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published in

Physical Review Letters
1988

document version

Publisher's PDF, also known as Version of record

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citation for published version (APA)

Baerends, E. J., Ravenek, W., & van den Hoek, P. J. (1988). MSi₂/Si(111) (M=Co,Ni) interface chemical bond. *Physical Review Letters*, 60(17), 1743-1746.

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$MSi_2/Si(111)$ ($M = Co, Ni$) Interface Chemical Bond

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(Received 3 September 1987)

With the aid of electronic structure calculations an explanation has been found for the experimentally observed difference in geometric structure between $CoSi_2/Si(111)$ and $NiSi_2/Si(111)$ interfaces.

PACS numbers: 68.35.Bs, 61.50.Lt, 73.20.Hb, 73.40.Ns

The metallic disilicides $CoSi_2$ and $NiSi_2$ (both CaF_2 structure) grow epitaxially on $Si(111)$ surfaces.¹ Therefore, $CoSi_2/Si(111)$ and $NiSi_2/Si(111)$ interfaces are interesting from both technological and fundamental points of view. A detailed insight into the chemical bonding at these interfaces is of vital importance for the understanding of Schottky barriers. Directly related to the interface chemical bond is the atomic arrangement at the interface. Recent experiments show that the atomic arrangements at the $CoSi_2/Si(111)$ and $NiSi_2/Si(111)$ interfaces are quite different: In the case of $CoSi_2$, the *metal* atoms of the disilicide bind to the silicon substrate^{2,3} [Figs. 1(a) and 1(b)], whereas in the case of $NiSi_2$ the *silicon* atoms of the disilicide do³⁻⁶ [Fig. 1(c)].

In this Letter, we present an explanation for the observed difference between $CoSi_2/Si(111)$ and $NiSi_2/Si(111)$. The argument is based on a detailed understanding of the interface chemical bond. Such an understanding has been obtained by analysis of electronic structure calculations. To this end we used the concept of "frontier orbitals" (a frontier orbital is a candidate orbital for a chemical bond). This concept has been proven to be a powerful tool in the explanation both of molecular⁷ and of crystal⁸ structures.

In the case of disilicide-silicon to substrate-silicon bonding, the metal atoms closest to the interface are sevenfold coordinated [Fig. 1(c)]. In the case of disili-

cide-metal to substrate-silicon bonding, the interface metal atoms are fivefold coordinated [Fig. 1(a)] if one assumes that all Si atoms are tetrahedrally coordinated. If, however, this constraint is lifted, the possibility exists to saturate the three interface metal dangling bonds by Si atoms [Fig. 1(b)], which are then threefold coordinated (for a "B-type" interface). In this case the coordination number of the interface metal atoms is eight. There is no experimental evidence which favors either the fivefold or eightfold structure. Our calculations indicate that the addition of a silicon layer to the fivefold structure (thus making the eightfold structure) lowers the total energy of the system.⁹ Therefore, in our comparison of silicon-silicon bonding with metal-silicon bonding, we will use the sevenfold [Fig. 1(c)] and eightfold [Fig. 1(b)] structures, respectively.

In order to get a full insight into the nature of the frontier orbitals at the interface, we also performed calculations on the bulk disilicides. Below, we present our results as follows. First, we discuss bonding in the bulk disilicides. Next, we consider the "cutoff" of the bulk disilicides along the (111) plane and argue which disilicide orbitals are candidates for the interface chemical bond. Finally, the interface chemical bond itself is discussed.

We have performed self-consistent-field local-density-approximation (LDA) linear-combination-of-atomic-orbitals¹⁰ calculations on clusters modeling the bulk disilicides and the disilicide-silicon interfaces. The Vosko-Wilk-Nusair parametrization¹¹ of the LDA functional was used. From a Mulliken orbital-population analysis, a picture of the interface chemical bond in terms of frontier orbitals could be derived. Although quantitative results from cluster calculations should be taken with care, the analysis of such calculations gives a simple intuitive picture of the electronic structure in terms of (local) chemical bonds. Such a picture helps one to understand results from experiments and from band-structure calculations on periodic systems. Trends in calculated bond energies will serve as a check on the

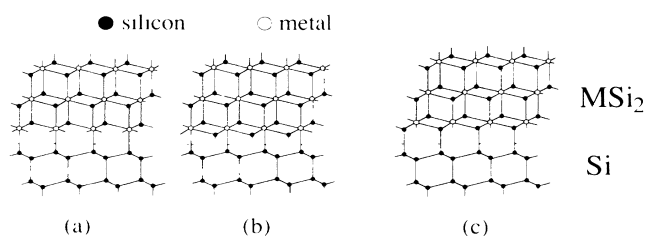


FIG. 1. Possible structures for the epitaxial $MSi_2/Si(111)$ ($M = Co, Ni$) interfaces: (a) fivefold, (b) eightfold, and (c) sevenfold coordination of the interface metal atoms. All structures shown are of the B type.

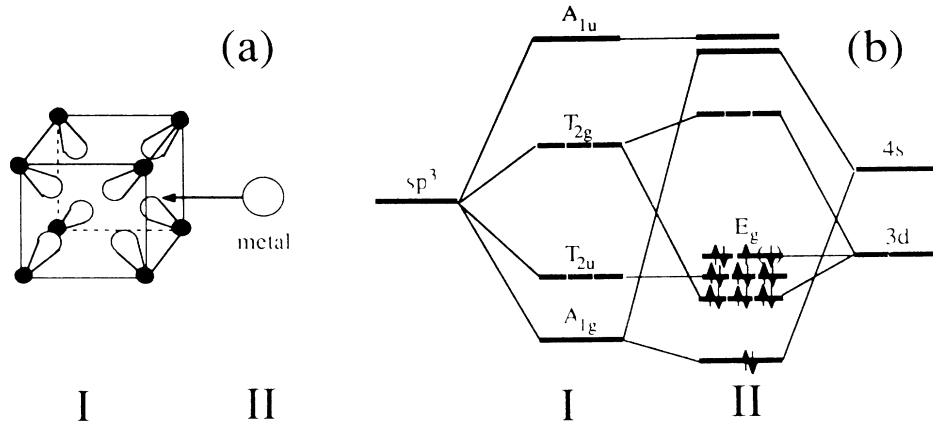


FIG. 2. (a) Chemical bonding within the bulk disilicides. (b) Energy-level diagrams for steps I and II (see text). In the energy-level diagram for step II the extra Ni electron is indicated between brackets.

correctness of the interface chemical bond picture.

Bonding in the bulk disilicides is modeled with the smallest representative unit, i.e., a cluster consisting of one metal atom surrounded by eight silicon atoms. For the clusters modeling the interfaces, we varied the cluster size by building model clusters containing one and three metal atoms. The number of Si atoms in the interface clusters varied, depending on the cluster geometry, but was on the average equal to 15. The silicon parts of the interface clusters were, as usual, saturated by hydrogen atoms.¹² The Si-H distance was set equal to 1.52 Å. This value was obtained from an optimization procedure in a cluster representing bulk silicon; in fact, it is very close to the silane value of 1.48 Å. An appropriate saturation of the disilicide parts of the interface clusters is more complicated, since in this case the bonding is not strictly covalent. Here, we followed a special "saturation scheme,"⁹ in which the disilicide parts were saturated both by hydrogen and by "pseudohydrogen" atoms. The latter have a number of electrons (and, in order to guarantee charge neutrality, consequently a nuclear charge) not equal to one.

We start by considering the chemical bonding in the bulk disilicides. Here, the metal atoms are eightfold coordinated. Therefore, we may view the local environment of a metal atom as a cube with Si atoms at the corners and the metal atom at the center. We now "build up" the chemical bonds within this cube, starting with the sp^3 hybridized Si orbitals, which point to the cube center. Two steps are considered [Fig. 2(a)]: the mutual interaction between the sp^3 orbitals within the cube (step I), and next the interaction of the resulting orbitals with the metal atom (step II). Figure 2(b) gives a schematic energy-level interaction diagram based on the calculations. Because of a large mutual overlap, the sp^3 orbitals interact strongly with each other, resulting in bonding (A_{1g}, T_{2u}) and antibonding (T_{2g}, A_{1u}) levels (step I). The labels A_{1g}, T_{2u}, \dots indicate the irreducible representations of the cubic point group. The E and T

levels are twofold and threefold degenerate, respectively. Next, we consider step II. As a result of the symmetry, the metal s orbital can only interact with the A_{1g} orbital, as indicated in Fig. 2(b). Three of the five metal d orbitals (xy, xz, yz) can interact with the T_{2g} orbital, whereas the other two remain nonbonding. Now, if we fill up the levels within the cube with the electrons available (one electron per sp^3 orbital, and the metal electrons), we see that the Fermi level will be in a region of mainly metal-silicon (step II) nonbonding levels [Fig. 2(b)]. For NiSi_2 , all (step II) nonbonding levels (E_g, T_{2u}) are filled, whereas for CoSi_2 there is still a place for one electron per unit cell. This explains why the difference in cohesive energy between both disilicides is only small (about 0.06 eV/atom expt.¹³) (Table I): The extra Ni electron per unit cell goes into a metal-silicon nonbonding orbital. Finally, we note that the main features of density-of-states pictures based on band-structure calculations¹⁴ for bulk CoSi_2 and NiSi_2 are consistent with our cluster results presented in Fig. 2(b): The d -level contribution to the density of states splits into a metal-silicon bonding and nonbonding part, a "quasigap" separates metal-silicon nonbonding and antibonding states, and the extra NiSi_2 electron per unit cell goes into (mainly) nonbonding states.

Next, we discuss what happens when the bulk disili-

TABLE I. Interaction energies per interface bond (in electronvolts) calculated with clusters containing one and three metal atoms. For the bulk disilicides, the interaction energies are given per metal-silicon bond.

	1 metal atom		3 metal atoms	
	Co	Ni	Co	Ni
Sevenfold	2.3	2.2	1.9	1.9
Eightfold	3.2	2.1	2.9	1.4
Bulk $M\text{Si}_2$	2.3	2.3		

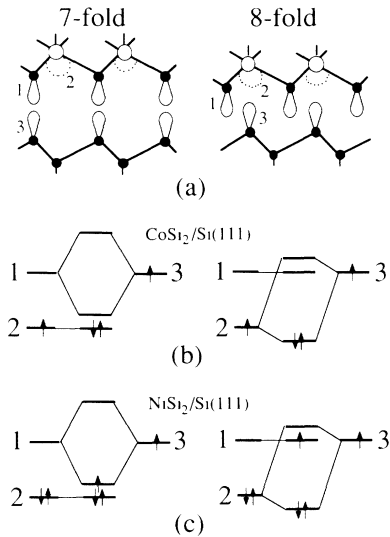


FIG. 3. Energy-level diagrams for the interface chemical bonds for (a) sevenfold- (left) and eightfold- (right) coordinated interface metal atoms. (b) CoSi₂/Si(111) and (c) NiSi₂/Si(111) are compared.

cide is cut along the (111) plane in such a way that it is silicon terminated; no surface reconstruction is assumed. For the "unit cubes" [Fig. 2(a)] closest to the surface, the cutoff means that one of the Si atoms at the cube corners is removed. The three Si atoms sitting next to this atom become surface Si atoms, each with a dangling sp^3 orbital pointing in the [111] direction. Now, if we assume that the energy-level diagram within the cube is not considerably affected by the removal of one Si corner atom, the only effect is that one electron is "taken away" from the cube. The level energies of the surface Si dangling bonds, however, are higher than those of the metal-silicon nonbonding orbitals (E_g, T_{2u}). Therefore, the electrons in the surface Si dangling bonds will prefer these lower-lying orbitals. Consequently, the Si atoms of the $MSi_2(111)$ surface will have empty dangling bonds, and the orbitals within the cube will be filled the same way as in the bulk disilicide. The latter means that for CoSi₂(111) surfaces, apart from the empty Si dangling bond, there is also a not completely filled orbital centered around the metal atom; in the case of NiSi₂(111) surfaces, this orbital is completely filled. Figure 3(a) shows the above-mentioned orbitals: the MSi_2 Si (empty) dangling bond (No. 1), the orbital centered around the metal atom (No. 2), and the Si substrate dangling bond (No. 3). Note that the orbital energy of No. 2 is much lower than those of Nos. 1 and 3.

Finally, we discuss the formation of the disilicide-silicon interface chemical bond. Figure 3(a) shows the difference between sevenfold and eightfold-coordinated disilicide-silicon (111) interfaces: In the case of the sevenfold structure, the substrate Si dangling bond (No.

3) interacts with the MSi_2 Si dangling bond (No. 1), whereas in the case of the eightfold structure the substrate Si dangling bond interacts with the metal-centered orbital (No. 2). The interaction between orbitals 1 and 3 is stronger than between 2 and 3 because of larger overlap and less orbital energy difference. This is also clear from an inspection of Table II. This table shows the orbital overlap populations between the p_z orbitals of the substrate and disilicide silicon atoms, and between the substrate Si p_z orbitals and metal d orbitals. For comparison, we calculate between p orbitals of neighboring Si atoms in (a cluster representing) bulk Si an overlap population of 0.15. Clearly, we see from this table that in the sevenfold case, there is a strong interaction between the Si-centered dangling bonds (which have mainly p_z character); the p_z - d interaction {mainly corresponding to the 2-3 interaction [Fig. 3(a)]} in the eightfold structure is weaker by about 50%. Figures 3(b) and 3(c) show schematic energy-level interaction diagrams for CoSi₂/Si(111) and NiSi₂/Si(111), respectively. These diagrams are based on our calculations. We find that the orbital energy of the bonding combination between 1 and 3 (left) is higher than that of the bonding combination between 2 and 3 (right). In the sevenfold CoSi₂/Si(111) case [Fig. 3(b), left] the two electrons available for one interface chemical bond go into a nonbonding orbital, whereas in the eightfold case [Fig. 3(b), right] they go into a bonding orbital. Therefore, eightfold coordination of the interface metal atom will be energetically more favorable at the CoSi₂/Si(111) interface than sevenfold coordination. Although the interaction diagrams for NiSi₂/Si(111) are roughly the same as those for CoSi₂/Si(111), the one extra Ni electron has different effects on the interaction energy. In the eightfold NiSi₂/Si(111) structure, two electrons go into a bonding orbital and the third goes into a nonbonding one [Fig. 3(c), right]. In the sevenfold structure, however, although two electrons go into a nonbonding instead of bonding orbital, the third one goes into the strongly bonding combination between frontier orbitals 1 (disil-

TABLE II. Orbital overlap populations (in electrons) between the p_z orbitals of the substrate Si and disilicide Si atoms, and between the substrate Si p_z orbitals and disilicide metal d orbitals. The z axis is defined perpendicular to the (111) interface plane. The orbital overlap populations are given per interface bond. They have been calculated with interface clusters containing one and three metal atoms.

	1 metal atom		3 metal atoms	
	Co	Ni	Co	Ni
Sevenfold Si p_z -Si p_z	0.15	0.15	0.11	0.12
Si p_z -M d	0.0	0.0	0.0	0.0
Eightfold Si p_z -Si p_z	0.0	0.0	0.01	0.0
Si p_z -M d	0.06	0.06	0.08	0.07

cide) and 3 (silicon). The latter configuration (one electron in a strongly bonding orbital) turns out to be energetically more favorable than the first one (two electrons in a more weakly bonding orbital), although the energy difference between the two configurations (corresponding to the sevenfold and eightfold structures) will be smaller here than for $\text{CoSi}_2/\text{Si}(111)$. Thus, we see that for $\text{NiSi}_2/\text{Si}(111)$ the extra Ni electron changes the picture: The strongly bonding orbital between Nos. 1 and 3 in the sevenfold structure is empty for $\text{CoSi}_2/\text{Si}(111)$, whereas it gets partially filled for $\text{NiSi}_2/\text{Si}(111)$, making the sevenfold-coordinated interface energetically more favorable in the latter case. Table I shows the interaction energies per interface bond calculated with the model clusters containing one and three metal atoms. These energies were calculated with Ziegler's transition-state method.¹⁵ Although there are differences between the clusters, we see that both clusters reproduce the trends in binding energies very well; for $\text{CoSi}_2/\text{Si}(111)$ the eightfold structure is energetically more favorable, whereas for $\text{NiSi}_2/\text{Si}(111)$ the sevenfold structure is. Moreover, the difference in bond energy between the two structures is smaller for $\text{NiSi}_2/\text{Si}(111)$ than for $\text{CoSi}_2/\text{Si}(111)$, as expected.

In summary, we have shown why CoSi_2 binds with its Co atoms to the Si substrate at the (111) interface, whereas NiSi_2 prefers binding with its Si atoms.

The authors thank J. F. van der Veen and I. Ohdomari for their critical reading of the manuscript. Financial support from the Dutch Committee for the Use of Supercomputers is gratefully acknowledged. This work is part of the research program of FOM and is financially supported by the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (ZWO).

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