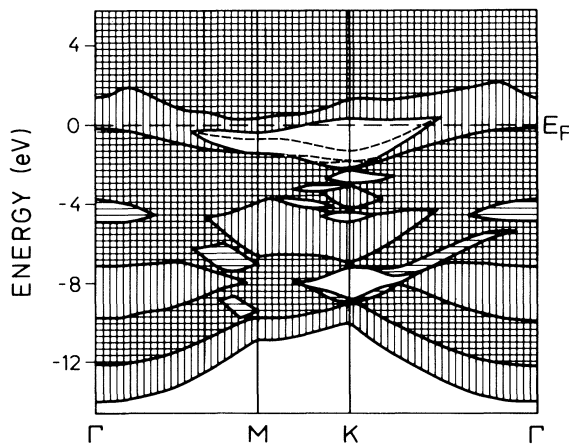


FIG. 2. Two-dimensional band structure of the *A* interface. The interface bands (dashed curves) were calculated using the (8+6) supercell. The bulk band structures of NiSi₂ (vertically hatched) and Si (horizontally hatched) were calculated using the potentials from the bulklike layers of the supercell.

band structure in the two-dimensional, hexagonal Brillouin zone. For bulk NiSi₂ there is a partial gap around the zone boundary (*KM*) for energies near E_F . This gap is inside the Si gap. For both the *A* and *B* types, there is an interface band running through the central part of the common gap and crossing the Fermi level close to where it emerges into the continuum. It is occupied by about 1.3 electrons (per interface and two-dimensional cell), and the integrated density is shown in the right-hand part of Fig. 1. Common to all states in this band is a σ antibonding linear combination of a $d(3z^2-1)$ orbital on the Ni atom near the interface (*z* is perpendicular to the interface) and an sp^3 orbital on the Si atom lying in the *z* direction inside the disilicide.

The dipole of the charge distribution near the interface determines the lineup of the bulk NiSi₂ bands with respect to the bulk Si bands and, hence, the Schottky barrier. This is seen in Fig. 2 as the 0.1 eV difference between E_F and the top of the Si valence band E_v at Γ . Experimentally, $\epsilon_F - \epsilon_v \approx 0.5$ eV. This 0.4 eV discrepancy is small on the scale of the bandwidths, but significant on the scale of the Si gap. It is comparable to the 0.6 eV error of the Si LDA gap. For the difference between $E_F - E_v$ for the *A* and *B* types we find 0.14 eV, in perfect agreement with the experimental barrier difference. We shall now explain details of these results, discuss the dipole formation, and seek reasons for the 0.4 eV discrepancy.

In Fig. 3 we show various potential profiles across the *A* or *B* interface calculated using (8+6) or (5+3) supercells and with or without the ASA. In Fig. 3(a) we show for each layer the potential (*V*) averaged over the sphere surface, minus the average over the corresponding sphere surface of the respective bulk potential (V^0), plus the Fermi energy, or valence-band top, calculated for the bulk (E_F^0 or E_v^0). Moving away from the interface, in either direction, the potential approaches the respective bulk potentials, so that the profile in Fig. 3(a) approaches, respectively, E_F or E_v . We see that the variations of the potential which exceed 0.2 eV are limited to a few layers near the interface, but that variations exceeding 0.02 eV extend considerably further. For the Schottky-barrier height we find, using the ASA and the (8+6) cell (triangles), $E_F - E_v = 0.12$ eV (*A* type), and -0.02 eV (*B* type).¹⁴ The experimental results are 0.52 and 0.38 eV. The difference between the *A*- and *B*-type barrier heights is building up in the second *EESiSi* layer away from the interface. We shall return to this point later.

The results obtained with the (8+6) cell are size converged, as judged from the shape of the profiles. The (5+3) cell (filled circles) yields essentially the same profile near the interface, but the asymptotic value is not quite reached on the Si side. In order to demonstrate that the spherical averaging of the potential inside the spheres in the ASA, and hence the neglect of intrasphere

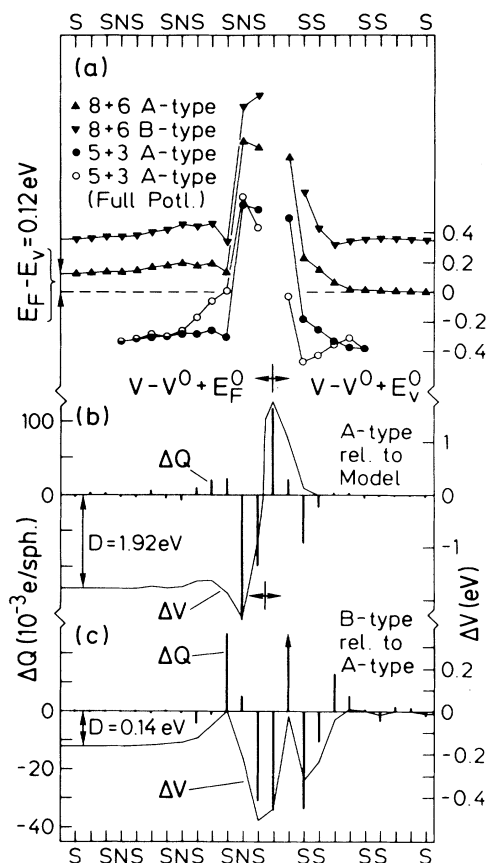


FIG. 3. Potentials and sphere charges as functions of z perpendicular to the interface. Layers of Si and Ni atoms are labeled by S and N , respectively, and layers of interstices (E) are unlabeled. (a) Potential profiles (as defined in text) for various supercells ($n+m$) calculated using the ASA and the full potential. (b) Charges and potential calculated for the A -type ($8+6$) supercell relative to those of the reference as explained in the text. The fictitious charges of the reference are not shown. (c) Charges and potential calculated for the B -type ($8+6$) supercell minus those of the A type. The charge of the double E layer at the B interface has been distributed onto the two E layers of the A interface, conserving the total charge and dipole moment.

dipole contributions, is unimportant, we have performed a full-potential calculation for the ($5+3$) cell (open circles). Although some details of the potential profile are changed near the interface, the barrier height ($E_F - E_v = 0.05$ eV) is as in the ASA ($E_F - E_v = 0.04$ eV) due to efficient screening after a few layers.

We next consider the charge transfer. This is defined with respect to a *reference charge density*⁹ which we choose to be the bulk densities, cut and joined like $\dots E\text{SiNiSi} | E\text{ESiSi} \dots$. To each of the two semi-infinite bulk densities a fictitious surface density is added such that the electrostatic potential tends to some chosen *reference level* in the vacuum. When the two half-

crystals are joined to form the reference system, the reference levels will be lined up. In the ASA, the intersphere part of the electrostatic potential V is one of point charges Q , and it is customary to use the average of the point-charge potential, the so-called ASA zero, as reference level. For the reference barrier height this yields: $E_F^0 - E_v^0 = 1.92$ eV. Having defined the references, we show in Fig. 3(b) for the A interface the profiles of the charge transfer, $\Delta Q(z)$, and of the corresponding electrostatic potential, $\Delta V(z)$, averaged in the x - y plane. The interface dipole is $D \equiv \Delta V(\infty) - \Delta V(-\infty) = (8\pi c/A) \sum_l \Delta Q(z_l) \approx 0.81 \sum_l \Delta Q(z_l)$. Here, l is the sublayer index, c is the distance, A is the area, Q is in units of electrons/sphere, and D is in rydbergs. For the Schottky barrier we find again: $E_F - E_v = E_F^0 - E_v^0 - D = 1.92 - 1.80 = 0.12$ eV. The electron transfer is seen to be from the NiSi_2 side to the Si side; it is essentially limited to the five sublayers $\text{NiSi} | E\text{ESi}$, and the transfer is mostly less than 0.1 electron/sphere.

Figure 3(c) shows the charge differences between the A and B interfaces. They merely amount to some hundredths of an electron per sphere, but they oscillate and extend throughout the first NiSi_2 and the first and second Si_2 layers. Their dipole moment lowers $E_F - E_v$ for the B type relative to the A type by 0.14 eV, in agreement with the experimental result. The charge differences most relevant for this lowering are those in the second $E\text{ESiSi}$ layer, and we ascribe them to the occupied interface states (right-hand side of Fig. 1) which are screened more efficiently in the A than in the B geometry. This is concluded from the following: Self-consistent calculations in which we did *not* occupy the interface band gave essentially *no* difference between the barrier heights for the A and B types. Whereas the *bare* interface states shown in Fig. 1 give a dipole difference which is an order of magnitude too large and has the wrong sign, the potential profile for the B - A difference of the *screened* interface states; that is, the profile in Fig. 3(c) minus the one obtained without occupying the interface band has the same dipole and the same behavior as in Fig. 3(c), but with strongly reduced oscillations on the NiSi_2 side and in the first Si layers.

The calculations reported above were for unrelaxed interfaces. X-ray standing-wave experiments indicate a contraction perpendicular to the A interface by about 4%.¹ Squeezing the E layers correspondingly, we calculate a *lowering* of $E_F - E_v$ by 0.05 eV, and essentially the same result is obtained when we assume a 4% reduction of the perpendicular bond between the first and second SiNiSi layers, or between the first and second SiSi layers. The two latter relaxations should, respectively, have a maximal influence on the position of the interface band and on the screening and, yet, the effect on $E_F - E_v$ is far too small to explain our 0.4 eV error. The experimental situation for the B interface is less clear, but it gives no basis for assuming that the relaxation

differs sufficiently from that of the A type, as to be the cause for the 0.14 eV difference. This is in accord with pressure experiments¹⁵ which indicate that for a 1% decrease of the lattice constants $\epsilon_F - \epsilon_v$ is lowered by about 0.02 eV; this holds for both interfaces. Hence, it seems that relaxations can neither be the reason for the 0.4 eV discrepancy between calculation and experiment, nor for the measured and calculated 0.14 eV difference between the A - and B -type barrier heights.

We believe that the too small value for the calculated Schottky barrier is due to the LDA. Using different LDA parametrizations,⁷ or applying an external, orbital-dependent potential to the Si layers so as to yield the correct gap in bulk Si, in any case changed $E_F - E_v$ by less than 0.01 eV. Many-body calculations in the GW-approximation¹⁶ indicate that the LDA value for E_v in bulk Si is 0.1–0.2 eV too high. This suggests that there may also be errors of this type in the relative depths of the LDA exchange-correlation potential on the two sides of a metal-semiconductor interface. As discussed below, such errors are, however, very efficiently screened out, and they merely lead to errors of order 0.01 eV in the barrier height, unless $\Delta v_{xc} \neq 0$. Therefore, Δv_{xc} is likely to be an essential contribution to $\epsilon_F - \epsilon_v$ in Eq. (1). That Δv_{xc} may be nonzero can be illustrated¹⁷ by a simple (Hubbard-type) model which consists of a linear chain of atoms with a spin-degenerate orbital on each site, an on-site Coulomb interaction U , and nearest-neighbor hopping. A metal-semiconductor interface is modeled by setting $U=0$ on the metal side, and very large on the semiconductor side. In this model, the barrier is entirely due to Δv_{xc} .

The extreme nonlocal part Δv_{xc} can presently not be calculated for a realistic interface, but we shall try to mimic its effects by applying, in the LDA, an external potential with a similar spatial behavior. This must be fairly constant, except near the interface where it switches from $v_{xc}(-\infty)$ to $v_{xc}(\infty)$. This follows if we assume that a perturbation of the density in the region $z > 0$ cannot influence the density, and hence the spatial variation of the potential, in the region $z < 0$ far away from the interface, and vice versa. Moreover, Δv_{xc} hardly depends on the interface structure. The result of the LDA calculation, in which the potential of the Si side is shifted down with respect to that of the NiSi₂ side, is now that this potential step is screened out almost completely within a few layers near the interface ($\epsilon_{\text{eff}} > 20$). In order to reproduce the experimental barrier, the shift must be 0.4 eV. The Kohn-Sham bands and, hence, $E_F - E_v$ therefore change by merely a few hundredths of an eV, i.e., they are virtually unchanged, and so are all our previous results, except details of the charge transfer at the interface.

In conclusion, for Schottky-barrier heights there seems

to be a sizable, highly nonlocal correction to the LDA. Nevertheless, structural dependences seem to be well accounted for in the LDA. The existence of the interface band, which we believe is responsible for the barrier heights of the A and B interfaces being different, could be experimentally verified.

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