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CoSi₂/Si(111) interface: Determination of the interfacial metal coordination number

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The morphology and the surface and interface structure of flat CoSi₂ films (thickness ~ 2 Si-Co-Si triple layers) epitaxially grown on Si(111) have been investigated using medium-energy ion scattering with ultrahigh energy resolution. The data show that the silicide is attached to the substrate through Co-Si bonds rather than through Si-Si bonds. At the interface, the silicide is terminated by a full Si-Co-Si triple layer. The interface metal atoms are thus eightfold coordinated. The silicide-substrate distance is expanded by 0.16 ± 0.08 Å. The first Si substrate layer is relaxed outward by 0.08 ± 0.08 Å. The length of the Co-Si interface bond is thus dilated by 0.08 Å. At the silicide surface, the first Co-Si interplanar distance is found to be relaxed inward by 0.14 ± 0.04 Å. Our measurements suggest that the silicide lattice strain is almost fully relaxed. We propose that such relaxation occurs through a high density of microcracks in the film. The average spacing between cracks is then smaller than roughly 50 Å.

I. INTRODUCTION

The growth of the epitaxial silicides of Co and Ni on Si(111) has been investigated extensively. CoSi₂ and NiSi₂, which both have the cubic CaF₂ structure, have a small lattice mismatch with Si (1.2% and 0.4%, respectively). They may be grown on this substrate material to form atomically flat epitaxial interfaces.¹ The silicides are important from a technological point of view² and serve as model Schottky barriers, offering the opportunity to directly correlate interface atomic structure to electrical properties.³⁻⁶ Clearly, knowledge of the atomic structure is a prerequisite to make such a correlation. This paper provides a detailed analysis of the atomic structure at the CoSi₂/Si(111) interface.

Figure 1 shows three possible atomic arrangements at an MSi_2 /Si(111) ($M=Co, Ni$) interface with the film 180° rotated with respect to the substrate (type *B*). The silicide may be attached to the substrate either through Si-Si bonds or M -Si bonds. In the case of Si-Si bonding, the silicide is terminated by a Si- M -Si triple layer and the interface metal atoms are sevenfold coordinated with Si [Fig. 1(a)]. In the case of M -Si bonding the silicide is terminated by either a Si- M double layer [Fig. 1(b)], with the interface metal atoms coordinated fivefold, or by a Si- M -Si triple layer [Fig. 1(c)] corresponding to eightfold coordination. The structural difference between the latter two interface geometries in the "interface Si layer" marked by the arrow in Fig. 1(c).

Considerable effort has already been devoted to the CoSi₂/Si(111) and NiSi₂/Si(111) interfaces, both theoretically and experimentally. Calculations by van den Hoek, Ravenek, and Baerends^{7,8} and Hamann⁹ have shown that the interfaces should be markedly different. For CoSi₂/Si(111) eightfold coordination of the interface Co atoms is predicted, while in the case of Ni the sevenfold structure model is expected to be lower in energy. For both interfaces the model with fivefold-coordinated metal atoms is found to be energetically unfavorable because of the presence of unsaturated metal-centered bonding or-

bitals at the interface for that model.

Experimentally, the NiSi₂/Si(111) interface registry has been investigated using high-resolution transmission electron microscopy (HRTEM),¹⁰ medium-energy ion scattering (MEIS),^{11,12} x-ray standing waves (XSW),^{13,14} and surface x-ray diffraction.¹⁵ For this interface there is agreement on the sevenfold structure model, i.e., the silicide is attached to the substrate with Si-Si bonds across the interface. This is in accordance with the theoretical predictions.⁷⁻⁹

In contrast, the experimental evidence for the CoSi₂/Si(111) interface structure is less clear cut. Most techniques mentioned above have also been applied to this system. In an early HRTEM study, Gibson *et al.*¹⁶ found that the Co atoms at the interface were most likely fivefold coordinated. These authors did not consider the eightfold model. In high-resolution MEIS (Ref. 17) and XSW (Refs. 18-20) investigations the silicide-substrate registry was studied and strong evidence in favor of Co-Si bonding across the interface was found, consistent with either fivefold or eightfold coordination of the interface Co atoms.

Evidence for eightfold-coordinated Co atoms at differently prepared CoSi₂/Si(111) interfaces has been ob-

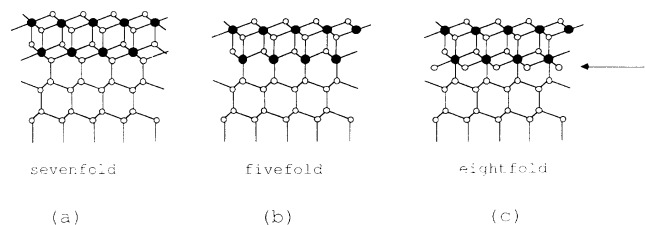


FIG. 1. Different possible bonding arrangements at an MSi_2 /Si(111) ($M=Co, Ni$) interface. The interface metal coordination numbers corresponding to the different structures are (a) seven, (b) five, and (c) eight. The structure with eightfold-coordinated atoms contains an additional "interface Si layer" (arrow) as compared to the fivefold structure.

tained from comparisons between simulated and observed images in an extensive HRTEM study by Bulle-Lieuwma *et al.*²¹ Rossi *et al.*²² also claimed evidence for eightfold coordination on the basis of surface extended x-ray-absorption fine-structure (SEXAFS) data on very thin (1–2 Si-Co-Si triple layers) CoSi₂ films. However, under the preparation conditions of Rossi *et al.* we always observe the formation of islands with an average height of more than ~6 ML. If that is the case, the SEXAFS has effectively probed the eightfold Co coordination number in bulk CoSi₂. In a photoemission study on the CoSi₂(111) surface in different stoichiometries, Haderbache *et al.*²³ established a relation between the eightfold Co coordination number at the Si-rich surface and that at the CoSi₂/Si(111) interface, which has been suggested in other studies.^{24,25} However, no epitaxial interfaces were studied in that work.

Conflicting evidence for Si-Si interface bonds, i.e., sevenfold-coordinated metal atoms at the CoSi₂/Si(111) interface, has been obtained in a HRTEM study by Catalana *et al.*²⁶ Moreover, alternative configurations in which the silicide is laterally shifted with respect to the substrate have also been reported.²⁷ The quality and structure of the CoSi₂ films and their interfaces with Si(111) are sensitive to small variations in the substrate quality and silicide preparation. Such variations may result in silicide films, which are essentially unstrained, as in this work, or in a peculiar metastable interface structure.^{28–30} Differences in sample preparation might explain the differences in interface structure reported. Clearly, experiments on well-characterized interfaces are necessary to resolve this issue.

In the previous MEIS study,¹⁷ relatively thick CoSi₂ layers (thickness ~9 Si-Co-Si triple layers) were investigated. The issue of the presence or absence of the interface Si layer, which resides on buried silicide lattice sites, was not addressed.

In this paper, we present a detailed structure determination on well-characterized interfaces of very thin CoSi₂ films (thickness ~2 Si-Co-Si triple layers) grown on Si(111) using medium-energy ion scattering with monolayer sensitivity. We show that the interface consists of metal-Si bonds and that the interface Si layer is present. Thus the interface metal atoms are eightfold coordinated, in agreement with theory. Interface relaxations from bulk distances are observed. The data suggest that the silicide consists of essentially unstrained patches separated by microcracks. On the assumption of complete strain relaxation a characteristic patch size may be inferred from the data.

II. EXPERIMENT

The experiments were performed in an ultrahigh-vacuum (UHV) system (base pressure ~7×10⁻⁹ Pa) that has facilities for medium-energy ion-scattering (MEIS) analysis, low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and sputtering.³¹ Co was sublimed from thoroughly outgassed wires. Absolute metal coverages were determined using ion scattering. Samples were heated using direct-current Ohmic heating.

Temperatures were monitored with an accuracy of 50°C using an infrared pyrometer.

The silicide films were prepared as follows. Si(111) substrates (*n*-type, miscut less than 0.5°, dimensions 7×0.5×16 mm³) were cleaned using mild sputtering and annealing.²⁵ Surface cleanliness was monitored using ion scattering (detection limit ~10⁻²–10⁻³ ML for elements heavier than Si) and AES [intensity ratios $I(C(KLL))/I(Si(LVV))$ and $I(O(KLL))/I(Si(LVV))$ smaller than 1×10⁻³]. After cleaning sharp (7×7) LEED patterns were obtained. Next, 1.75 or 1.90 ML of Co was evaporated at room temperature at a rate of ~0.02 ML s⁻¹. Type-*B* oriented silicide was formed by annealing at ~330°C for 5 min. This resulted in good (1×1) LEED patterns. Occasionally half-order spots, indicative of part of the surface being (2×2) reconstructed, were observed. Those samples were not considered further in the analyses.

For ion scattering a well-collimated proton beam (energy 100 keV, energy stability 10 eV) was used. A three-axis goniometer allowed for alignment of the crystal axes with respect to ion beam and detector to within 0.1°. Backscattered ions were simultaneously detected over a 20° angular range using an electrostatic analyzer with an energy resolution of 0.09% (90 eV at 100-keV ion energy). With this resolution sensitivity to signal backscattered from individual monolayers is obtained.^{32,33} A small part of the data set was obtained using a less good energy resolution of ~360 eV. The detector was rotated around the sample by means of a rotary table. By combining scans taken at different detector positions angular ranges larger than 20° were covered.

All measurements were carried out in the (1 $\bar{1}$ 0) scattering plane. The channeling and blocking axes in the type-*B* oriented silicide do not coincide with those in the substrate and are marked with an asterisk. The experiments were performed with the beam incident along either the [00 $\bar{1}$], the [$\bar{2}$ 21], or the [$\bar{1}$ 10] substrate ([$\bar{2}$ 21]*, [00 $\bar{1}$]*, or [$\bar{1}$ 14]* silicide) crystal axis corresponding to incident angles of 35.26°, 35.26°, or 54.74° with respect to the surface plane. Note that the [00 $\bar{1}$] and [$\bar{2}$ 21] directions both reside in the (1 $\bar{1}$ 0) scattering plane at the same angle, but at 180° rotated azimuths. Only atoms in the silicide and in the interface region are hit; the deeper substrate atomic layers are shadowed.

Backscattered ions are blocked on their way to the vacuum in directions which are specific to the silicide and the interface structure. These directions are visible as minima (“blocking minima”) in the angular distributions of the ion yield obtained from the energy spectra of backscattered protons: a “blocking pattern” is an angular distribution of the integrated (total) intensity in the surface peak while a “constant depth profile” is an angular distribution of the energy-resolved intensity corresponding to one particular backscattering depth (see Sec. IV A).^{32,33}

The measured ion yields were calibrated using a standard method with an accuracy of 6% (Ref. 34) and either expressed in units of monolayers visible to both ion beam and detector or normalized to the random height using tabulated values for the random stopping power.³⁵ One monolayer (ML) is taken to be equivalent to 7.83×10¹⁴

atoms cm^{-2} , which is the areal density of Si atoms in one Si(111) atomic plane.

The conclusions of this work rely heavily on computer simulations of the ion-scattering experiments.³⁶ Ion intensities calculated for different structure models were compared with the experimental scattering yields.

We have also employed ion trajectory-dependent energy losses for structure analysis.^{32,33} For the simulation of those measurements, the energy loss along the trajectories through the crystal was evaluated. The ion-atom impact parameter dependence of the inelastic energy loss was assumed to obey the semiempirical exponential relation introduced by Oen and Robinson.^{37,38} Additional energy spreads related to ion energy straggling effects and detector energy resolution were taken into account.

In the simulations, values for root-mean-square (rms) vibration amplitudes were taken from our earlier work:^{6,17,25,39} 0.095 and 0.110 Å for Co and Si in CoSi_2 and 0.078 Å for the Si substrate atoms. The vibrations were assumed to be uncorrelated.

III. SILICIDE MORPHOLOGY AND SURFACE STRUCTURE

In this section we discuss the morphology and surface structure of the epitaxial CoSi_2 films, knowledge of which is needed for the interface structure analysis.

Backscattering data were taken with the beam incident along the $[00\bar{1}]/[\bar{2}\bar{2}1]^*$ direction [Fig. 2(a)]. Figure 2(b) shows the blocking pattern of the Co signal taken from the as-prepared sample with 1.75-ML Co coverage. The type-*B* orientation of the film is evident from the presence of strong minima in the $[001]^*$ and $[113]^*$ type-*B* silicide directions ($\sim 35^\circ$ and $\sim 60^\circ$ exit angle) due to blocking of ions backscattered from second-layer Co by surface Co and Si atoms. The virtual absence of blocking minima in the $[\bar{1}\bar{1}9]^*$, $[115]^*$, and $[112]^*$ directions shows that the surface stoichiometry is Co rich, i.e., the silicide is terminated by a Si-Co-Si triple layer.^{24,25}

The Co-rich surface of the silicide film is converted into a Si-rich one by deposition of 2 ML of Si and annealing to 300°C, in agreement with earlier work.^{25,40,41} After this the blocking minima caused by the two additional Si monolayers, in the $[\bar{1}\bar{1}9]^*$, $[001]^*$, $[115]^*$, and $[112]^*$ directions, are readily observed [see Fig. 2(c)]. The angular positions of the minima are consistent with the atomic coordinates as determined in Ref. 25. This is confirmed by a Monte Carlo simulation assuming these coordinates (first and second Si layers relaxed outward by 0.15 and 0.075 Å; third Si layer relaxed inward by 0.05 Å with respect to the CoSi_2 bulk positions). The fit (solid curve) matches the data well.

The virtual absence of minima in the blocking pattern from the Co-rich surface [Fig. 2(b)] along the $[\bar{1}\bar{1}9]^*$, $[117]^*$ (not indicated), $[115]^*$, and $[112]^*$ blocking directions further shows that the silicide film is rather flat. The roughness of the film can be estimated by fitting the data to a linear combination of patterns calculated for patches having heights of 1, 2, and 3 Si-Co-Si triple layers. The solid curve through the data shows the best fit for the film with 1.75-ML Co, obtained for fractional cov-

erages of the first, second, and third silicide Si-Co-Si triple-layer levels of 1.00, 0.67, and 0.08. For the film with 1.90-ML total Co coverage these fractional coverages are 1.00, 0.78, and 0.12. The error margins on these numbers are $\pm 15\%$. Thus the films are continuous. For both films the third-layer coverage is small. The silicide height distributions have been taken into account in all calculations presented in this paper.

The interplanar distance between the topmost Co and Si layers in the Co-rich surface has been determined in a residual energy difference measurement.^{32,33} In this experiment the difference of the Co and Si first-layer backscattering energies, corrected for the elastic backscattering energy difference, is measured as a function of exit angle. The distance then follows from the angular position of the strongly asymmetric minimum in the energy difference curve induced by the presence of the Si atom,

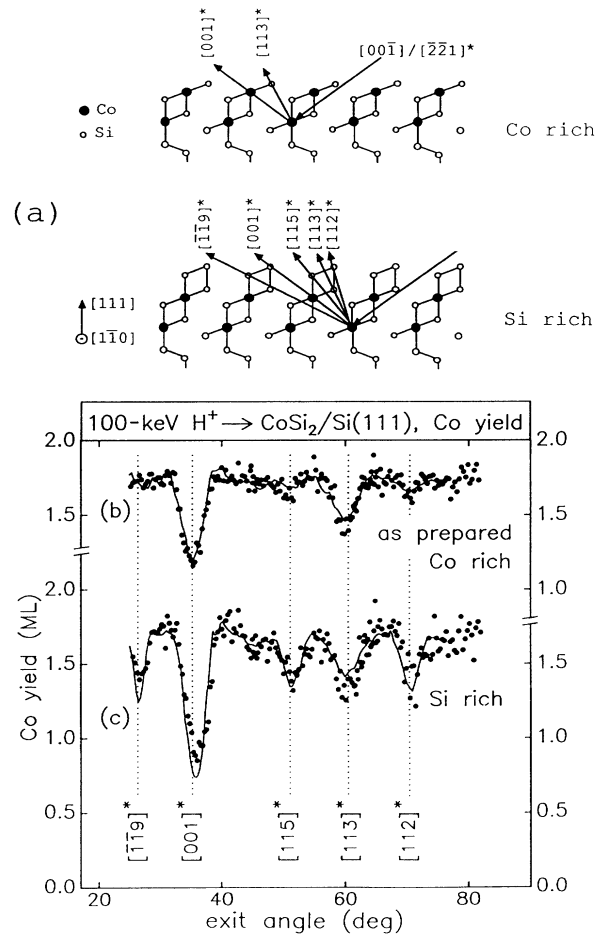


FIG. 2. Characterization of different CoSi_2 surface terminations. (a) Scattering geometry used for characterization of the silicide surfaces. Blocking directions for Co-rich and Si-rich type-*B* oriented silicides with a height of 2 Si-Co-Si triple layers are indicated. (b) Observed (circles) and simulated (solid curves, see text) Co yields for the as-prepared sample. The surface is Co-rich. The flatness of the film is evident from the virtual absence of blocking minima in the $[\bar{1}\bar{1}9]^*$, $[117]^*$, $[115]^*$, and $[112]^*$ directions (see text). (c) Co yields for the same sample after deposition of a Si double layer. The surface is then Si-rich.

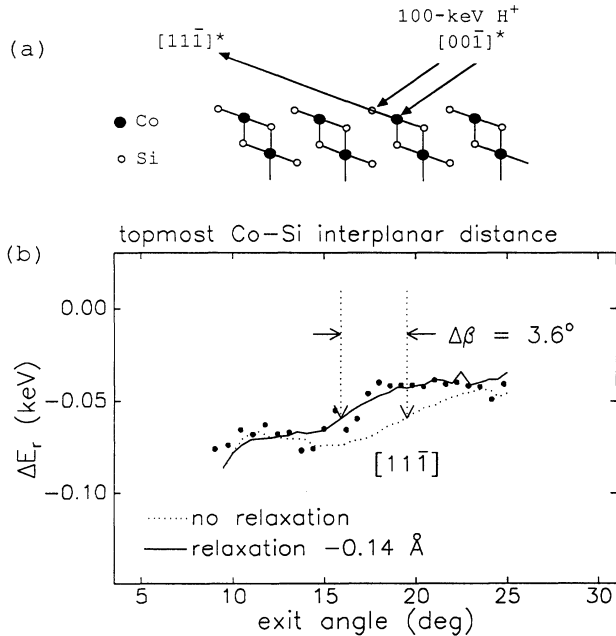


FIG. 3. Determination of topmost Co-Si interlayer spacing using energy losses. Scattering geometry (a) and energy residues observed [(b), circles] (Refs. 32 and 33). The first Co-Si interlayer distance relaxation (-0.14 ± 0.04 Å) is obtained from the position of the strongly asymmetric minimum. Calculated curves are shown for bulklike (dotted curve) and relaxed (solid curve) interlayer distances. Both calculations have been shifted up by 60 eV (Ref. 42).

which affects the ion energy in each exit direction along a Co-Si internuclear axis. This method is described in detail elsewhere.³³ Figure 3(a) shows the scattering geometry used. The data have been taken with the ion beam incident along the $[00\bar{1}]^*$ silicide axis. Backscattered ions have been recorded in a 20° angular range around the $[11\bar{1}]^*$ blocking direction. Figure 3(b) shows the experimental energy residues [shifted over 60 eV (Ref. 42)] together with calculated curves for relaxed (solid curve) and bulklike (dotted curve) Co-Si interplanar distances. The solid curve matches the data well, both in shape and in angular position. We conclude that the Co-Si interplanar distance is 0.63 ± 0.02 Å, which corresponds to an inward relaxation by 0.14 ± 0.04 Å with respect to the bulk CoSi₂ spacing. This value for the interplanar distance is consistent with the position of the $[11\bar{3}]$ minimum observed in the blocking pattern [Fig. 2(b)], as is demonstrated by Monte Carlo simulations assuming this value (solid curve). The value for the interplanar distance agrees with LEED results.⁴³

For the Co-rich surface [see Fig. 2(a)] the silicide-substrate interface is better accessible to ion beam and detector than for the Si-rich surface. This allows an easier analysis. Therefore we have studied the interface mainly on samples with Co-rich terminated surfaces.

IV. INTERFACE STRUCTURE DETERMINATION

A. Sevenfold versus eightfold (fivefold) coordination

First, we have examined whether the silicide is attached to the substrate through Co-Si or Si-Si bonds. To

distinguish between these different silicide-substrate registries we have performed an experiment in the scattering geometry of Fig. 4(a). The data have been obtained from the sample with 1.90-ML coverage. The ion beam was incident along the $[\bar{2}\bar{2}1]$ substrate, $[00\bar{1}]^*$ silicide axis. Atoms in the second to fifth layers in the substrate have a large hitting probability; the silicide and the sixth- and deeper-layer substrate atoms are shadowed. Therefore most backscattered ions originate from the interface region. On their way back to the vacuum these ions are blocked by silicide atoms in directions which are characteristic for the silicide-substrate bonding registry.

An experiment in this geometry is only weakly sensitive to the difference between the fivefold and eightfold models because the interface layer present in the eightfold model is shadowed and hardly contributes to the total yield. Blocking effects by this layer are weak as well.

We have labeled characteristic substrate-silicide blocking directions for either the sevenfold or the fivefold or eightfold registries 1 and 2 [Fig. 4(a)]. Direction 1 is

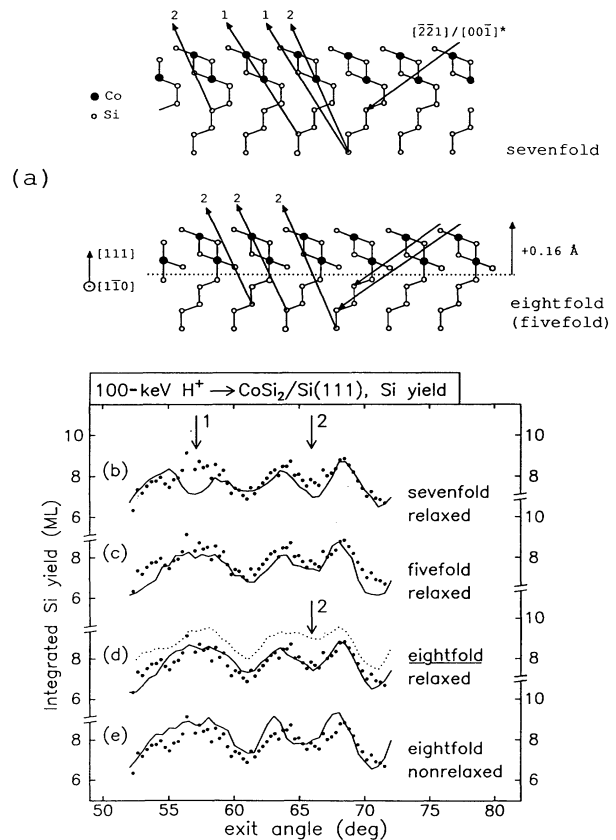


FIG. 4. Determination of silicide-substrate registry. (a) Scattering geometry. Characteristic blocking directions in the Si yield, labeled 1 and 2, are indicated for both the sevenfold and eightfold silicide-substrate registries. Direction 1 is expected for the sevenfold model only. (b)–(d) Observed Si yields (circles) compared to simulations for each of the three models for the interface with optimized coordinates (solid curves). A calculation for the eightfold model with bulklike silicide-substrate distance is shown for comparison (e). The dotted curve is described in Sec. V.

present in case of the sevenfold Si-Si bonding registry only. On the other hand, direction 2 is expected for both the sevenfold and fivefold/eightfold interface structure models.

The Si blocking pattern is shown in Figs. 4(b)–4(e) (circles). The presence of a blocking minimum in direction 2 and the absence of a minimum in direction 1 in the data suggest a fivefold or eightfold registry of the silicide with respect to the substrate. An angular shift of minimum 2 to a larger exit angle with respect to its bulk position indicates a silicide-substrate distance that is larger than that expected for bulklike Si bond lengths and bond angles.

In the simulations for each of the different structure models, we have varied the silicide-substrate distance and first substrate plane position to obtain the best fits to the data (solid curves). The simulations confirm the qualitative arguments given above. As expected, the calculations for the sevenfold model (b) indeed predict a minimum in direction 1, in disagreement with the data. By contrast, both the simulations for the fivefold (c) and eightfold (d) interface registries are in very good agreement with the data on an absolute scale, showing no minimum in direction 1 and predicting minimum 2 with the correct intensity. To obtain these fits, the silicide-substrate distance had to be increased by $0.16 \pm 0.08 \text{ \AA}$. The error margin has been determined in a visual comparison of patterns calculated using different relaxation values to the data. To demonstrate the sensitivity of the data to the interface expansion we have included a calculation for the eightfold-coordinated interface with the bulklike silicide-substrate distance (e), which predicts minimum 2 at the wrong exit angle.

From the data taken in this geometry we conclude that the silicide is attached to the substrate through Co-Si bonds, consistent with either fivefold or eightfold coordination of the interface Co atoms. Si-Si bonding across the interface (the sevenfold structure) is ruled out.

B. Fivefold versus eightfold coordination

Next, we have investigated whether the silicide is terminated at the interface by a Si-Co-Si triple layer [Figs. 1(a) and 1(c)] or a Si-Co double layer [Fig. 1(b)], i.e., whether or not the interface Si layer, which should saturate the metal-centered orbitals, is present. To this end, we used the geometry of Fig. 5(a). The ion beam was incident along the $[\bar{1}\bar{1}0]$ substrate channeling axis. In this geometry the silicide atoms, including the interface Si layer, have a large hitting probability whereas the substrate atoms are shadowed.

The presence of the interface Si layer is detected as follows. The yield from the atoms in that layer is efficiently blocked along the $[33\bar{1}]^*$ silicide blocking axis ($\sim 41.5^\circ$ exit angle) by the topmost Co atoms. Because of the flatness of the silicide, a minimum in a similar direction is not expected in the yield from any other Si atom in the silicide-substrate system, neither for the sevenfold, nor for the fivefold or eightfold interface bonding registries. Its presence or absence is therefore directly indicative of the presence or absence of the interface layer.

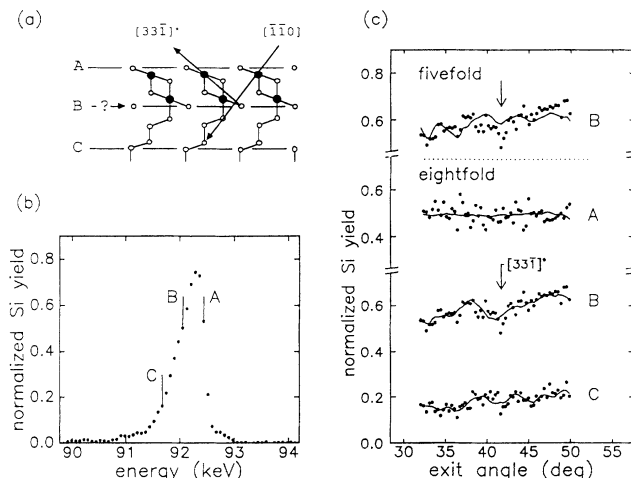


FIG. 5. Presence of interface Si layer. (a) Scattering geometry used. A blocking minimum is expected in the $[33\bar{1}]^*$ silicide direction if the interface layer is present. (b) Energy spectrum observed at 42° exit angle. Yields in the spectrum at positions *A*, *B*, and *C* correspond to ions backscattered from surface, interface, and substrate atoms. (c) Constant depth profiles *A*, *B*, and *C* (circles) and calculated curves for the fivefold and eightfold structure models (solid curves, see text). In profile *B* a blocking minimum is observed in the $[33\bar{1}]^*$ direction (arrow), indicative of the presence of the interface atoms.

The data have been recorded from the sample with 1.90-ML Co coverage using an energy resolution $\Delta E/E$ of 9×10^{-4} , with which monolayer sensitivity is attained.³² The Si part of the energy spectrum taken at 42° exit angle is shown in Fig. 5(b). The shape of the spectrum reflects the depth distribution of hitting probabilities: the yields from the silicide and first substrate layers form the surface peak; the low minimum yield behind the peak reflects the small hitting probability of deep substrate atoms. Accordingly, we have taken angular “constant depth profiles” of the ion yields in the energy spectra corresponding to a constant backscattering depth³³ in the surface (*A*), interface (*B*), and substrate (*C*) regions [Fig. 5(c), circles]. Profile *B* does have a distinct blocking minimum at 41.5° exit angle, indicative of the presence of the interface Si layer. As expected, no minimum is observed at this angle in either profiles *A* or *C*.

To demonstrate the sensitivity of the experiment to the presence or absence of the interface Si layer we have produced fits (solid curves) to the constant depth profiles with linear combinations of calculated monolayer yields from each of the single Si layers in the silicide and interface region.³³ The fitting has been performed for the eightfold (interface Si present) and fivefold (no interface Si) structure models.

First, we discuss the fits for the eightfold model. As profile *A* is due to ions backscattered from surface Si, no blocking minima are observed. This profile is described by only a first-layer contribution (flat curve). Interface profile *B* is described well by a fit containing a 30% contribution from the interface Si layer. Profiles taken at slightly different “depth” around profile *B* (not shown)

also have the minimum and are satisfactorily described using a relative contribution of ~ 0.3 from the interface Si layer. Substrate profile *C* does not show a minimum. The fit is obtained using a large contribution from substrate Si atoms.

The sevenfold model would yield results similar to that for the eightfold model, but that structure has been ruled out in the preceding section.

The best calculation assuming the fivefold interface structure (no interface Si) is shown separately. It does not predict the $[3\bar{3}\bar{1}]^*$ minimum in profile *B*.

The data in this geometry are described satisfactorily by the eightfold structure model, i.e., the silicide is terminated at the interface by a Si-Co-Si triple layer. The fivefold structure model is ruled out.

C. Interface expansion

Additional evidence in favor of an expanded interface has been obtained from Si yields taken with the ion beam

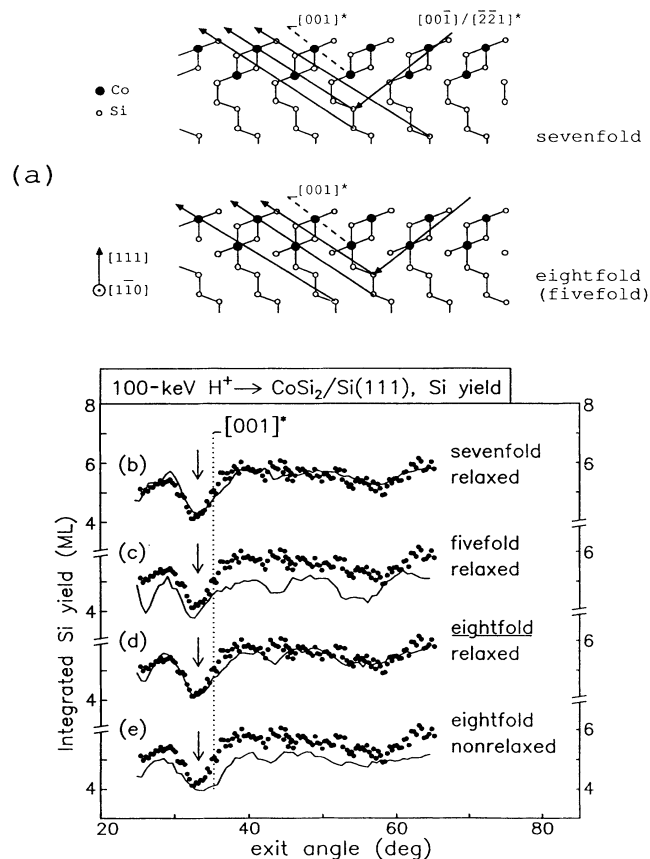


FIG. 6. Determination of interface relaxations. (a) Scattering geometry. In the case of an outward relaxed silicide the substrate atoms have an increased hitting probability, which gives rise to an increase in yield from these atoms and an apparent shift in the silicide $[001]^*$ direction (arrows). An additional shift is induced by the inward relaxation of the topmost Si atom (0.14 \AA , see Sec. III). (b)–(d) Si yields (circles) compared to simulated intensities for different models with an interface expansion (solid curves). A simulation for the eightfold model without the expansion is shown for comparison (e).

incident along the substrate $[00\bar{1}]$, silicide $[\bar{2}\bar{2}1]^*$ axis [see Fig. 6(a)]. The experiment has been performed on the sample with 1.75-ML coverage. In this case all silicide atoms are hit by the ion beam. Due to the interface expansion the first substrate atoms have a large hitting probability as well. Ions backscattered from these substrate atoms are blocked in directions at angles slightly below that of the $[001]^*$ silicide blocking axis (arrows). Our previous conclusions concerning the interface structure are confirmed by a comparison with simulations for different models. The solid curves [Figs. 6(b)–6(d)] show the best fits to the data obtained for the three structures including optimized relaxations.

For the *fivefold-coordination* model (c) yields are predicted which are $\sim 1 \text{ ML}$ lower than the data, because of the absence of the interface Si layer (in the eightfold structure model the layer is almost fully visible to beam and detector). Moreover, the shape of the calculated pattern does not match the data. Again the fivefold coordination is ruled out.

The fits for the structure models with either *sevenfold*- or *eightfold-coordinated* Co atoms at the interface satisfactorily describe the data [Figs. 6(b) and 6(d)]. These two models are thus not distinguished in this geometry. For both curves the silicide-substrate distance is expanded by 0.16 \AA in accordance with the results in Sec. IV A (Fig. 4). The expansion causes an increase in absolute yield and a shift in the $[001]^*$ blocking minimum to lower angle, as is evident from a comparison to a calculation for the eightfold model with a bulklike silicide-substrate distance [Fig. 6(e)]. These changes are related to an increased hitting probability of the first substrate atoms for the dilated interface. The corresponding simulation faithfully reproduces the $[001]^*$ minimum, both in shape and in angular position. In contrast with the experiment of Fig. 4, the measurement in Fig. 6 is also sensitive to the distance between the first and second Si layers of the substrate (deeper-layer spacings were assumed to be bulklike). The best fit in Fig. 6 is obtained if this distance is expanded by $0.08 \pm 0.08 \text{ \AA}$. In other words, the 0.16-\AA displacement of the silicide with respect to the substrate bulk is divided over the 0.08-\AA expansion of the first substrate interlayer spacing and a 0.08-\AA Co-Si interface bond length increase.

Interface data taken from a sample with a Si-rich surface (not shown) yield the same conclusion. The data are consistent with a dilated eightfold interface structure model.

The data taken in this geometry are completely consistent with the conclusions derived in the preceding sections. CoSi₂/Si(111) has Co-Si bonds across an expanded interface. The interface Co atoms are eightfold coordinated. A dilation of the silicide-substrate distance is observed.

V. STRAIN RELAXATION

For thin CoSi₂ films prepared as described in Sec. II we always observe that they are essentially undistorted by lattice strain (we have studied thicknesses ranging from 1.4 to 3.5 Si-Co-Si triple layers). This can be seen from

the position of the $[001]^*$ silicide blocking minimum [see, e.g., Fig. 2(b)], which coincides with the unstrained $[001]^*$ bulk axis (exit angle 35.26°). This suggests that the lattice strain is almost fully relaxed and that the films have the CoSi_2 bulk lattice constant.

We now present a simple model for our films assuming that no residual strain or other elastic distortions are left in the film. Under this assumption we conclude that the strain relaxation should occur through microcracks. Consider the blocking profile in Fig. 4 (circles). The minimum labeled 2 is due to blocking of the substrate yield by silicide atoms (see Sec. IV A). Its presence and depth show that most silicide atoms reside in the vicinity of a perfectly epitaxial site. That is possible only if the silicide, which is in principle incommensurate with the substrate, contains a large concentration of cracks. Figure 7 shows a possible configuration of silicide patches. We note that the experiment is insensitive to the atomic bonding configuration at the cracks in between the patches. The average lateral misfit is proportional to the size of the unstrained patches. The depth of blocking minimum 2 in Fig. 4 is sensitive to the average misfit Δx and decreases with increasing patch size.

In order to obtain an estimate for the average patch size we have performed Monte Carlo simulations for several sizes. An excellent fit to the data is obtained for a size of 35 \AA [see Fig. 4(d), solid curve], and less good agreement for a diameter of 55 \AA (dotted curve). The latter simulation indeed predicts a shallower minimum 2. The substrate is less efficiently shadowed and blocked by the silicide, which results in a too high overall yield. Minimum 2 completely disappears for even larger patches. On the other extreme, fair agreement with the data, with minimum 2 only slightly too deep, is obtained in a simulation for a fully coherent strained silicide (not shown).

From this we infer an upper limit for the average distance between cracks, which is roughly 50 \AA . The data indicate that the average silicide lateral misfit does not exceed $\sim 0.15 \text{ \AA}$. For a typical patch size of 35 \AA the maximum lateral misfit between the silicide and the sub-

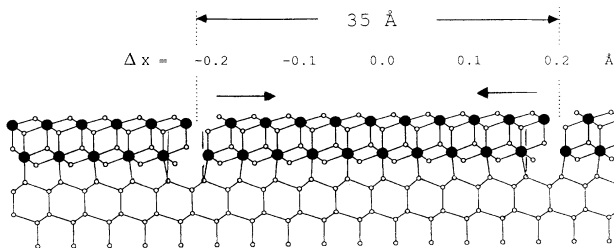


FIG. 7. Possible model of a silicide film in which the lattice strain is fully relaxed. The lattice mismatch is exaggerated. From the data (Fig. 4) we conclude that most of the silicide atoms reside in or near perfect registry with the substrate. For a strain-relaxed film, that is possible only if the silicide has a large number of microcracks. For unstrained patches of $\sim 35 \text{ \AA}$, as used in the fits, the lateral misfit Δx of the silicide atoms with respect to the substrate increases linearly from zero in the center to $\sim 0.2 \text{ \AA}$ at the patch perimeter.

strate at the patch perimeter is $\sim 0.2 \text{ \AA}$. The corresponding silicide-substrate bond-angle distortion amounts to $\sim 5^\circ$ (see Fig. 7). From the silicide height distribution (first-layer fractional coverage 1.00 ± 0.15) we know that the patches should fit closely together as sketched in Fig. 7. For patches which are much smaller than 35 \AA the cracks themselves might cover a considerable fraction of the surface and thus affect the Si and Co blocking patterns. In all calculations in this paper a patch size of 35 \AA has been assumed.

We admit that on the basis of our data alone we cannot exclude the possibility of a fully strained and coherent silicide. Most fits would not become significantly worse than those obtained for small unstrained patches. However, in order to be consistent with the observed bulklike $[001]^*$ silicide direction a strained film would have to be stretched in all three directions (i.e., parallel and perpendicular to the surface) by 1.2% . This behavior would have to remain unchanged over the range of coverages studied, from 1.4 to 3.5 triple layers. In addition we note that strained CoSi_2 films can in fact be prepared and that they combine the lateral stretching by 1.2% with a perpendicular contraction by 1.1% , which corresponds to a Poisson ratio of $\alpha = -\epsilon_{\perp}/\epsilon_{\parallel} = 0.9$.^{25,44}

Note that all previous conclusions on the topology and the relaxations of the interface are not affected by the small difference between strained and unstrained silicide.

VI. DISCUSSION

The determination of the $\text{CoSi}_2/\text{Si}(111)$ interface structure completes a consistent picture concerning the silicide-substrate and silicide-vacuum interfaces of $\text{CoSi}_2(111)$ and $\text{NiSi}_2(111)$. These silicides exhibit the different chemical behavior predicted by van den Hoek *et al.* and Hamann (see Fig. 8),⁷⁻⁹ not only at the interfaces, but also at the surfaces: at the bulklike-terminated $\text{NiSi}_2(111)$ surface, the metal-centered orbital is completely filled with electrons. This results in a stable surface with sevenfold-coordinated Ni atoms. As to the interface, because of the complete filling of the metal-centered orbital, the only candidate for an interface chemical bond with the substrate is the empty Si dangling bond of the disilicide. This results in an interface with Si-Si interface bond and sevenfold-coordinated Ni atoms. By contrast, Co has one electron less than Ni. At the $\text{CoSi}_2(111)$ surface the metal-centered orbital is half filled and is an ideal candidate for formation of a Co-Si bond. The latter then

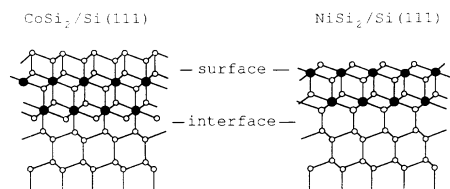


FIG. 8. Comparison of $M\text{Si}_2/\text{Si}(111)$ interface and $M\text{Si}_2(111)$ surface structures ($M = \text{Co}, \text{Ni}$). The Co atoms are eightfold coordinated and the Ni atoms are sevenfold coordinated, both at the most stable surfaces and at the interfaces.

makes the Co coordination number 8. This happens at both the Si-rich CoSi₂(111) surface and the CoSi₂/Si(111) interface.

We observe an expansion of the silicide-substrate distance by 0.16 Å. In other experiments dilations were found of 0.14 Å,¹⁹ 0.05 Å,¹⁸ 0.04 Å,²⁰ and zero.¹⁷ No interface structure determinations have been reported on fully strained silicides:⁴⁴ the lattice strains in the silicide films were found to be either fully^{17,18} or for a large part^{19,20} relaxed, as in our case.

Apart from the work by Rossi *et al.*,²² we are not aware of any investigations on the interface between epitaxial CoSi₂ films with a thickness of ~2 triple layers and Si(111). The silicide-substrate distance expansion might be specific for a very thin silicide film. However, we suspect that the interface expansion is caused by the anti-bonding interaction between the dangling-bond orbital of the threefold-coordinated interface Si layer and the filled Si substrate orbitals.⁸ The interface relaxation observed (0.16 Å) is similar to that present at the Si-rich surface.²⁵ The latter relaxation, between the topmost surface Si and Co atoms, amounts to 0.15 Å. The Si-rich surface may be viewed as a type-*A* oriented interface.²³⁻²⁵

The complete strain relaxation at the low coverages studied in this work is somewhat unexpected. In heteroepitaxial systems strain relaxation is believed to occur beyond a certain critical thickness⁴⁵ and fully strained epitaxial CoSi₂/Si(111) films have been obtained at much larger thickness (40 Å).⁴⁴ It could be that the structure of the "unreacted" metal film before annealing⁴⁶ and the formation kinetics of the film at 330°C govern the final structure. We have observed that upon annealing at ~550°C the relaxed film converts into an islanded structure in which each island is strained.

We note that in the case of a complete relaxation of the lattice strain the formation of *small* patches is the only way for CoSi₂ to grow on Si(111) without steps or defects at the interface. Let us consider the interatomic distances for the rather close-packed eightfold interface configuration (see Fig. 9) for different lateral misfits. In the center of the patch there is no lateral misfit. The interface Si atom and the surrounding first Si substrate atoms, with which it does *not* form bonds, are ~2.74 Å apart [Fig. 9(a), double arrow]. At the edge of a patch of 35-Å size, a lateral misfit of 0.2 Å [Fig. 9(b), exaggerated] reduces this distance to ~2.58 Å and brings it much closer to a regular Si-Si bond length (2.35 Å). In the case of 0.3-Å misfit (50-Å patch) the interatomic distance reduces further to 2.51 Å. It might be that the maximum unstrained patch size observed is related to the maximum

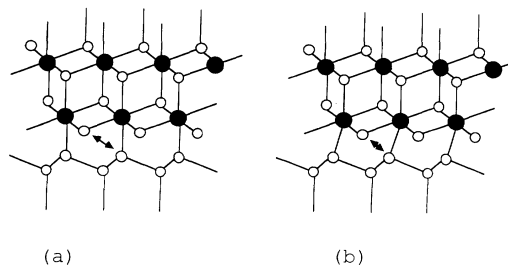


FIG. 9. (a) Center and (b) edge parts of a CoSi₂ patch on Si(111). The misfit (exaggerated) at the perimeter of the patch results in a reduction of interatomic distances in the densely packed eightfold interface (see double arrows) which puts an energetic constraint on the maximum unstrained patch size (see text).

lateral misfit energetically allowed by the eightfold interface. It remains to be investigated what the atomic structure at the cracks is and what role, for example, steps play in their formation.

VII. CONCLUSIONS

We have prepared flat CoSi₂ films (thickness ~2 Si-Co-Si triple layers) on Si(111) substrates. The topmost Co-Si interlayer spacing in the Co-rich surface is relaxed inward by 0.14±0.04 Å. The silicide is attached to the substrate through Co-Si bonds. The interface Co atoms are eightfold coordinated with Si atoms, in agreement with theoretical predictions.⁷⁻⁹ The silicide-substrate distance is observed to be dilated by 0.16±0.08 Å. The first Si substrate layer is relaxed outward by 0.08±0.08 Å. The interface Co-Si bond length is thus expanded with respect to the Si-Si bulk distance by 0.08 Å.

The lattice strain in the silicide is probably almost fully relaxed. The silicide then contains a large concentration of cracks. On the assumption of complete strain relaxation the average distance between cracks is estimated to be smaller than roughly 50 Å.

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