# Surface structure of epitaxial CoSi<sub>2</sub> crystals grown on Si(111)

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The structural and electronic properties of a Co monolayer condensed on the (111) surface of epitaxial CoSi<sub>2</sub> on Si(111) are studied by low-energy electron diffraction (LEED), x-ray photoemission spectroscopy (XPS), angle-resolved ultraviolet photoemission spectroscopy (ARUPS), and workfunction measurements. A room-temperature Co deposit is disordered, but mild annealing (420 °C, 5 min) results in a sharp (1×1) surface structure. Such a surface can be clearly distinguished from the starting surface previously annealed at 550 °C for 5 min. The work function is 0.2 eV higher, the LEED intensities versus electron energy are quite different, and the ARUPS curves show surface features with two-dimensional (1×1) dispersion behavior. These surface states are attributed to an ordered (1×1) surface layer of Co atoms with four rather than eight Si neighbors for bulk CoSi<sub>2</sub> Co atoms. The initial CoSi<sub>2</sub>(111) surface is recovered by further annealing at 550 °C, which results in Si segregation at the surface. We suggest that both surfaces, Co rich on the one hand and Si rich on the other hand, essentially represent truncations of the ideal CoSi<sub>2</sub> crystal exposing Co and Si (111) planes, respectively. The consequence of the present finding is that the previous observation by ARUPS of a two-dimensional structure in the course of epitaxial CoSi<sub>2</sub> growth on Si(111) should be interpreted in terms of CoSi<sub>2</sub> formation with a Co-rich (111) surface.

#### I. INTRODUCTION

The question of the structure, composition, and reactivity of transition-metal silicide surfaces is of both technological and fundamental importance. Yet, except for the oxidation properties, little work has been devoted to the subject. For Ni, <sup>1</sup> Co, <sup>2</sup> and other near-noble-metal<sup>3</sup> silicides, it appears that oxygen generally bonds to silicon atoms and the oxidation process is considerably enhanced in the silicides of increasing metal content. Metal oxides are also formed for the silicides containing metals with very stable oxides such as Ti.<sup>4</sup> Actually, a better knowledge of the stoichiometry as well as crystallographic and electronic structure of the clean surface is desirable, particularly for understanding the oxidation behavior. For instance, it has been found that depending on the annealing conditions, a variable amount of Si segregates on the surface of epitaxial NiSi<sub>2</sub> (Ref. 5) and CrSi<sub>2</sub> (Ref. 6) crystals grown on Si(111).

The purpose of the present study is to investigate the (111) surface structure of epitaxial  $CoSi_2$  crystals grown on Si(111) and to relate the findings to the previous observation<sup>7</sup> of an intriguing intermediate silicide phase, displaying two-dimensional characteristics, during the  $CoSi_2(111)/Si(111)$  interface formation. The outline of the paper is as follows. Section II presents experimental details. Section III is devoted to the study of a Co monolayer condensed on  $CoSi_2(111)$  and subsequently annealed at various temperatures. A model for the  $CoSi_2(111)$  surface structure, based on these experimental data, is proposed. Section IV contains a discussion of the relationship of the present results to the  $CoSi_2(111)/Si(111)$  interface formation.

#### II. EXPERIMENTAL PROCEDURE

The experiments were carried out in a UHV chamber equipped with low-energy electron diffraction (LEED) and angle-resolved ultraviolet (ARUPS) and x-ray (XPS) photoemission techniques. The ARUP spectra were measured with HeI (21.2 eV) and NeI (16.8 eV) photons impinging on the surface at 45° with respect to the normal. The resolution in angle and energy was  $\pm 1.5^{\circ}$  and 0.2 eV (HeI), respectively.

The epitaxial  $\text{CoSi}_2$  films on Si(111) were prepared as described previously by Co sublimation onto a clean Si(111) surface and subsequent annealing at 550 °C. The Co coverage in monolayers (ML) [in terms of the Si(111) surface atomic density] was measured with a quartz thickness monitor. In this way, high-quality uniform epitaxial films are grown with thicknesses in the 3–200 Å range as evidenced by very sharp (1×1) CoSi<sub>2</sub>(111) LEED patterns and characteristic photoemission spectra.<sup>7–9</sup>

The surface structure obtained by evaporating small amounts (in the monolayer range) of Co onto such  $CoSi_2(111)$  surface was studied as a function of annealing by LEED, ARUPS, XPS, and work-function measurements. It should be noted here that it is necessary to use angle-resolved UPS in order to observe some subtle changes in the valence-band region. From ARUPS as well as from angle-integrated UPS, absolute values of the work function  $\phi$  can be evaluated by measuring the width of the photoelectron energy distribution curve  $\Delta E$  according to

$$\phi = \hbar\omega - \Delta E$$

in the case of metals. These measurements were performed at normal emission for the photoelectrons. The sample was biased by a negative voltage of -10 eV with respect to the ground in order to distinguish the lowenergy electrons emitted by the sample from those emitted (via scattering) by other parts of the spectrometer. The accuracy of such measurements is better than  $\pm 0.05 \text{ eV}$ .

#### III. SURFACE STRUCTURES OF CoSi<sub>2</sub>(111)

### A. LEED observation

The clean  $\cos_2(111)$  surface displays a sharp  $(1 \times 1)$ LEED pattern which indicates that no major reconstruction occurs on such surfaces. With a ~1-ML Co deposit at room temperature, the  $(1 \times 1)$  spot intensity decreases and an important diffuse background is observed. The surface layer at room temperature is therefore disordered. Annealing at 420°C for a few minutes restores a fairly good  $(1 \times 1)$  LEED diagram as shown in Fig. 1(a). Fur-





FIG. 1. LEED diagrams as observed after annealing one Co monolayer deposited on epitaxial  $CoSi_2(111)/Si(111)$ : (a) 420 °C, 5 min, (b) 550 °C, 5 min.

ther annealing at higher temperatures ( $\sim 550$  °C) results in some reduction of the diffracted beam width and incoherent scattering and finally the diffraction pattern of the starting surface is essentially recovered [Fig. 1(b)]. Actually we observe that the diffraction intensities versus primary-electron energy of low-temperature (420 °C) and high-temperature (550 °C) annealed surfaces show major qualitative differences. Thus both surfaces represent distinct ordered (1×1) surface structures.

#### **B.** Work-function measurements

Typical results for the work-function changes upon annealing are presented in Fig. 2(a). The work function of the starting clean  $CoSi_2(111)$  surface is found to be  $\phi = 4.73 \pm 0.05$  eV. Room-temperature deposition of  $\sim 1$ ML of Co results in a slightly higher value:  $\phi \sim 4.75$  eV. As the sample is annealed at low temperature (420 °C) one notices that  $\phi$  increases by  $\sim 0.15$  eV and reaches a plateau within 1 min. From Fig. 2(a) it can be seen that further changes in  $\phi$  can be achieved by heating at higher temperatures. Annealing a few minutes at 550 °C again yields  $\phi = 4.73$  eV, the work function of the initial clean  $CoSi_2(111)$  surface.

#### C. XPS measurements

The Si(2s) and Co(2p) core-level lines were recorded during the annealing experiments described above. Fig. 2(b) shows the evolution of the Co(2p)-to-Si(2s) photoemission intensity ratio versus annealing. The data of Fig. 2(b) are relevant to a thick ( $\sim 100$  Å) CoSi<sub>2</sub> film so that the contribution to the Si(2s) line from underlying Si substrate is negligible. The photoelectron collection angle is set to 45° with respect to the surface normal. The important result here is that the Co(2p)-to-Si(2s) intensity ratio remains essentially constant during annealing at low temperature (420°C). This means that at this stage of annealing the ordering process consists in a lateral rear-



FIG. 2. (a) Work function and (b) XPS core-level Co(2p)-to-Si(2s) intensity ratio for one Co monolayer deposited on epitaxial  $CoSi_2(111)/Si(111)$  as a function of annealing. The  $CoSi_2$  film thickness is ~100 Å. The regions corresponding to ordered Co-rich and ordered Si-rich  $CoSi_2(111)$  surfaces are indicated.

rangement of the Co surface species rather than any diffusion of Co (or Si species) along a direction normal to the surface. In contrast, annealing at higher temperatures leads to an important decrease of the Co-to-Si intensity ratio. Actually the ratio of about 4.5 relevant to clean  $CoSi_2$  is quickly recovered by annealing at 550 °C. This observation indicates Si (Co) diffusion towards the surface (into the bulk) at higher temperature. Finally a small but distinct shift to lower binding energies by ~0.1 eV can be detected for Co(2p) at grazing photoelectron ejection on the low-temperature annealed surface. This result suggests that the chemical environments of Co species in the ordered layer of that surface and in bulk  $CoSi_2$  are different.

### **D.** ARUPS measurements

Let us now discuss the evolution of the ARUPS spectra during annealing. Fig. 3 shows a series of energy distribution curves (EDC's) collected at normal emission with HeI radiation. Curve 1 corresponds to the initial  $CoSi_2(111)$  surface and the conspicuous features at -1.8and -3.8 eV were assigned previously to nonbonding and bonding Co(3d) states, respectively.<sup>7,8</sup> From curve 2 it can be seen that deposition of a Co monolayer reflects in a broadening of the feature at -1.8 eV with a shoulder at  $\sim -1.1$  eV and a filling of the valley present in the clean surface spectrum near -2.8 eV. Curve 3 shows the result of low-temperature annealing (420°C, 5 min.). One recognizes new features at -1.4 and -2.8 eV which should be attributed to surface states associated with the ordered Co overlayer. The bulk peaks are still dominant but the prominent peak at -1.8 eV moves sightly towards higher binding energies by 0.1 eV. This latter effect might be due to the presence of a third surface state peak superimposed on the bulk emission at -1.8 eV. Further annealing at higher temperatures leads to a progressive decrease of the surface state peaks relative to the bulk ones (curve 4). We attribute this behavior to the onset of the diffusion along the direction normal to the surface and incorporation of the ordered Co surface layer. Finally the clean surface spectrum (curve 5) is recovered upon annealing for 5 min at 550 °C.

The data of Fig. 3 are collected from a  $\text{CoSi}_2$  film of 20 Å in thickness. In fact, the surface-state nature of the peaks at -1.4 and -2.8 eV can be nicely demonstrated by varying the thickness of the underlying  $\text{CoSi}_2$  film. Figure 4 presents a series of EDC's collected at normal emission from an ordered monolayer of Co (lowtemperature annealed) on a  $\text{CoSi}_2$  film for various film thicknesses d (3-20 Å). For instance, starting with the clean Si(111) surface, the sample relevant to the 3 Å trace in Fig. 4 can be prepared by successively evaporating 1 ML of Co, annealing at 550°C for 5 min. to get a  $\sim$ 3-Åthick uniform  $\text{CoSi}_2$  layer and further evaporating 1 ML of Co and annealing for 5 min. at 420°C in order to form an ordered Co overlayer. For such thin silicide layers, the peaks at -1.2 and -2.8 eV essentially dominate the spec-





FIG. 3. Normal emission ARUPS spectra for one Co monolayer evaporated on epitaxial  $CoSi_2(111)/Si(111)$  as a function of annealing. The  $CoSi_2$  film thickness is ~20 Å. The angle of incidence of light is 45° and the photon energy 21.2 eV. The dashed lines indicate surface-state emission.

FIG. 4. Normal emission ARUPS spectra for one Co monolayer evaporated on epitaxial  $CoSi_2(111)/Si(111)$  and subsequently annealed at 420 °C for 5 min for various  $CoSi_2$  film thicknesses. The angle of incidence of light is 45° and the photon energy 21.2 eV. The dashed (dotted) lines indicate surface-(bulk) state emission.

trum and the  $\cos i_2$  bulk peak at -1.8 eV is just visible as a weak shoulder. Clearly this demonstrates that the features at -1.2 and -2.8 eV have to be assigned to surface state emission from the ordered Co overlayer. In the present case there is one Co monolayer on the surface and only one Co monolayer incorporated in bulk  $\cos i_2$ . Hence the surface to bulk photoemission intensity ratio *s* is actually greater than one if we assume similar photoionization cross section for bulk and surface Co species and take into account the finite inelastic mean-free-path  $\lambda$  of the photoelectron. The data of Fig. 4 show that *s* decreases with increasing  $\cos i_2$  thickness and reaches a limiting value for  $d \sim 15-20$  Å. This implies  $\lambda \sim 4-5$  Å, in agreement with our general knowledge of electron meanfree paths in solids at about 20 eV of kinetic energy.

The two-dimensional character of the electron states associated with the peaks at -1.2 and -2.8 eV can be further asserted by varying the photon energy and emission angle. For instance, the position of the peaks at normal emission is found to be the same for He I and Ne I photons as it should be if the initial energy E is a function of the component of the wave vector parallel to the surface  $k_{\parallel}$ only. Figure 5 summarizes our data at both normal and off-normal emission in the form of energy dispersion curves  $E(k_{\parallel})$ . These data display a  $(1 \times 1)$  periodicity in reciprocal space. In particular note the energy location at equivalent  $\overline{\Gamma}$  points of the extended Brillouin zone scheme. This confirms that the surface Co atoms are ordered in a  $(1 \times 1)$  overlayer.

### E. Structural models

So far, our experimental results can be summarized as follows. By annealing mildly (420 °C) a Co monolayer deposit on a  $CoSi_2(111)$  surface (previously annealed at 550-600 °C) it is possible to prepare a Co-rich  $CoSi_2(111)(1 \times 1)$  surface which can be clearly distinguished from the starting Si-rich surface by LEED, XPS, ARUPS, and work-function measurements. Both surfaces, the Co-rich one and the Si-rich one [hereafter referred to as  $CoSi_2(111)$ -Co and  $CoSi_2(111)$ -Si respectively], are well ordered and quite stable at room temperature.

The surface structure of the  $\text{CoSi}_2(111)$ -Si surface is not known at the moment, but the present observations allow us to get more insight into this problem.  $\text{CoSi}_2$  has the cubic fluoride structure  $(\text{CaF}_2)$  which can be thought of as a fcc lattice of Co atoms with every tetrahedral site occupied by a Si atom. Along the [111] direction the  $\text{CoSi}_2$ structure can be seen as a stacking of hexagonal (111) planes containing either Si or Co atoms. The three possible ideal (nonreconstructed)  $\text{CoSi}_2(111)$  surface structures representing truncations of the  $\text{CoSi}_2$  crystal are depicted in Fig. 6 (surface *a*, *b*, and *c*).

From an oxidation study of  $\text{CoSi}_2(100)$  surfaces, Castro *et al.*<sup>2</sup> came to the conclusion that the top layer and most probably the second layer are composed of Si atoms. It is reasonable to assume that the  $\text{CoSi}_2(111)$ -Si surface





FIG. 5. Experimental energy-dispersion curves for one Co monolayer evaporated on epitaxial  $\text{CoSi}_2(111)/\text{Si}(111)$  and subsequently annealed at 420 °C for 5 min. The high binding energy peak (-2.8 eV at  $\overline{\Gamma}$ ) shows a strong periodic dispersion along the  $\overline{\Gamma}$ - $\overline{M}$ - $\overline{\Gamma}$  symmetry line. The data around -0.5 and -1.8 eV include important contributions from bulk transitions which are difficult to distinguish from surface-state emission.

FIG. 6. Three possible surface structural models for  $CoSi_2(111)$  as obtained by truncation of the ideal  $CoSi_2$  crystal. The figure is a projection on the  $(\overline{0}11)$  plane. Possible relaxation or reconstruction is shown in case c.

prepared by annealing at 550 °C has also a top layer which contains only Si. We are then left with structural models of type b and c. Of course some reconstruction or relaxation of the topmost layers should occur especially in surface c (see Fig. 6). Actually we favor the latter model with two Si layers on top of the first Co layer for the following reasons.

First, a monolayer Co deposit on surface c might be easily converted into an ordered  $(1 \times 1)$ -Co overlayer with minimum atomic displacements since the local stoichiometry in the first three atomic layers is already CoSi<sub>2</sub>. A simple lateral rearrangement in the overlayer is needed in order to form the CoSi<sub>2</sub>-like structure of surface a. In this regard, let us recall that the XPS measurements actually rule out any diffusion along the surface normal during the ordering process, i.e., annealing at 420 °C. In fact, if we put one Co monolayer on surface c we just supply the right species (Co) in the stacking sequence of CoSi<sub>2</sub> along (111) allowing further growth of the crystal by one atomic layer. The ordered surface Co atoms in surface a have four rather than eight Si neighbors for bulk sites. Thus it is expected that the reduced coordination results in prominent surface states derived from Co 3d orbitals in agreement with the ARUPS data. In this model, annealing at higher temperature would cause the segregation of two Si monolayers on top of the Co overlayer and restore the initial surface. As a matter of fact, a rough estimation of Si segregation during annealing at 550°C based on the XPS data yields a value of 2 rather than 1 ML. Second, we find that the  $CoSi_2(111)$ -Si and CoSi<sub>2</sub>(111)-Co surfaces have the same oxidation properties, very similar to pure Si. Clearly, a monolayer Co deposit on surface b would result in a local stoichiometry of CoSi rather than CoSi<sub>2</sub> for the topmost atomic layers. However, as to the oxidation behavior, CoSi is comparable to Co metal, i.e., it is very active with respect to oxide formation in contrast to pure Si.<sup>2</sup> Thus, one would expect the  $CoSi_2(111)$ -Co surface to be much more reactive than CoSi<sub>2</sub>(111)-Si in disagreement with experiment. Furthermore, the CoSi stoichiometry should remain unchanged upon annealing at 420°C, since experiment shows that there is no diffusion along the surface normal. Yet, considering the known bulk structure of CoSi, the observed  $(1 \times 1)$  hexagonal overlayer could be hardly explained.

In conclusion, we proposed that both surfaces,  $CoSi_2(111)$ -Co on the one hand and  $CoSi_2(111)$ -Si on the other hand, represent essentially two possible truncations of the  $CoSi_2$  crystal exposing either a Co(111) or a Si(111) plane as depicted in Figs. 6(a) and 6(c), respectively.

## IV. FORMATION OF THE CoSi<sub>2</sub>(111)/Si(111) INTERFACE

The results of Sec. III shed some light on previous investigations concerning the formation of the  $CoSi_2(111)/Si(111)$  interface. Actually in a previous paper<sup>7</sup> we reported on the observation by ARUPS of an "in-

termediate silicide phase" characterized by electron states displaying a marked two-dimensional behavior. We have already mentioned in Sec. II that epitaxial CoSi<sub>2</sub> films on Si(111) are usually prepared by Co evaporation and annealing at 550-600 °C. It is demonstrated in Sec. III that films grown in this way have a  $CoSi_2(111)$ -Si surface structure. What happens if a Co deposit on clean Si(111) is annealed at lower temperatures (< 550 °C)? We have investigated this issue quite extensively.<sup>7,10</sup> As a matter of fact ARUPS experiments show that a room-temperature Co deposit of less than  $\sim 8$  ML annealed at 420 °C results in a surface compound displaying the same spectra as those presented in Fig. 4. In other words, considering for instance the 3-A curve in Fig. 4, the relevant sample can be prepared either by successive evaporation of 1 ML of Co on clean Si(111), anneal at 550°C, further deposition of 1 ML of Co and final anneal at 420 °C or by evaporation of 2 ML of Co at once and subsequent anneal at 420°C. In fact LEED, XPS, ARUPS, and work-function measurements all agree in that both preparation methods vield the same surface compound. Thus, considering the results of Sec. III, we are led to the conclusion that the so-called intermediate silicide phase can be thought of as true  $CoSi_2$ , but with a (Co-rich)  $CoSi_2(111)$ -Co surface.

Finally, the lowest trace in Fig. 4 deserves some comment. The relevant sample is prepared by annealing at 420 °C a 1-ML Co deposit on clean Si(111). The interesting point here is the absence of the prominent surface state features at -1.2 and -2.8 eV, which arise from surface Co atoms. In contrast, a peak at  $\sim -2$  eV close to the characteristic  $CoSi_2$  peak near -1.8 eV can already be seen in spite of the dominant contribution from Si substrate. This result strongly supports a model in which Co is incorporated into the silicon lattice in sixfold hollows between the first and second Si layers, as proposed by Comin et al.<sup>11</sup> for the similar Ni(111)/Si(111) system. In this model the first Si layer expands outward by  $\sim 0.8$  Å and the resulting overlayer has already a CoSi<sub>2</sub>-like structure. Furthermore, one would expect a sevenfold coordination for the Co atoms at the CoSi<sub>2</sub>(111)/Si(111) interface. Note that ion scattering experiments favor such an interface structure in the case of the similar NiSi<sub>2</sub>(111)/Si(111) system.<sup>12</sup>

# **V. CONCLUSIONS**

In summary, we have demonstrated that cobalt disilicide can exhibit two distinct (111) surface structures either Co rich or Si rich depending on the annealing conditions. The "intermediate silicide phase" identified in the course of the  $CoSi_2(111)/Si(111)$  interface formation should be interpreted as  $CoSi_2$  with a Co-rich surface.

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(a)



FIG. 1. LEED diagrams as observed after annealing one Co monolayer deposited on epitaxial  $CoSi_2(111)/Si(111)$ : (a) 420 °C, 5 min, (b) 550 °C, 5 min.