

New Epitaxially Stabilized CoSi Phase with the CsCl Structure

H. von Känel, C. Schwarz, S. Goncalves-Conto, and E. Müller

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich, CH-8093 Zürich, Switzerland

L. Miglio, F. Tavazza, and G. Malegori

Dipartimento di Fisica dell'Università, via Celoria 16, I-20133 Milano, Italy

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We report the first synthesis of CoSi in the CsCl structure, as an epitaxial film on Si(111). Experimentally and theoretically we find that the lower stability of this phase, relative to that of FeSi with the same structure, can be understood only by taking into account the energy contribution for the interface bonding, in addition to the elastic energy.

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The epitaxial stabilization of crystal structures, which do not exist in bulk form, has found much interest recently [1,2]. Ordinary phase transformations occur as a result of changing temperature or pressure. In order to be accessible by such a phase transition, the target phase must either be close in energy to the original phase (energy differences of order kT) or it must be of smaller volume, since hydrostatic pressure is necessarily positive. Neither condition applies to epitaxial phase transitions, since for coherent interfaces the biaxial pressure exerted by the substrate may be both large and negative. A phase transformation induced by epitaxy may therefore lead to structures which cannot be reached by external changes in pressure or temperature. An example is FeSi, which has recently been discovered to crystallize in the CsCl structure, when grown by molecular beam epitaxy (MBE) on Si(111) [3]. The stable bulk phase, i.e., ϵ -FeSi, is characterized by a simple cubic cell with 8 atoms (usually referred to as "FeSi" structure, Pearson symbol $cP8$ [4]) and is semiconducting. According to a band structure calculation the new FeSi phase is metallic and exhibits a low density of states (DOS) at the Fermi level E_F [5]. Electrical transport measurements have also given evidence for Kondo behavior at low temperatures. This is due to magnetic impurities, originating from deviations from the exact 1:1 stoichiometry of perfect FeSi [6]. Our search for an epitaxially stabilized CoSi phase with the CsCl structure has been motivated by the following considerations. First, the stable bulk phases of Fe and Co monosilicides crystallize with the same FeSi structure and with comparable lattice parameters [4] (see also Table I). Second, only a few bulk monosilicides are known to crystallize "sometimes" with the CsCl structure: OsSi, RuSi, and RhSi [7]. Since in the periodic table Ru and Rh are the two $4d$ metals situated right below Fe and Co, respectively, it is reasonable to suspect the existence of an epitaxially stabilized CoSi phase with the same structure [5].

It is the aim of this Letter to show that the hypothetical new CoSi phase does in fact exist, and to provide an explanation for why it has escaped discovery for so long.

The substrates used were n -type, 800 Ω cm Si(111) wafers with an unintentional misorientation of less than 0.2°. CoSi with the CsCl structure was grown in two ways: (1) A thin (3–10 Å) template of epitaxial CoSi₂ was formed by stoichiometric codeposition of Co and Si from two electron gun evaporators onto the (7 × 7) reconstructed substrates kept at room temperature (RT) and subsequent annealing to ~350 °C. CoSi could then be grown by MBE onto this template up to a thickness of ~100 Å. During the deposition the substrate temperature was kept close to RT. (2) In place of the CoSi₂ template 1 to 2 monolayers (ML) of pure Co were first deposited, immediately followed by the MBE growth of CoSi, again on the cold substrate. Both methods yielded essentially the same results except for the improved crystalline quality of films formed by the former. The Kikuchi band pattern, observed by reflection high-energy electron diffraction (RHEED), indicated that an epitaxial CoSi phase of cubic symmetry had formed, with an orientation given by CoSi(111)||Si(111) and CoSi[11 $\bar{2}$]|Si[$\bar{1}\bar{1}2$], i.e., the interface is of type B [8]. X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements confirm that our CoSi films do crystallize with the CsCl structure. As an example, Fig. 1(a) shows a cross-sectional TEM image of a 70 Å thick CoSi film on top of a 10 Å thick CoSi₂ template at low resolution. The corresponding diffraction pattern is displayed in Fig. 1(b). It is indexed according to a cubic unit cell with the lattice parameter a_{Si} of Si, with the result that all odd-order reflections of CoSi are absent. This is consistent with the CsCl structure and a lattice parameter a_0 of

TABLE I. Lattice constants of the bulk stable and unstable Fe and Co monosilicides and trigonal strain observed for coherent interfaces by XRD and RBS.

	(CsCl)CoSi	(CsCl)FeSi	ϵ -CoSi	ϵ -FeSi
a_0 (Å)	2.74 ± 0.02	2.77 ± 0.01	4.445 ^a	4.48 ^a
e_t (%)	2.80 ± 0.30	3.48 ± 0.20		

^aAfter Ref. [4].

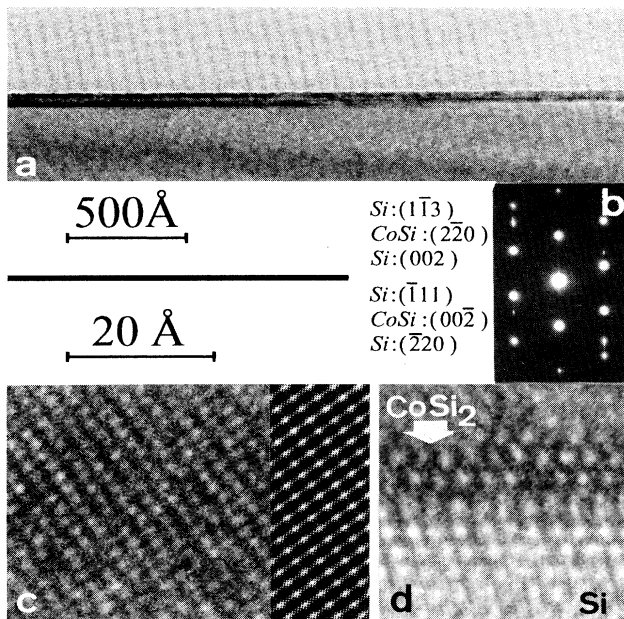


FIG. 1. (a) Low-resolution cross-sectional TEM image of a 70 Å thick CoSi film with the CsCl structure, grown on a 10 Å thick CoSi₂ template on Si(111). (b) Selected area diffraction pattern of the silicide region. All spots in the leftmost column are indexed according to a cubic unit cell with the lattice parameter of Si. (c) High-resolution image and corresponding computer simulation of the CoSi layer, taken along the [110] zone axis. Input parameters for the contrast simulation were as follows: layer thickness $d = 38$ Å, accelerating voltage $V = 300$ kV, spherical aberration constant $C_s = 1.1$ mm, beam semiconvergence angle $\alpha = 0.7$ mrad, focus spread = 8 nm, and defocus value $\delta = -80$ nm. (d) High-resolution image of the interface region between the CoSi₂ template and the Si substrate, taken along the [110] zone axis.

the film close to $a_{\text{Si}}/2$ [3]. Figure 1(c) shows a high-resolution image of the CoSi layer, together with a computer simulation, taken along the [110] zone axis. An image of the interface region with the CoSi₂ template is displayed in Fig. 1(d). Since a_0 is slightly larger than $a_{\text{Si}}/2$, the CoSi films are under a biaxial compressive strain, as long as the interfaces remain coherent, i.e., for sufficiently small thicknesses [9]. The resulting trigonal distortion e_t was measured by Rutherford backscattering (RBS) channeling. Table I shows the lattice constants and the maximum trigonal distortion, $e_t = e_{\parallel} - e_{\perp}$, obtained for CoSi and FeSi [10] phases with coherent interfaces. The lattice parameters of the stable bulk phases are also shown for comparison. From Table I the misfit η of the various phases can be calculated by taking into account their different epitaxial orientation relationships [11]. For (CsCl)FeSi and (CsCl)CoSi, we obtain $\eta = 2\%$ and 0.9% , respectively. The corresponding numbers for the stable bulk phases, ϵ -FeSi and ϵ -CoSi, are -4.7% and -5.5% .

The main reason for the epitaxial stabilization of a bulk unstable phase is, for coherent interfaces, the larger elastic

energy of the competing bulk phase, due to its larger misfit [1,2]. With increasing thickness the elastic energy of a film is, however, lowered by misfit dislocations [9], and the bulk stable phase eventually wins [1,2]. Experimentally, the new CoSi phase was found to exist up to film thicknesses of ~ 100 Å, above which the phase transition to the ϵ phase took place even at RT. A mild anneal to 200 °C was sufficient to trigger the transition for film thicknesses below 100 Å. As grown films of (CsCl)FeSi did not transform up to the largest thicknesses (~ 900 Å) investigated [12]. Annealing to 200–300 °C, depending on thickness, was necessary to initiate the phase transition.

In Fig. 2(a) the valence band spectra are displayed, obtained by angle integrated ultraviolet photoelectron spectroscopy (UPS) at $h\nu = 21.2$ eV, on a 44 Å thick CoSi film before and after the thermally induced phase transition to the stable bulk phase. Except for the pronounced peak at a binding energy of ~ 0.3 eV the spectral features corresponding to the stable bulk phase are in good agreement with those obtained at higher photon energies [13,14]. The main d -band derived peak is located at ~ 1.1 eV for both crystal structures. The two phases can, however, be easily distinguished by the fact that only one peak is present in the CsCl phase, whereas three are found in ϵ -CoSi.

In order to get a more quantitative understanding of the experimentally observed features, and in particular of the low stability of (CsCl)CoSi with respect to FeSi, we performed a semiempirical estimation of the DOS and of the cohesion energies for all phases. Our calculations are based on a parametrized, tight-binding (TB) Hamiltonian, where the matrix elements (involving s,p orbitals for silicon and s,p,d orbitals for the transition metal) are fitted onto muffin tin (LMTO) [15] and augmented plane wave (FLAPW) [5] evaluations of the CoSi₂ and FeSi₂ electronic bands, respectively. Transferability to the other configurations is obtained by scaling the hopping elements of the TB matrix (up to d - d , second neighbor interactions in a Koster-Slater representation [16]), following

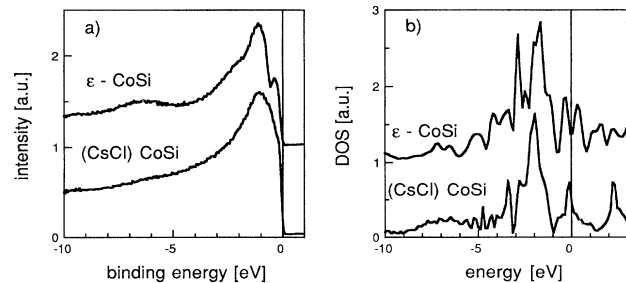


FIG. 2. (a) UPS spectrum of a 44 Å thick CoSi film on a 7 Å CoSi₂ template, obtained at a photon energy of 21.2 eV, before (bottom) and after (top) the phase transformation from the pseudomorphic CsCl to the bulk stable ϵ -CoSi phase. (b) Corresponding DOS.

Harrison's universal law with interatomic distance [17]. Also, the on-site energies of the TB matrix are adjusted, if charge transfer occurs, by a local neutrality condition [18]. In particular, we tested our TB DOS for (CsCl) and ϵ -FeSi to be in good agreement with FLAPW [5] and LMTO [19] calculations, especially near E_F [20]. No such *ab initio* results are present for CoSi. In Fig. 2(b) we report our TB DOS for ϵ -CoSi and (CsCl)CoSi. The relative energies of the peaks confirm the experimental findings, but with respect to E_F they are shifted by nearly 0.8 eV [21]. A three-peak structure characterizes the ϵ phase, the central main peak coinciding in energy with the single peak of (CsCl)CoSi. The total energy for different atomic configurations R is calculated by summing the TB states up to the current Fermi level (the attractive part) and by adding a short range, central potential, which takes into account the repulsion between occupied orbitals [22]

$$E_{\text{tot}}(R) = E_{\text{att}}(R) + E_{\text{rep}}(R) \\ = \sum_{n,k}^{\epsilon_F} \epsilon_{n,k}(R) + \frac{1}{2} \sum_{i,j} \frac{\phi}{r_{ij}^n}, \quad (1)$$

where $\{n, k\}$ label the electronic TB states and $\{i, j\}$ indicate an atom pair. ϕ and n are different for Si-Si, Si-Co, and Co-Co interactions and the set of six parameters is fitted by a minimization procedure to the lattice parameter and the bulk modulus of fluorite CoSi_2 and the lattice parameters of ϵ -CoSi and (CsCl)CoSi. Since relative cohesive energies are the key feature, we checked that our calculation reproduces the energy differences between fluorite and adamantane CoSi_2 [15] and between fluorite and β -FeSi₂ [23], obtained by *ab initio* total energy calculations. Our results are reported on the left-hand side of Fig. 3(a) (FeSi) and Fig. 3(b) (CoSi), as a function of the relative difference from the Si lattice parameter. Strictly speaking, the curves apply to the hydrostatic pressure case, whereas in reality the epitaxial films are under a biaxial stress. Including the (neglected) c -axis relaxation [1] would not, however, change any of the conclusions drawn below. We note that the cohesive energy of the ϵ phase (filled circles) is lower than the one of the CsCl structure (filled squares) by 0.75 eV per formula unit in CoSi and 0.54 eV per formula unit in FeSi. By considering only the elastic energy contribution for a coherent interface, the ϵ phase remains thus the most stable phase in both cases. Higher in energy lie the NaCl curves (filled triangles), which indicate a very small misfit of the monosilicides with the NaCl structure [11]. The energy is too high for these phases to occur in either bulk or epitaxial form.

Until now we have neglected the contribution of the interface bonds to the stability. The coherent registry of the Bravais lattices does not, however, imply the same for the atomic basis. It is easy to see that the atomic planes of the CsCl phase map perfectly onto those of Si(111). The ϵ phase, however, yields a mapping of the Si(111) atoms by one in three at best. If we assume that the bonds

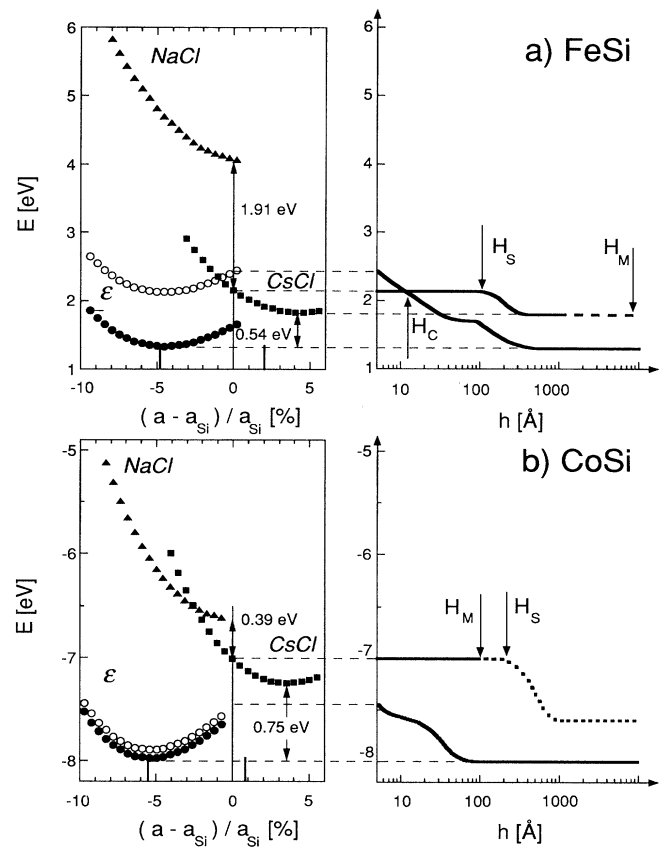


FIG. 3. (a) Left panel: Total energy curves of FeSi with the NaCl (filled triangles), the CsCl (filled squares), and the ϵ phase (filled circles) as a function of the lattice parameter, expressed in terms of the relative deviation from a_{Si} . Open circles indicate the total energy increase in the monolayer limit of the ϵ -FeSi phase with respect to (CsCl)FeSi, when its unfavorable interface contribution is taken into account. Right panel: Qualitative variation of the total energy per formula unit of ϵ and CsCl phases as a function of the layer thickness h . For small thicknesses the energy of ϵ -FeSi decreases proportional to $1/h$ because of the diminishing contribution from the interface. The further drop at larger thicknesses indicates schematically the loss of interface coherence due to the generation of misfit dislocations. H_s marks the (experimental) value of the critical thickness, where strain relaxation of the (CsCl)FeSi phase sets in at RT. The metastability limit, H_M , is not known experimentally [10]. (b) Left panel: Total energy curves of the CoSi phases corresponding to those in (a). Right panel: Same as in (a) for CoSi. The (CsCl)CoSi phase is predicted to be unstable for all thicknesses. Experimentally, (CsCl)CoSi films with coherent interfaces have been grown up to a thickness of $H_M \sim 100$ Å.

emanating from the two other atoms are broken, then the bond energies can be used to estimate the maximum cohesive energy loss with respect to the bulk situation at the first ϵ -phase layer on top of Si(111). A rough estimate for the bond energies in FeSi and CoSi can be obtained from the difference between the total energy curves for the

CsCl and NaCl phases at the silicon interatomic distance. This difference is seen to be 1.91 eV in FeSi [Fig. 3(a)] and 0.39 eV in CoSi [Fig. 3(b)]. Taking into account the coordination numbers, differing by 2 between these two phases, the average energy per bond is just half as large, namely, 0.96 eV for FeSi and 0.2 eV for CoSi. With two out of three bonds broken, the cohesive energy loss is found to be approximately 0.66 eV per formula unit in FeSi and 0.13 eV in CoSi. In the CsCl phase no relevant loss can be expected. Getting back to Fig. 3(a), we draw by open circles the energy curve of ϵ -FeSi with this interface contribution included, whereupon the CsCl phase becomes lower in energy. Very likely this is not the case for CoSi, where the interface contributes much less [Fig. 3(b)].

On the right-hand side of Fig. 3, qualitative diagrams of the average energy per layer with respect to film thickness are reported. For FeSi, there exists a region of absolute stability of the CsCl phase up to a critical thickness H_c (a few angstroms). This is supported by the fact that experimentally no transition is found below 10–15 Å, even at high annealing temperatures [10]. It is not the case for CoSi, where no positive H_c can be estimated. At larger thicknesses we are in a metastable region in both FeSi and CoSi, where an activation barrier prevents a phase transformation at RT up to a maximum thickness H_m . In the metastable region, the annealing temperature for the transition decreases with film thickness, as a result of a complex interplay of elastic and thermodynamic factors, which should be analyzed by simulation techniques.

In conclusion, we think the larger stability and the easy growth of (CsCl)FeSi, compared with (CsCl)CoSi despite its unfavorable misfit situation, to be related to the fact that FeSi is thermodynamically stable in the early stage of the growth. (CsCl)CoSi, by contrast, should be metastable even at film thicknesses of a few monolayers. Its growth must therefore be attributed to kinetic factors. Our results point out that the common interpretation of epitaxial stability just in terms of purely elastic criteria is not generally exhaustive and that direct estimations of the interface energetics will be very recommendable.

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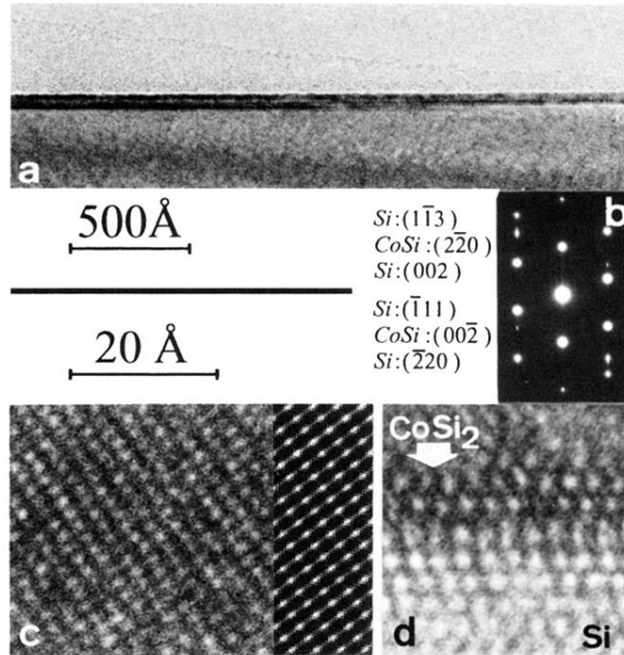


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