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Structure determination of the $CoSi_2$:Si(111) interface by x-ray standing-wave analysis

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The atomic structure at the interface of $CoSi_2$ films on Si(111) has been investigated with x-ray standing waves. The Co atoms at the interface are five-fold-coordinated. The bonds across the interface are dilated by 0.05 ± 0.03 Å. For the range of film thicknesses studied (9–28 Å), the $CoSi_2$ lattice was measured to be almost free of strain in the direction perpendicular to the interface plane.

I. INTRODUCTION

Epitaxial silicide layers of the near-noble metals Co and Ni can be grown on Si(111) with a high degree of perfection and with abrupt interfaces.[1] These heterostructures are extensively studied because of their fundamental interest and possible applications in diversified fields.[2] They serve as model systems for Schottky-barrier formation;[3] the Schottky-barrier height may be directly correlated to the electronic bonding arrangement at the interface, provided the geometric interface structure is accurately known. In this paper we present a structural investigation of the $CoSi_2$:Si(111) interface with x-ray standing waves (XSW) using synchrotron radiation. In studies of epitaxial layers, this method has previously been applied to determine the atomic bonding arrangement at the $NiSi_2$:Si(111) interface.[4]

The silicides $CoSi_2$ and $NiSi_2$ have the cubic CaF_2 structure with bulk lattice parameters smaller than that of Si by 1.2% and 0.46%, respectively. For $CoSi_2$ the commonly observed epitaxial relationship with Si(111) is one in which the film is (111) oriented but 180° rotated about the [111] substrate normal, labeled as type-*B* epitaxy.[5] The silicide may also have the same in-plane orientation as the Si(111) substrate (type-*A* epitaxy), but it appears that such a heterostructure can only be obtained free of *B*-type grains for $NiSi_2$.[1] In modeling the corresponding interface structures one is left with only two distinct possibilities, if the tetrahedral coordination of the Si atoms is to be preserved in passing over from the silicon to the silicide lattice. Figure 1 shows these two possibilities for a *B*-type film. The two models are distinguished by the silicide being terminated with either fivefold- or sevenfold-coordinated metal atoms, as opposed to eightfold coordination for metal atoms in bulk disilicide. For the $NiSi_2$:Si(111) system the results of various techniques agree on both *A*- and *B*-type interfaces being sevenfold coordinated.[4,6,7] The chemical and structural similarity of nickel and cobalt silicides has led several authors to believe that also for the $CoSi_2$:Si(111) interface a sevenfold coordination is favored.[8,9] But by comparing measured cross-section transmission electron microscope (TEM) lattice images with calculated ones, Gibson *et al.*[10] identified fivefold coordination as the most likely model (a definite structure assignment was hampered by uncertainties in the TEM image parameters). Recently we reported preliminary ion scattering data which gave evidence for a fivefold-coordinated $CoSi_2$:Si(111) interface.[11] The XSW measurements presented here rule out the sevenfold model and show that the model based on fivefold coordination is indeed correct. Furthermore, the (111) interplanar distance has been determined at the interface and in the $CoSi_2$ overlayer. Across the interface this distance is slightly dilated. In the overlayer lattice the interplanar distance is equal to that in bulk $CoSi_2$, i.e., essentially free of strain for the range of thicknesses studied (9–28 Å).

II. X-RAY STANDING-WAVE ANALYSIS

With regard to the XSW method, the relevant difference between fivefold and sevenfold coordination is the distance $d_{\rm IF}$ of the first Co layer to the last (111) diffraction plane in the substrate (Fig. 1). The (111) interplanar spacing is $d_{\rm H}=3.135$ Å for Si and 3.097 Å for bulk $CoSi_2$. The bond across the interface can be assumed to be part of either the silicon substrate or the silicide; in what follows the former is assumed. Then, using bulk bond lengths, the interface distance is calculated to be 2.74 and 3.52 Å for unrelaxed fivefold- and sevenfold-coordinated interfaces, respectively.

XSW is by now well established as a structure probe

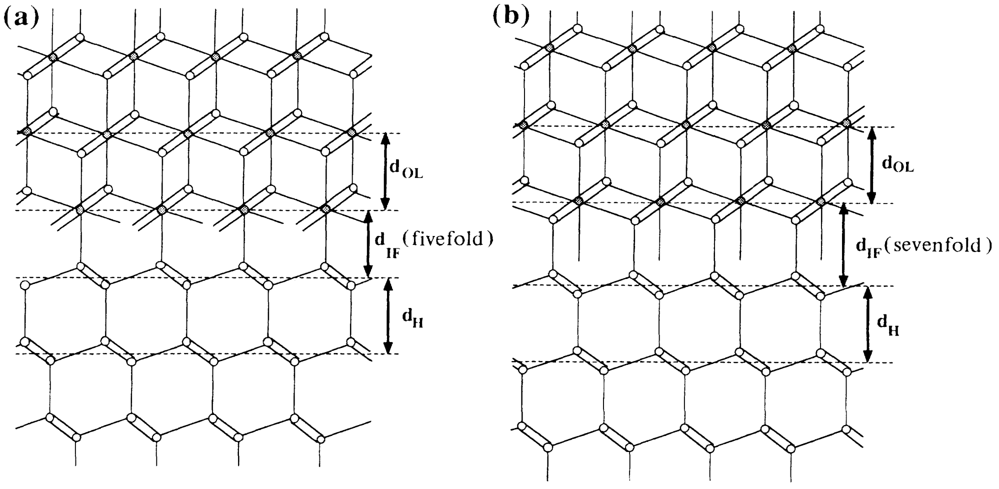

FIG. 1. Ball-and-stick models of the *B*-type CoSi$_2$:Si(111) interface in a projected view down the $[1\bar{1}0]$ direction. Open and solid circles represent Si and Co atoms, respectively. The Co atoms are (a) fivefold or (b) sevenfold coordinated at the interface.

of surface adsorbates[12] and epitaxial overlayer systems.[4] When a monochromatic x-ray beam is Bragg reflected from the Si substrate lattice, the interference between the incident and reflected waves gives rise to a standing-wave field which extends across the interface. According to the dynamical theory of x-ray diffraction the phase of the standing-wave field changes by π radians as the crystal is rocked through the Bragg reflection.[13] On the low-angle side of the reflectivity curve the antinodal planes of the standing-wave field lie halfway between the diffraction planes and move with increasing angle towards a position coinciding with the diffraction planes. The positions of the overlayer lattice planes are determined by measuring as a function of rocking angle the fluorescence radiation yield emitted by the Co atoms, which is proportional to the local **E** field intensity of the standing-wave field. Henceforth the overlayer is assumed to be composed of N lattice planes of the fluorescing element Co with a spacing d_{OL} and starting at a distance d_{IF} from the topmost diffraction plane of the substrate (Fig. 1). For convenience we introduce the structural parameters $\delta_{\mathrm{IF}} \equiv d_{\mathrm{IF}}/d_{\mathrm{H}}$ and $\gamma \equiv d_{\mathrm{OL}}/d_{\mathrm{H}} - 1$, as in Ref. 4.

In principle, any periodic overlayer influences the standing-wave pattern generated in the substrate. Here this effect can be neglected, since the layers are very thin compared to the extinction depth in the layer material. Under this condition the total fluorescence yield $Y(\theta)$ emitted by the N overlayer planes as a function of reflection angle θ is given by[4]

$$Y(\theta)/NC = 1 + R(\theta) + 2\sqrt{R(\theta)}F\cos[v(\theta) - 2\pi D] \ , \quad (1)$$

where the reflectivity $R(\theta)$ and the phase $v(\theta)$ can be calculated from dynamic diffraction theory.[13] D and F are defined by

$$D \equiv \delta_{\mathrm{IF}} + (N-1)\gamma/2 \ , \quad (1a)$$

$$F \equiv f_c \sin(\pi N \gamma)/N \sin(\pi\gamma) \ , \quad (1b)$$

and C includes constant geometry parameters. If the fluorescence selected overlayer atoms occupy just one site coherently, the parameter f_c in Eq. (1b) gives the coherent fraction, i.e., the fraction of overlayer atoms which are positioned exactly in the N planes. The parameters D and F describe all possible yield curves and are determined experimentally by fitting the measured yield curves to Eq. (1). The quantities δ_{IF} and γ then follow from determining D for (at least) two different coverages N and solving Eq. (1a).

Once γ is known, the coherent fraction f_c for each sample can be calculated from Eq. (1b). The coherent fraction is a measure of the crystalline quality of the overlayer.

The above XSW analysis depends on precise knowledge of the number of overlayer planes N. Since N cannot be uniquely determined from the shape of a fluorescence yield curve, it should be acquired from another independent method. Here Rutherford backscattering spectrometry (RBS) is employed.

III. EXPERIMENTAL PROCEDURE

The silicide overlayers were prepared in ultrahigh vacuum at the Fundamenteel Onderzoek der Materie (FOM)—Institute, where also the RBS analyses were performed. The XSW measurements were performed at the Hamburger Synchrotronstrahlungslabor (HASYLAB). The Si(111) substrates ($6\times10\times0.38$ mm^3 in dimension) were cleaned and annealed following the procedure outlined in Ref. 4. Cobalt was then deposited at room temperature by sublimation from resistively heated Co wires. The deposition rate was $\sim5\times10^{13}$ atoms cm^{-2} s^{-1}. The pressure rose to 7×10^{-8} Pa during deposition, but recovered quickly to base pressure (7×10^{-9} Pa) once the deposition was stopped

It is well known that upon heating to $\sim$550 °C for a few minutes a solid-state reaction takes place at the interface between the deposited Co layer and the Si substrate under UHV conditions. An epitaxial $CoSi_2$ layer is then formed.[14] However, unlike the Ni:Si(111) system, for thin films such a treatment generally yields discontinuous $CoSi_2$ layers with sizable holes in them (pinholes). This introduces a large uncertainty in the number of Co planes N contributing to the fluorescence yield. In the present study a substantial improvement in layer morphology was obtained by first depositing at room temperature a thin layer of Si on top of the unreacted Co film and then reacting the resulting Si/Co/Si(111) sandwich structure at elevated temperature. The Si layers were deposited *in situ* with use of an *e*-beam evaporator and were typically chosen to be of the same thickness as the Co films. The sandwich structures were heated for 3 min isochronally at stepwise increased temperatures starting at 300 °C. *In situ* reflection high-energy electron diffraction (RHEED) was used after each anneal step to verify the resulting surface periodicity. Once the surface exhibited the sharp 1×1 RHEED pattern which is typical for the formation of a well-ordered epitaxial disilicide,[15] the annealing procedure was stopped. The temperature at which the 1×1 pattern appeared was $\sim$400 °C.

In the above manner we have prepared overlayer systems of different thickness, containing, on average, $N\cong4.7$, 7.9, and 9.2 Co planes. One sample, with $N=3.0$, was prepared by annealing a sandwich structure having a top Si layer ten times thicker than the Co layer at a temperature of 550 °C. The N value for each sample was determined by measuring with RBS the areal density of deposited Co atoms and noting that a single Co plane in bulk silicide ($N=1$) contains 8.02×10^{14} atoms cm^{-2}. Clearly, the conversion of areal densities into N values is accurate only if the $CoSi_2$ layer is reasonably uniform and covers most of the substrate surface area. In order to check upon the latter point, the overlayer morphology has been studied using high-resolution ion backscattering[16] and high-resolution TEM in planar and cross-sectional view. All silicide layers are found to be continuous and free of pinholes, justifying the direct conversion of areal density to number of Co planes. For the layers under investigation the epitaxial relationship observed is entirely type B, in good agreement with other results.[17] Details on morphology and structure of the $CoSi_2$ layers will be published elsewhere. The TEM micrographs show that for $N>4.7$ the interface contains steps of height $3d_H$. On either side of these distinct steps the interface is structurally perfect and flat. The inclusion of these steps in structure models of the interface hardly affects the XSW analysis and can therefore be ignored.

In order to protect the ultrathin silicide overlayers from contamination during transport to HASYLAB and during XSW analysis (all in air), the samples were capped by an amorphous layer of Si with a thickness of 50–80 Å. (The amorphous caps were "densified" by annealing at 200 °C for 2 min.) The presence of this layer does not influence the XSW analyses.

The experimental arrangement at HASYLAB for XSW measurements has been described elsewhere.[18–20] With use of an asymmetrically cut double-crystal monochromator the synchrotron radiation from Doppel-Ring Speicheranlage (DORIS) was collimated at an energy of 14.2 keV and directed onto the sample. Scans through the rocking curve were made by varying the energy of the monochromatized beam, while the sample remained fixed in position. The Co $K\alpha$ fluorescence yield (at 6.9 keV photon energy) was measured with a Si(Li) solid-state detector at a distance of 10–20 mm from the sample. The (111) Bragg-reflected x-ray intensity was detected by a NaI scintillation counter. The quality of each sample as generator of standing waves was examined through high-resolution double-crystal topographs.[21] Perfect regions on the sample were then selected for XSW measurements. The reflectivity and fluorescence yield were measured simultaneously as a function of $\lambda-\lambda_B$, where λ_B is the wavelength determined by Bragg's equation $2d_H\sin\theta_B=\lambda_B$.

IV. RESULTS AND DISCUSSION

A typical reflectivity curve is shown in Fig. 2(a). The angular profiles of the measured fluorescence yields are shown in Figs. 2(b)–2(e) in order of increasing overlayer thickness. For each of the samples the parameters D and F [Eqs. (1a) and (1b)] were determined by least-squares fitting the theoretical expression for the fluorescence yield given by Eq. (1) to the experimental data. Prior to the fits the theoretical yield curves were convoluted with the experimental resolution function, as determined from the shape of the reflectivity curve.[22] The results of the fits are shown in Figs. 2(b)–2(e) as solid curves. The corresponding optimal values for D and F are listed in Table I. The D values are plotted in Fig. 3 against $N-1$. The data are consistent with a linear dependence on $N-1$, as in Eq. (1a). The straight solid line in Fig. 3 represents the best fit to the data points, which is obtained for

$$\delta_{\mathrm{IF}}=0.891\pm0.011\ ,$$

and

$$\gamma=(-11\pm5)\times10^{-3}\ .$$

Note, that this δ_{IF} value corresponds to the intercept of the solid line with the ordinate axis and that $\gamma/2$ is given by the slope of the line. For comparison, Fig. 3 shows also the expected dependencies of D on layer thickness for unrelaxed fivefold- and sevenfold-coordinated interfaces, assuming for both interface models a bulklike interplanar spacing in the overlayer (dashed lines). The data are very close to the prediction for fivefold coordination. Clearly, a sevenfold-coordinated interface is ruled out. The ease with which the two interface models can be distinguished from one another is illustrated for the sample with $N=7.9$ in Fig. 2(d), where the angle-dependent fluorescence yields for the unrelaxed fivefold- and sevenfold-coordinated interfaces are shown as dashed curves.

The sensitivity of the XSW method to the structural

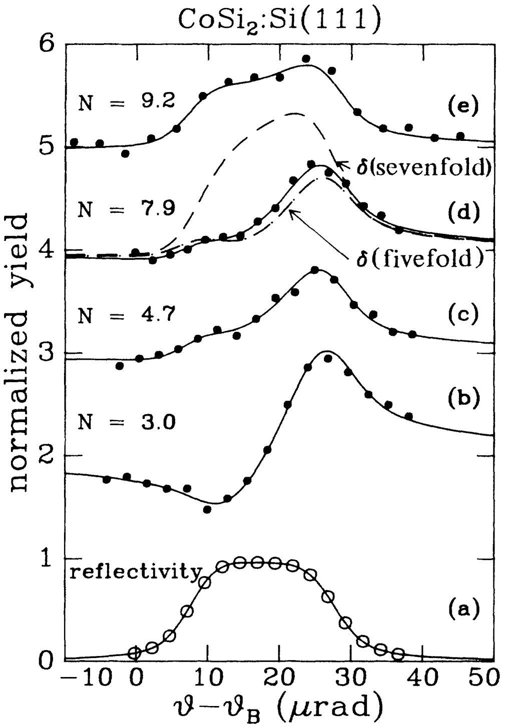

FIG. 2. Angular profiles of the reflectivity and the Co $K\alpha$ fluorescence yield for CoSi$_2$:Si(111) samples of different thickness. The reflection angle scale refers to the crystal angle of the monochromator. The circles are the data points, the solid lines are the best fits. The data were obtained using the (111) Bragg reflection at an x-ray energy of 14.2 keV. Curves b–e have an accumulative vertical offset of 1 unit. Curve a: typical reflectivity curve of the Si(111) substrate, taken on the sample with $N=7.9$. Curves b to e: fluorescence curves for samples with overlayer thicknesses of (b) $N=3.0$, (c) $N=4.7$, (d) $N=7.9$, and (e) $N=9.2$. The dash-dotted and dashed curves represent the yields calculated for unrelaxed fivefold and sevenfold-coordinated interfaces, assuming for both interface models a bulklike interplanar spacing in an overlayer, containing $N=7.9$ planes of Co atoms.

TABLE I. The parameters D and F measured on CoSi$_2$:Si(111) samples with different number of Co planes N in the silicide. The error in the number of Co planes is determined by the accuracy of the RBS measurements. The coherent fraction f_c of Co atoms is approximately equal to F. Sample 1 was annealed at 550 °C, the other samples were annealed at 400 °C.

Sample	Number N of Co planes	D	$F\approx f_c$
1	3.0±0.2	0.883±0.002	0.79±0.01
2	4.7±0.3	0.859±0.006	0.40±0.02
3	7.9±0.5	0.863±0.006	0.46±0.01
4	9.2±0.6	0.847±0.016	0.19±0.03

parameters δ_{IF} and γ depends on the perfection of the CoSi$_2$ overlayers. The perfection in turn is described by the coherent fraction f_c. The measured coherent fractions are listed in Table I in order of increasing overlayer thickness. They have been derived from Eq. (1b). Since both γ and N are very small for the samples under investigation, f_c is equal to F. The coherent fractions ranged from 0.8 to 0.4, with the exception of the thickest overlayer ($N=9.2$), for which f_c is only 0.19. The values suggest a correlation with layer thickness and possibly with annealing temperature. Presumably, for the thickest overlayer the annealing procedure described in Sec. III does not adequately order the lattice. The much higher coherent fractions for the other samples are still lower than those for NiSi$_2$ overlayers.[4] The lower quality is possibly related to local disorder in the CoSi$_2$ lattice at atomic steps at the interface. This corroborates the findings of other studies[17] that CoSi$_2$ layers of good crystal quality are more difficult to grow.

The overlayers were found to be completely relieved of strain along the direction perpendicular to the interface plane. If the CoSi$_2$ layers were to grow pseudomorphic on Si(111), as is the case for NiSi$_2$ layers of similar thickness,[23] then a substantial perpendicular strain would be present. Assuming the same ratio of perpendicular to parallel strain as for NiSi$_2$,[4] a pseudomorphic growth of CoSi$_2$ would correspond to $\gamma=-23\times10^{-3}$. On the other hand, complete absence of strain implies $\gamma=-12\times10^{-3}$. These values are to be compared with the experimental one, $\gamma=(-11\pm5)\times10^{-3}$. It is concluded that the 1.2% mismatch between CoSi$_2$ and Si is largely accommodated by defects (e.g., dislocations) in the layer rather than by lattice strain. It was noted in Sec. III that steps are present at the interface. Their existence is known to be one of the mechanisms for strain relief.[10]

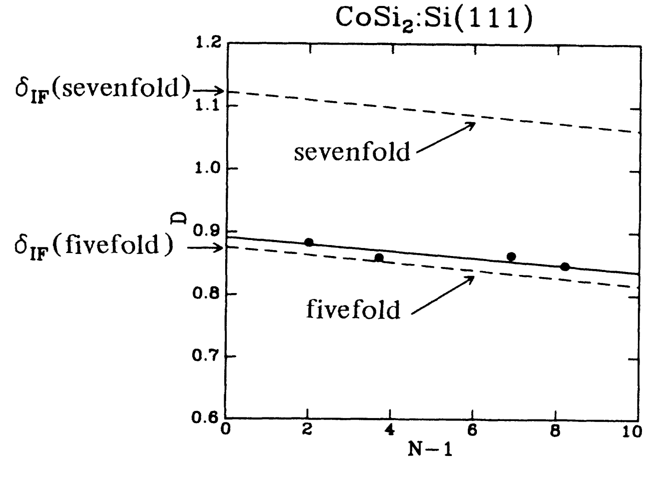

FIG. 3. The fitted D values as a function of overlayer thickness $N-1$. Solid circles denote the data points. The solid line represents a least-squares fit to the data points. The dashed lines show the expected dependencies of D on $N-1$ for unrelaxed sevenfold- and fivefold-coordinated interfaces, assuming for both interface models a bulklike interplanar spacing in the overlayer.

The lowered crystal symmetry at the fivefold-coordinated interface may give rise to a local lattice distortion in the form of bond-length or bond-angle changes. In our XSW analysis such lattice distortions would be evident as a change in d_{IF}. A distance parameter of $\delta_{IF}=d_{IF}/d_H=0.891\pm0.011$ was measured, yielding $d_{IF}(\text{expt})=2.79\pm0.03$ Å. Comparing this value with $d_{IF}=2.74$ Å expected for an unrelaxed fivefold interface, we conclude that the interface bonding arrangement, if distorted at all, is such that d_{IF} is dilated by 0.05±0.03 Å. This may be the result of an expansion of the Si—Co bond across the interface and/or an angular distortion of the Si—Si bonds at the substrate side of it [Fig. 1(a)].

In summary, the geometric structure of the epitaxial $CoSi_2$:Si(111) interface has been determined by x-ray standing wave analysis. The Si atoms in the top layer of the Si(111) substrate are bonded to the Co atoms in the silicide, corresponding to fivefold coordination of the Co atoms at the interface. This is in striking contrast with XSW (Ref. 4) and ion scattering[7] results for $NiSi_2$:Si(111), which both gave conclusive evidence for sevenfold coordination at that interface. The reason for the difference in coordination number between Co and Ni is not yet known. Quantum chemical calculations on cluster models of the different interfaces are now in progress in an attempt to resolve this issue.[24]

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