Supersoft Transition Metal Silicides

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Candidates for epitaxially stabilized structures of Fe, Co, and Ni silicides are searched by *ab initio* calculations. We find that the pseudomorphic phases of $FeSi_2$ in the $C1$ structure and CoSi and NiSi in the $B2$ structure soften dramatically under compressive biaxial strain induced by epitaxy on a (100) substrate. This supersoft effect is reflected by zero strain energy, constant volume, and constant bond energies. [S0031-9007(98)06930-0]

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Epitaxial growth of silicides on silicon or metallic substrates is of considerable scientific and technological importance. In particular, $CoSi_2$ and $NiSi_2$ grow with excellent structural quality [1] on Si substrates for the [111] direction and even reepitaxy of Si on top of these silicides is possible. The coherent growth of semiconducting $FeSi_2$ films is more complex, because depending on the growth conditions several pseudomorphic structures may form. In contrast to the stable bulk phases of β-$FeSi_2$ and FeSi ($B20$ structure), which are semiconductors, Fe-Si films on Si along the [111] direction prefer the $B2$ (CsCl) or the $C1$ (CaF_2) structures [2,3] being metallic conductors. For these cubic pseudomorphic silicides, despite the several reports on [111] epitaxy, no experiments of molecular-beam epitaxy have been performed until now for the [100] direction.

In this Letter we provide structural and elastic properties of artificial materials using *ab initio* calculations. We calculate elastic and bonding properties of a possible pseudomorphic $B2$ structure for MSi (M stands for Fe,Co,Ni) and of a $C1$ structure for MSi_2. For each case we determine the strain energies corresponding to a wide range of biaxial strains modeling epitaxial growth for substrate planes corresponding to [100], [110], and [111] orientations. In the direction perpendicular to the growth planes the structures are relaxed. The results for the undistorted cubic $B2$ (MSi) and $C1$ (MSi_2) structures are taken as references. By expanding the strain energy as a sum of nearest-neighbor bond energies we attribute the epitaxial constraint effects to the change of the M-M, Si-Si, and M-Si bond strengths. Our *ab initio* results describe quantitatively the anharmonic effects due to the misfit strain and clearly demonstrate the limitation of harmonic elastic theory. We neglect the actual chemical interaction of film and substrate which is a reasonable first approximation for sufficiently thick deposited films and to the extent where the kinetic growth effect does not play a major role.

The calculations were performed using the Vienna *ab initio* simulation package (VASP) [4] which is based on ultrasoft pseudopotentials [5,6]. For the exchange-correlation functional the generalized gradient approximation (GGA) of Perdew and Wang [7] was used. Our *ab initio* results describe well the structural properties of all studied transition metal silicides and predict the correct experimental ground state phases [8]. Effects of lattice vibrations are neglected by our calculations.

A rather normal elastic behavior was derived for FeSi, $CoSi_2$, and $NiSi_2$ for which we did not find stable strained phases. For all investigated compounds with the exception of FeSi only, the largest strain energies occur for [110] and [111] epitaxy. CoSi, NiSi, and $FeSi_2$, however, are strongly anomalous because the strain energy is zero for the [100] growth over a rather wide range of compressive strains of about 0.3 Å. The extreme softness of these tetragonally distorted compounds is characterized by a constant M-Si bond strength and length during the deformation.

According to the total energies of the unstrained pseudomorphic structures, Fe-Si stabilizes the $B2$ over the $C1$ structure by 0.19 eV/atom while for Co-Si and Ni-Si compounds the $C1$ structure is preferred now compared to the $B2$ structure by 0.09 eV/atom.

FeSi, CoSi, and NiSi compounds of $B2$ structure are not stable bulk phases. The total energy differences ΔE_{B2} between $B2$ and the ground state structures are 0.03, 0.22, and 0.24 eV/atom for FeSi, CoSi, and NiSi, respectively. FeSi and CoSi bulk stable compounds crystallize in the $B20$ structure while the $B31$ structure becomes more favorable for NiSi. For FeSi, the $B2$ equilibrium volume is smaller by about 4.5% than the volume of the $B20$ ground state structure and because of the small ΔE_{B2} we predict a transition from $B20$ to $B2$ at a pressure of 150 kbar. The Fermi level falls into a pseudogap of the density of states (DOS) which separates the occupied bonding states from the empty antibonding states. On the other hand, the Fermi level of $B2$ CoSi cuts through a sharp peak of $3d$ states, making the cubic $B2$ structure unstable also with respect to a tetragonal distortion. Differently to FeSi, the $B20$-$B2$ phase transition for CoSi is predicted at an unrealistic very large critical pressure of 1840 kbar. The small ΔE_{B2} for FeSi compared to CoSi reflects the experimental finding that, for the [111] epitaxy, FeSi grows in the $B2$ structure up to 900 Å, whereas CoSi up to only 100 Å [9]. For NiSi a significant contribution of antibonding Si-s Ni-d states leads to a ΔE_{B2} similar to CoSi.

The calculated equilibrium lattice parameters a_0 of $B2$ FeSi, CoSi, and NiSi are 2.77, 2.79, and 2.85 Å and, because $2 \times a_0 > a_{\mathrm{Si}} = 5.43$ Å, coherent epitaxy on Si is achieved under compressive strain. Comparison to experiment is possible for FeSi for which recent x-ray diffraction data [3] on thin epitaxial film on Si(111) yield $a_0 = 2.77$ Å. According to our calculation the energy cost due to straining for a coherent epitaxy of $B20$ FeSi on Si(100) is about 1.20 eV/atom compared to less than 0.01 eV/atom for $B2$ FeSi. The good matching of $B2$ onto the Si substrate indicates a possible experimental stabilization of the $B2$ structure.

The bonding properties of the $C1$ compounds $\mathrm{FeSi_2}$, $\mathrm{CoSi_2}$, and $\mathrm{NiSi_2}$ are understood in terms of hybridized M-d Si-p states [10–12]. This covalent bonding stabilizes the $C1$ structure for $\mathrm{CoSi_2}$ and $\mathrm{NiSi_2}$ but not for $\mathrm{FeSi_2}$ [12], because for $\mathrm{FeSi_2}$ the Fermi level is located in a large peak of the DOS. The actual ground state structure of $\mathrm{FeSi_2}$ is the semiconducting orthorhombic β phase which is derived from $C1$ by a Jahn-Teller distortion [8,13]. The calculated equilibrium lattice parameters of $\mathrm{FeSi_2}$, $\mathrm{CoSi_2}$, and $\mathrm{NiSi_2}$ are 5.40, 5.37, and 5.47 Å, accordingly. The very small lattice mismatch with the Si substrate and the similarity between the fluorite and diamond structure makes the formation of ideal interfaces and coherent epitaxial films plausible. For $\mathrm{FeSi_2}$ the possible $C1$ stabilization against the β phase requires a calculation of the actual interface [8] because the strain energies are comparable for both structures: they differ by only 0.01 eV/atom while the total energy difference of the unstrained phases is 0.17 eV/atom.

The strained or epitaxial structures of MSi and $M\mathrm{Si_2}$ were obtained by biaxial strains imposed on the (100), (110), and (111) planes of the $B2$ and $C1$ structures. The corresponding total energies were computed as a function of the substrate lattice parameters a_s, spanning a wide range of about ±10% for compressive and tensile strains. When biaxially strained the structure was free to relax in the perpendicular direction $\hat{G}$. We define the total energy of such a structure as $E^{\mathrm{epi}}(a_s, \hat{G})$ and its unstrained bulk reference as $E_0 = E^{\mathrm{bulk}}(a_0)$.

FeSi, $\mathrm{CoSi_2}$, and $\mathrm{NiSi_2}$ are stable against the discussed straining and for a lattice mismatch of ±2% the corresponding distorted structures exhibit no significant anharmonic anomalies. They behave according to harmonic theory, because under compressive strain ($a_s < a_0$) their c axis along $\hat{G}$ elongates while under tensile strain ($a_s > a_0$) it shrinks keeping the slope of the c/a_s ratio constant. For $\mathrm{CoSi_2}$ and $\mathrm{NiSi_2}$, [100] epitaxy leads to smaller strain energies than for the [110] or [111] growth which reflects a weaker strain dependence of the volume and a larger relaxation of the c axis of the [100] epitaxial structure.

Very anomalous epitaxial behavior (which we call supersoft) characterizes the pseudomorphic $\mathrm{FeSi_2}$, CoSi, and NiSi phases. For $\mathrm{FeSi_2}$ and CoSi, Fig. 1 presents the epitaxial energies $\Delta E^{\mathrm{epi}}(a_s, \hat{G}) = E^{\mathrm{epi}}(a_s, \hat{G}) - E_0$ versus a_s and $\hat{G}$ together with the corresponding bulk total energy change, $\Delta E^{\mathrm{bulk}}(a_s) = E^{\mathrm{bulk}}(a_s) - E_0$. There, the striking observation is that under compressive biaxial strain of the (100) plane the corresponding total energies E^{epi} are degenerate with respect to E_0. This holds over a wide range of strains of about 0.3 Å for which, surprisingly, also the unit cell volumes are constant due to the nonlinear dependence of c/a. Our findings indicate that tetragonal phases of $\mathrm{FeSi_2}$, CoSi, and NiSi may be stabilized under compressive epitaxial constraints without any cost of strain energy.

The epitaxial softening function $q(a_s, \hat{G}) = \Delta E^{\mathrm{epi}}(a_s, \hat{G}) / \Delta E^{\mathrm{bulk}}(a_s)$ is used to emphasize the strain or a_s dependence of the epitaxial energy for all studied compounds as shown in Fig. 2. Harmonic elastic theory requires a constant value of q for each direction $\hat{G}$. Very small values of q indicate very soft epitaxial energies while a strong dependence of q versus a_s denotes anharmonic behavior. For [110] and [111] epitaxy of $M\mathrm{Si_2}$, q is nearly constant for small lattice mismatches, but a crossing of the corresponding q occurs under very large compressive strains. Under tensile and small compressive strain, FeSi is softest for the [111]

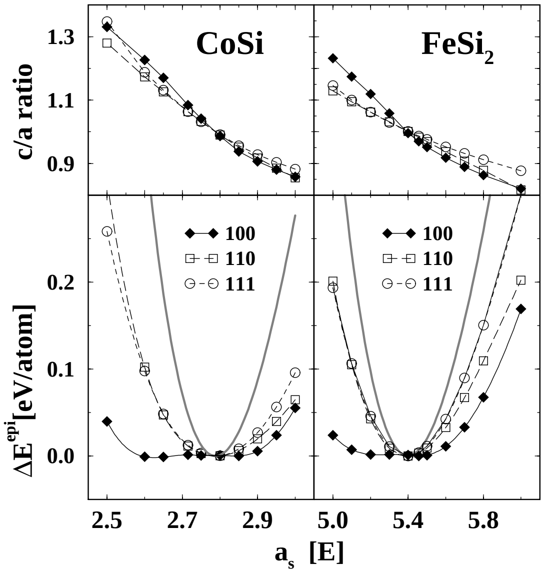

FIG. 1. Calculated epitaxial energies $\Delta E^{\mathrm{epi}}(a_s, \hat{G})$ and related c/a ratios of $\mathrm{FeSi_2}$ and CoSi versus substrate lattice parameter a_s for [100], [110], and [111] growth directions $\hat{G}$. The c/a ratios of the unstrained $B2$ and $C1$ structures are normalized to one independent of $\hat{G}$. $\Delta E^{\mathrm{bulk}}(a_s)$ is marked by a solid gray line.

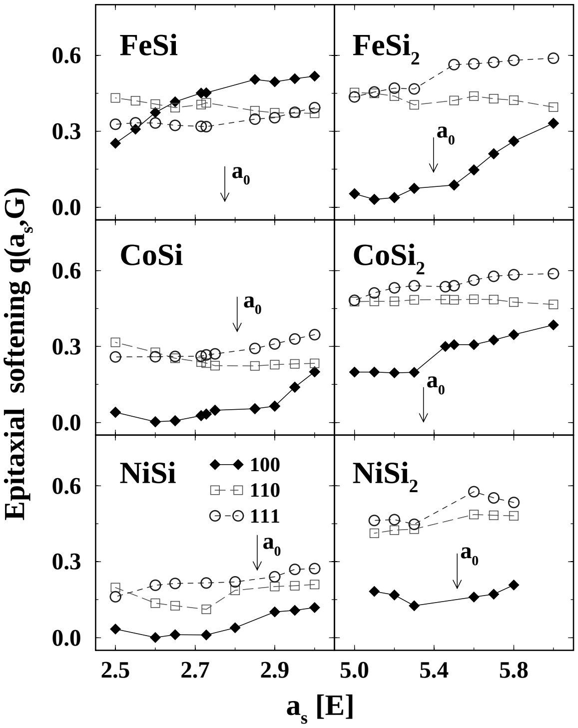

FIG. 2. Calculated epitaxial softening $q(a_s, \hat{G})$ versus substrate lattice parameter a_s for [100], [110], and [111] growth directions $\hat{G}$.

epitaxy, while under very large compressive strain, a significant reduction of the $q(a_s, [100])$ function occurs now crossing $q(a_s, [110])$ and $q(a_s, [111])$. The epitaxial softening in CoSi and NiSi is more pronounced than for $CoSi_2$ and $NiSi_2$. All of them possess the lowest q along [100] for both compressive and tensile strain and the largest q along [111]. For the Fe-Si compounds the softening expressed by $q(a_s, [100])$ is reversed compared to Co-Si and Ni-Si.

For the supersoft CoSi, NiSi, and $FeSi_2$ tetragonal structures, $q(a_s, [100])$ is practically zero under compressive biaxial strain as a consequence of zero strain energy displayed in Fig. 1.

Commonly, the strain energy versus $\hat{G}$ for epitaxial growth is estimated from harmonic theory. For that, the harmonic softening function $q(\hat{G})$ is conveniently expressed in terms of elastic constants [14,15] of the reference unstrained cubic medium. For $CoSi_2$, by using the computed GGA elastic constants [16], $c_{11} = 225$ GPa, $c_{12} = 147$ GPa, $c_{44} = 86$ GPa, we derived $q[100] = 0.23$, $q[110] = 0.36$, and $q[111] = 0.40$. These values are only slightly smaller than the $q(a_s, \hat{G})$ in Fig. 2 and predict correctly the sequence of $\hat{G}$ dependent strain energies. However, the harmonic elastic theory totally neglects the important dependence on a_s and is therefore not able to describe any crossing of q for different $\hat{G}$.

For the analysis of our results in terms of a simplified bond model each unstrained compound lattice is decomposed into its elementary sublattices [17]. The $B2$ structure of MSi compounds consists of two simple cubic lattices of Si and M atoms, while the atomic arrangements of the $C1$ structure of MSi_2 compounds are made of two interpenetrating fcc lattices for Si and one fcc lattice for atom M. The energy of M-M and Si-Si bonds in MSi and MSi_2 is derived from the cohesive energies of the sublattices divided by the respective number of bonds. From the cohesive energy differences (ΔE_{coh}) between the compound structures and the elementary sublattices, the energy of M-Si bonds is derived from ΔE_{coh} divided by the number of M-Si bonds. There are eight M-Si bonds for the $B2$ as well as the $C1$ structure, because the metal atom M is in the center of a cube of Si atoms. This procedure assumes that all energy gain ΔE_{coh} is due only to the formation of M-Si bonds leaving the M-M and Si-Si bond energy unchanged which worked reasonably well for the estimation of surface energies of $CoSi_2$ [17]. However, for the present study it should be noted that only changes of these bond energies due to the deformation of the compound are of relevance.

Deriving the M-M and Si-Si bond energies there is some ambiguity due to the atomic ground state which might be chosen spin polarized or nonmagnetic [18]. However, this ambiguity does not influence the M-Si bond energy. For $B2$ FeSi and CoSi the derived M-Si bond energies are 0.52 eV and 0.49 eV, respectively, and are increased to 0.88 eV for $FeSi_2$ and 0.87 eV for $CoSi_2$. Although the M-Si bond lengths are very similar for both structures, the M-Si bond energy for MSi_2 is much larger. For the $C1$ structure the M-Si bonds are dominant and the M-M bonding is weak [17], while for the $B2$ stability the M-M bonding is much more important. The M-M bond energy of MSi is stronger by a factor of ≈ 4 compared to MSi_2.

By application of the bond energy model to the strained structures, we analyzed the change of bond energies for a wide range of strains. Figure 3 shows the strain energy decomposed in changes of M-M, Si-Si, and M-Si bond energies summed over all bonds for the [100] epitaxy for FeSi, CoSi, $FeSi_2$, and $CoSi_2$. As a reference we used the bond energies of the unstrained $B2$ and $C1$ structures which make the bond energy changes free from the ambiguities due to the atomic references. A negative (positive) change of bond energy means that the bond is stronger (weaker) compared to the reference. It should be noted that, in general, all bond energies are averages over two different (constrained or relaxed) sets of nearest-neighbor bonds for the noncubic cases. Concerning [110] epitaxy, the geometry constraint splits the M-Si bonds into two sets of four strained in-plane and four relaxed out-of-plane bonds, while the [111] constraints produce two sets of six strained and two relaxed bonds. However, for [100] epitaxy, all eight M-Si bonds always have the same length.

For the normally behaving compounds FeSi and $CoSi_2$ the strain energy in Fig. 3 is rather parabolic with its minimum at a_0. Under compressive strain they are

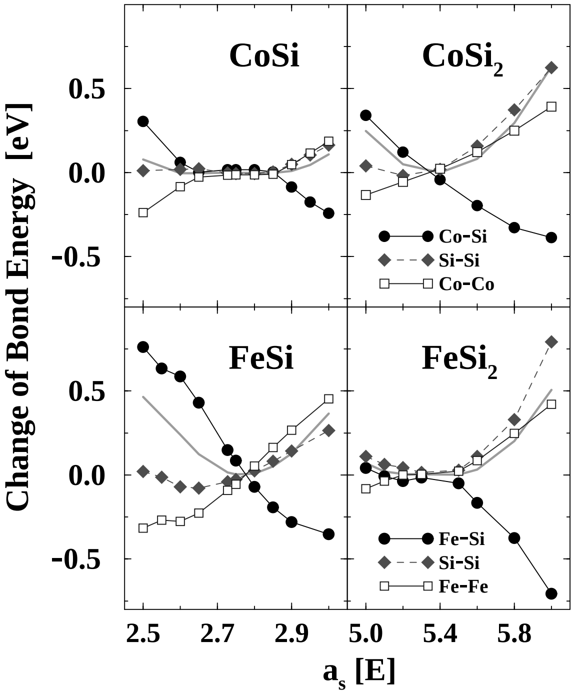

FIG. 3. M-M, M-Si, and Si-Si relative bond energies ($\times$ number of bonds) for [100] epitaxy versus the substrate lattice parameter a_s. The corresponding epitaxial energy $\Delta E^{\mathrm{epi}}(a_s, [100])$ is marked by a solid gray line.

characterized by a strengthening of M-M bonds and a weakening of M-Si bonds. The Si-Si bonds do not change significantly. For tensile strains the change of M-M and M-Si bond energies is just opposite to compressive strains. However, the Si-Si bonds are now weakened. The same holds for NiSi_2.

The bonding properties of CoSi and FeSi_2, which are supersoft for [100] epitaxy, are dramatically different as shown in Fig. 3, because all three bond energies remain constant over a broad range of ≈ 0.3 Å of epitaxial straining. According to [100] epitaxy the M-Si bonds are free to relax for both the $B2$ and $C1$ structures. The M-Si bond length stays constant which, to a certain degree, also holds for the normal compounds CoSi_2 and FeSi. The peculiarity of the supersoft compounds is due to the bonds pointing out of the (100) substrate plane which are free to relax in response to the biaxial in-plane strain. These bonds relax in such a way that the volumes of CoSi and FeSi_2 are constant in the critical strain region. For [110] and [111] epitaxy no supersoft effects are found, because the M-Si bonds are not all free to relax. Even FeSi_2 and CoSi behave like normal compounds.

Summarizing our approach, materials with artificial structures and unusual properties are predicted by a reliable *ab initio* technique. Our findings might hopefully stimulate the experimentalists to design and study the proposed supersoft silicides.

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