

## Evidence of Eightfold Coordination for Co Atoms at the CoSi<sub>2</sub>/Si(111) Interface

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We have studied two-dimensional and three-dimensional CoSi<sub>2</sub> epitaxial layers on Si(111) by polarization-dependent surface extended x-ray-absorption fine structure on the Co *K* edge (7707 eV). The Co interface atoms are coordinated with eight Si atoms, as in bulk CoSi<sub>2</sub>, with an interface bond length of 2.35(0.03) Å. Ultrathin three-dimensional CoSi<sub>2</sub> layers are 2.5% contracted in the direction perpendicular to the interface.

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CoSi<sub>2</sub> and NiSi<sub>2</sub> are metallic silicides which have the CaF<sub>2</sub> structure and can grow epitaxially on the low-index faces of Si.<sup>1</sup> Their importance in the progress of interface science is manifold: the epitaxy is easily reproduced and allows the growth of single-crystal metallic contacts on Si of primary interest for technological applications<sup>2</sup>; the interface with Si(111) is atomically sharp<sup>1</sup>; the modeling of these interfaces represents the frontier of theoretical analysis of metal silicide/silicon interfaces.<sup>3,4</sup> For all these reasons the detailed knowledge of the interface bonding geometry is a key point, and has already motivated a large number of studies.

NiSi<sub>2</sub> forms an interface with Si(111) where the Si atoms of the silicide bond to the top layer of Si atoms of the substrate.<sup>5</sup> The Ni atoms lying closest to the interface are therefore in sevenfold coordination with the first Si neighbors, instead of the eightfold coordination of Ni in bulk NiSi<sub>2</sub> (Fig. 1). The interface energy for the Ni-Si sevenfold coordination has been found to indeed be a minimum in total-energy calculations.<sup>3</sup>

There is clear evidence from recent experiments that the CoSi<sub>2</sub>/Si(111) interface is structurally different: The sevenfold coordination for Co has been excluded by x-ray standing-wave analysis (XSW),<sup>7</sup> ion channeling,<sup>8</sup> by cross-sectional TEM,<sup>1</sup> and by LEED.<sup>6</sup> This has opened a crucial question, given the chemical similarity of Ni and Co silicides. A model has been proposed of fivefold coordination for the Co at the interface (Fig. 1) where the five Si first neighbors would number three in the lowest CoSi<sub>2</sub> incomplete layer, one in the CoSi<sub>2</sub> layer above, and one from the Si(111) substrate.<sup>1,7,8</sup> This model has been recently questioned by two independent theoretical calculations of the interface energy,<sup>3</sup> and of the interface bonding configuration.<sup>4</sup> The theoretical results definitely favor a higher-than-fivefold coordination for Co at the interface. The determination of the bonding configuration of Co at the CoSi<sub>2</sub>/Si(111) interface is of crucial importance for the understanding of the energetics of the epitaxial growth and the stability of the interface in this model system.

We have directly addressed the problem of the Co-Si interface coordination by means of polarization-dependent surface extended x-ray-absorption fine-structure (SEXAFS)<sup>9</sup> experiments on the Co *K* edge on ultrathin layers of CoSi<sub>2</sub> produced *in situ*. We deposited thicknesses of  $6(\pm 2) \times 10^{14}$  Co atoms cm<sup>-2</sup> and  $1.5(\pm 0.3) \times 10^{15}$  Co atoms cm<sup>-2</sup> on virgin Si(111) 7×7 surfaces, in a vacuum of  $1 \times 10^{-8}$  Pa, and annealed at 630°C by direct Ohmic heating. The data used as standard phase and amplitudes were obtained from a 150-Å-thick CoSi<sub>2</sub> layer grown *in situ* by evaporation of Co onto Ohmically heated Si(111) held at 600°C. Different preparations of the CoSi<sub>2</sub> standards gave identical LEED and EXAFS results. No polarization effects were detected on the standard. The x rays from the DCI storage ring at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique were monochromatized by a double-crystal Si(311) device, separated from the UHV sample chamber by a Be window. The x-ray-absorption coefficient was measured by the total electron-yield technique.<sup>9</sup> The characterization of the

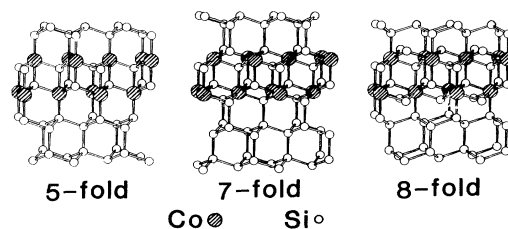


FIG. 1. Models [after Hamann (Ref. 3)] illustrating the 3D CoSi<sub>2</sub>/Si(111) interface discussed. The picture of the 2D interface is easily understood by removing one CoSi<sub>2</sub> triple layer. The epitaxial layers can maintain the substrate crystallographic axis (type *A*) or can be rotated by 180° around the [111] axis (type *B*). From the point of view of SEXAFS on first and second NN, the two orientations for each model interface are equivalent. There is independent evidence that only type-*B* interfaces are formed between CoSi<sub>2</sub> and Si(111) (Ref. 6).

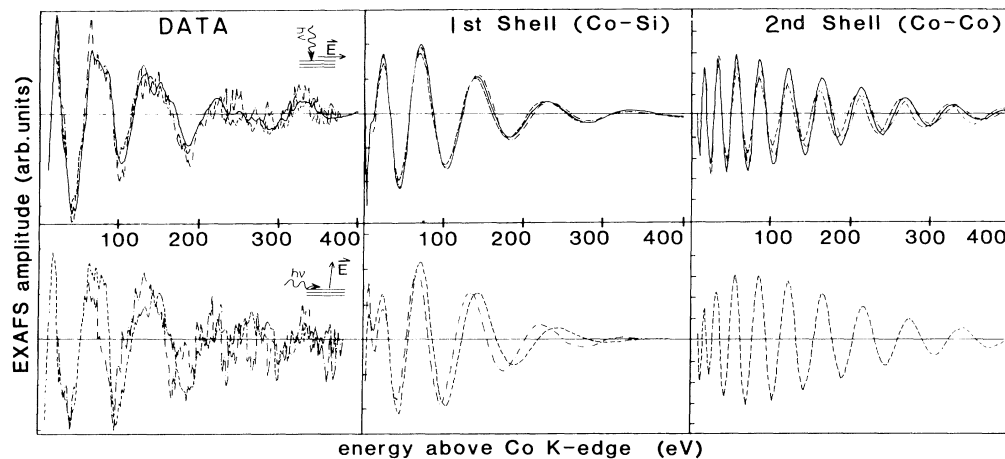


FIG. 2. SEXAFS data for  $\text{CoSi}_2$  2D and 3D epitaxial layers on Si(111), and for bulk  $\text{CoSi}_2$ : first column: background-subtracted raw data; second column: Fourier-filtered Co-Si first NN EXAFS oscillations; third column: Co-Co second NN EXAFS. The data were multiplied by  $k^2$  and Fourier transformed in the range  $k = 3.2\text{--}10.0 \text{ \AA}^{-1}$ . The first row shows the bulk  $\text{CoSi}_2$  reference (solid curves), and the results for normal x-ray incidence, i.e., polarization vector in the interface plane, for the 2D film (dot-dashed curves), and 3D film (dashed curves). The second row shows the results for grazing incidence (polarization vector almost normal to the interface).

silicide films was done with Auger, LEED, SEXAFS, and x-ray-absorption near-edge structure spectroscopies.<sup>10</sup>

LEED and Auger analyses of the thinnest film show that the interface is covered with Si, thermally migrated from the substrate during the annealing, displaying a clear  $7 \times 7$  LEED pattern, with superimposed  $\sqrt{3} \times \sqrt{3}$  beams. No Co low-energy Auger signal (54 eV, escape length 5–7 Å) is visible at the annealed surface, while the 775-eV Co peak is measured (escape length 15–20 Å) indicating that over two layers of Si are covering the surface. The LEED patterns arise from the layers of the sample which do not contain Co at the Auger detection level ( $< 3\%$  of a monolayer). The background-subtracted SEXAFS data and the Fourier-filtered Co-Si first-nearest-neighbor (NN) and Co-Co second NN signals are collected in Fig. 2. The thinnest film shows a full  $\text{CoSi}_2$  coordination for the Co atoms when the E vector of the x rays is in the plane of the interface (normal incidence), i.e.,  $N_{\text{Co-Si}} = 6$  ( $N^* = 8$ ; see caption of Table I), and  $N_{\text{Co-Co}} = 6$  ( $N^* = 9$ ). When the E vector is almost perpendicular to the interface (grazing incidence at  $18^\circ$  off the surface plane) no Co-Co signal is detected: This indicates the 2D character of the  $\text{CoSi}_2$  layer obtained in these conditions. The interface coordination is directly derived from the polarization dependence of the amplitude of the Fourier-filtered oscillations due to the first nearest neighbors (Co-Si). Perpendicular to the silicide plane there are two interfaces with Si: one with substrate Si and one with the Si overlayer. The alignment of the E vector with the interface bonds allows one to conclusively discriminate among the three possible (simple) interface models of Fig. 1: fivefold, sevenfold

[ $\text{NiSi}_2/\text{Si}(111)$ -like], and eightfold (bulklike with an added undercoordinated Si interface layer). From Table I, one can see the effective coordination numbers that should be measured by SEXAFS concerning the first and second coordination shells in the various models. In Table II one finds the measured bond lengths. Both the fivefold and sevenfold models present an (opposite) very large asymmetry of the polarization-dependent SEXAFS “effective” coordination number  $N^*$  with respect to the surface normal. No asymmetry is observed in the experimental  $N^*$ 's. The results are as follows: six Si neighbors in the  $\text{CoSi}_2$  layer ( $N^* = 8$ ) at  $2.32(0.02) \text{ \AA}$  interatomic distance and two at the interfaces ( $N^* = 8$ ) at  $2.35(0.03) \text{ \AA}$ , i.e., a total of eight Si neighbors. Clearly the data are conclusive as to the eightfold coordination for Co at both the lower and upper interfaces. This is the first conclusion of this Letter.

The eightfold interface coordination can be understood as being due to one layer of Si in  $\text{CoSi}_2$  lattice positions where the Si atoms are only threefold coordinated. This represents a new explanation for all the recent experimental results published in the references of this Letter, and nicely confirms the theoretical results of the bonding configuration and of the interface energy of Refs. 3 and 4. The interface layer of anomalously bound Si and the existence of an epitaxial Si overlayer which lowers the surface energy of the silicide,<sup>11</sup> imply that (1) the silicon epilayer is encountered by newly deposited Co during the thermally assisted growth of  $\text{CoSi}_2$ ; this allows the reaction to continue making single-crystal epitaxial layers up to several hundred Å possible even without the need of Si coevaporation.<sup>12</sup> (2) The availability of Si easily detached from the interface and then transported through

TABLE I. Effective polarization-dependent SEXAFS coordination numbers in the CoSi<sub>2</sub> plane (from normal-incidence data),  $N^*_{\parallel}$ , and perpendicular to the interface plane,  $N^*_{\perp}$ .  $N^*$  is given by  $N^* = 3\sum_i N_i \cos^2 \alpha_i$ , where  $\alpha_i$  is the angle between the electric vector  $\mathbf{E}$  of the x rays and the bonds of the excited atom with the  $i$ th neighbors. The measured data for the 2D and 3D silicides are given in the last column, with the experimental error bars indicated in parentheses. The  $A, B$  refer to the crystallographic type as demonstrated in Fig. 1.

	Fivefold $A$		Sevenfold $A$		Eightfold $A, B$		Experimental	
	Co-Si	Co-Co	Co-Si	Co-Co	Co-Si	Co-Co	Co-Si	Co-Co
1 CoSi <sub>2</sub> layer	2D data							
$N^*_{\parallel}$	4	9	8	9	8	9	8(0.5)	9(1)
$N^*_{\perp}$	7	0	5	0	8	0	8(0.5)	0(1)
2 CoSi <sub>2</sub> layers	3D data							
$N^*_{\parallel}$	4	10.5	8	10.5	8	10.5	8(0.5)	10(1)
$N^*_{\perp}$	7	6	5	6	8	6	8(0.5) <sup>a</sup>	10(1) <sup>b</sup>

<sup>a</sup>Fitted with a reduced  $\delta\sigma^2_{\text{Co-Si}\perp} = (2.5 \pm 1) \times 10^{-3} \text{ \AA}^2$ .

<sup>b</sup>The fitted number of the Co-Co $\perp$  neighbors in the 3D layer is consistent with a thickness of about three layers of CoSi<sub>2</sub>. The Co-Co $\perp$  Debye-Waller factor is reduced by  $\delta\sigma^2_{\text{Co-Co}\perp} = (4 \pm 1) \times 10^{-3} \text{ \AA}^2$ .

the layer requires the existence of some weakly bound Si at the interface. (3) The need of eightfold Co-Si coordination at the interface is likely the cause of the propagation in depth of the interface, with reproduction of the layer of undercoordinated "weakly bonded" Si.

The second experiment was done on an ultrathin 3D CoSi<sub>2</sub> layer obtained with the same procedure as above. In this case between two and three full layers of silicide are formed, buried under spontaneously migrated Si.<sup>11</sup> The LEED pattern shows a  $1 \times 1$  surface, and Auger analysis still shows only Si at the surface. The expected polarization-dependent SEXAFS amplitudes for Co-Si first neighbors, and Co-Co second neighbors for a double layer of CoSi<sub>2</sub> are listed in Table I. The results can be summarized as follows: the eightfold interface coordination is confirmed; the Co-Co second-neighbor coordination is present in both polarization, confirming the 2D-3D transition obtained with the increased coverage; the in-layer distances are those of CoSi<sub>2</sub>, while the perpendicular distances are shorter, indicating a 2.5% reduction of the silicide interlayer spacing  $d$ . This  $d$  contraction is consistently derived, from both the Co-Si first NN (the perpendicular distances are  $2.26 \pm 0.02 \text{ \AA}$ ) and Co-Co second NN measured distances ( $3.73 \pm 0.03 \text{ \AA}$  instead of  $3.78 \text{ \AA}$  as in the plane and in bulk CoSi<sub>2</sub>). This contraction must be imputed to the thinness of the CoSi<sub>2</sub> layer;

in fact, Co has an effective Co-Co coordination which is reduced to one-half in the perpendicular direction for most Co atoms in the 3D double layer of CoSi<sub>2</sub>. A much larger (20%) relaxation of the top layer was proposed in the analysis of the LEED data of Ref. 6 on an eight-layer thick CoSi<sub>2</sub> layer. XSW data for thicker CoSi<sub>2</sub> layers<sup>5</sup> allowed for an interface contraction of  $0.05 \text{ \AA}$ , i.e., the same value that we measure in a direct way on the perpendicular Co-Si distance. A consequence (and confirmation) of the  $d$  contraction in our 3D layer is the reduction of the mean-square relative displacements measured on both Co-Si ( $\delta\sigma^2_{\text{Co-Si}\perp} = 2.5 \pm 1 \times 10^{-3} \text{ \AA}^2$ ) and Co-Co ( $\delta\sigma^2_{\text{Co-Co}\perp} = 4 \pm 1 \times 10^{-3} \text{ \AA}^2$ ) distances perpendicular to the plane, with respect to CoSi<sub>2</sub> and to the in-plane values. The bond stiffening due to the  $d$  contraction is expected to increase the correlation of atomic motions in the CoSi<sub>2</sub> layer in the direction perpendicular to the interface plane. The increase in correlation is observed for both first and second NN distances, in spite of the relatively long Co-Co second NN bond length. This effect gives a higher weight in the spectra to the short perpendicular Co-Si bonds in the silicide layer than to the longer perpendicular Co-Si bonds at the interface. The same value of the perpendicular interface Co-Si bond length as derived from the 2D layer ( $2.35 \text{ \AA}$ ) can be used in the fitting of the data if a higher weighting factor (corresponding to the reduced Debye-Waller factor) than just counting neighbors is given to the short silicide perpendicular bonds.

The results discussed above add the following elements to the understanding of the epitaxial growth of CoSi<sub>2</sub> on Si(111) $7 \times 7$ : (1) The eightfold coordination of Co at the interface lifts one layer of substrate Si atoms in a nontetrahedral site; (2) the interface Co-Si perpendicular bond length is slightly longer than in the silicide parallel planes or bulk; (3) the surface energy minimization of CoSi<sub>2</sub> requires interface Si to migrate on top of

TABLE II. Measured bond lengths between Co and Si.

Measured distances ( $\text{\AA}$ )	2D CoSi <sub>2</sub>	3D CoSi <sub>2</sub>	Bulk CoSi <sub>2</sub>
Co-Si $\parallel$	2.31(0.02)	2.32(0.02)	2.31
Co-Si $\perp$	2.35(0.03)	2.26(0.03)	2.31
Co-Co $\parallel$	3.78(0.03)	3.78(0.03)	3.78
Co-Co $\perp$	...	3.73(0.03)	3.78

the silicide forming an epilayer; (4) at the first stages of 3D growth, the  $\text{CoSi}_2$  layer has a 2.5% reduced perpendicular lattice parameter; (5) the perpendicular motions of the atoms in the ultrathin 3D  $\text{CoSi}_2$  layer are more correlated than the parallel motions in the layer showing an asymmetry in the vibrational properties of ultrathin  $\text{CoSi}_2$  epitaxial layers on Si(111).

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