CoSi$_2$ on Si(100): LEED investigations of the c(2 × 2) and $(2\sqrt{2} \times \sqrt{2})$ phases and comparison to a bulk crystal CoSi$_2$(100) surface

U. Starke $^a$, W. Weiss $^a$, G. Rangelov $^b$, Th. Fauster $^b$, G.R. Castro $^c$, K. Heinz $^a$

$^a$ Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstrasse 7, D-91058 Erlangen, Germany
$^b$ Sektion Physik, Universität München, Schellingstrasse 4, D-80799 München, Germany
$^c$ Departamento de Física de la Materia Condensada, Universidad Autonoma de Madrid, Cantoblanco, 28049 Madrid, Spain

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Abstract

A CoSi$_2$(100) film of 12 Å thickness was grown on Si(100) and investigated by low-energy electron diffraction (LEED). Two surface phases of the film can be prepared depending on the annealing temperature. The c(2 × 2) phase appearing first (350°C) was compared to the c(2 × 2) structure of a bulk CoSi$_2$(100) sample. Diffraction spot intensities are very similar for bulk and film samples. By a quantitative LEED analysis both surfaces are found to be arranged in a CaF$_2$ structure terminated by its silicon layer. Additional Si adatoms in fourfold hollow sites form the c(2 × 2) periodicity. The second phase (600°C) has a $(2\sqrt{2} \times \sqrt{2})$-R45° periodicity. Here, the film is cracked and mixed with patches of clean (2 × 1)-Si(100), thus making the LEED pattern similar to a c(4 × 4) structure.

Keywords: Low-energy electron diffraction (LEED); Surface structure; Surface relaxation and reconstruction; Low index single crystal surfaces; Epitaxy; Solid phase epitaxy; Silicon; Cobalt; Silicides

1. Introduction

Thin metal films on silicon and their interface as well as silicide films developing upon thermal reaction are important for silicon based device technology for two reasons. On the one hand any electrical connection involves a metal–semiconductor interface which preferably should be of metallic nature. On the other hand the interface itself may already be used as part of the device e.g. as a metal–semiconductor diode. Then a well defined Schottky barrier is important. The structure of many transition metal silicides is strongly dependent on stoichiometry and temperature as mirrored by their complex phase diagram [1]. Among the various phases one can find metal as well as semiconductor properties. So, by selecting the appropriate preparation procedure one should be able to tailor the interface structure as desired for a specific purpose. However, in most cases the growth of a homogeneous epitaxial film on the silicon substrate seems extremely difficult. The crystallography of the surface and film structure during evaporation and reaction should provide information helpful to develop successful growth tech-
niques. For CoSi$_2$ the lattice mismatch of the interface is small enough (−1.2%) to generate epitaxial films which are believed to crystallize in the CaF$_2$ structure like the bulk crystal. We have chosen the (100) orientation of this system to study the atomic structure of an ultra thin film grown on Si(100) and compared it to a bulk CoSi$_2$ crystal using quantitative low-energy electron diffraction (LEED).

2. Film preparation

The experiments were carried out in a ultra-high vacuum chamber [2] equipped with a 3-grid rear-view LEED optics and a cylindric mirror analyzer for Auger electron spectroscopy (AES). For data acquisition of diffraction spot intensities we used a computer controlled video LEED system (AUTOLED) [3,4]. The samples could be introduced through a load-lock system. They were heated resistively with temperature measurement by means of an infrared pyrometer. By applying a sputter-anneal procedure clean flat Si(100) surfaces could be obtained as controlled by AES and the development of a sharp (2 × 1) LEED pattern. The diffraction intensities, i.e. $I(E)$ curves of the clean Si(100) samples compared well to published data [5].

Two electron beam heated evaporators for Si and Co were used to prepare the cobalt silicide films. Well ordered CoSi$_2$ films were obtained by a two step preparation. In a first step 2.6 ML of cobalt were evaporated at room temperature. This first amount of Co immediately reacts with the substrate [6,7]. In a second step 2 ML Co and 4 ML Si were deposited simultaneously (note the desired 1:2 stoichiometry) followed by subsequent annealing (~350°C). The film thickness was now about 12 Å. A well ordered LEED pattern developed with a c(2 × 2) periodicity with respect to the primitive Si(100) surface unit cell. The measurement of the Co(53 eV)-to-Si(92 eV) Auger peak intensity ratio (0.11) indicates that a silicon-rich termination phase has been obtained [8]. Further annealing to ~600°C made the structure change to a $(2\sqrt{2} \times \sqrt{2})$-R45° phase. In Fig. 1 LEED patterns of the two different film phases are presented: the c(2 × 2) (panel a) is mixed with weak [511] facet spots (see Ref. [9] for details). The $(2\sqrt{2} \times \sqrt{2})$-R45° (panel b) actually appears to be a c(4 × 4) LEED pattern due to additional spots originating from a (2 × 1) superstructure. Note that no "2 × 1" spots are visible in the c(2 × 2) LEED pattern. A $(3\sqrt{2} \times \sqrt{2})$-R45° that had been found in previous STM experiments [10] could only be observed in small surface areas at the edge of the evaporation region and thus apparently is not the dominant structure.

![Fig. 1. LEED patterns of the CoSi$_2$(100) films grown on Si(100). (a) c(2×2) phase at 82 eV, (b) $(2\sqrt{2} \times \sqrt{2})$-R45° at 61 eV (energy chosen to make the "2×1" spots visible).](image-url)
3. The c(2 × 2) phase: film and bulk CaF₂ structure

Intensity spectra were measured from 30 up to 400 eV for the c(2 × 2) phase of the film. In addition we investigated a CoSi₂(100) bulk sample [11] that exhibits a similar c(2 × 2) LEED pattern. I(E) spectra acquired from the bulk sample compare well to the film data in shape and structure for both, integer-order and fractional-order beams (see Fig. 3). So, using LEED I(E) spectra as fingerprints of the surface geometry the c(2 × 2) phases of film and bulk sample are found to have a fairly similar structure. In order to determine the actual geometry we carried out a detailed structure analysis for both data sets. Full dynamical LEED intensity calculations were performed using standard LEED programs [12,13]. Guided by the good agreement between bulk and film sample we concentrated on CaF₂ models. However, also another proposed structure for CoSi₂ i.e. the adamantane model [7,14] was tested both, as single structure and mixed with CaF₂. For each crystal structure and surface termination the detailed geometry was varied including stoichiometries deviating from the nominal 1 : 2 ratio. For the model search approximations had to be used in order to save computer time as outlined in detail elsewhere [9]. The only model yielding a reasonable agreement between experimental and calculated data was a CaF₂ structure terminated by a Si layer with additional Si adatoms in a c(2 × 2) arrangement as displayed in Fig. 2. Even just omitting the Si adatoms worsened the fit significantly. The Pendry R-factor [15] was used to quantitatively judge the agreement. In the final fit geometry a considerable contraction of the first substrate interlayer spacing is observed. The silicon adatoms reside in fourfold hollow sites with a Si–Si bond length of 2.45 Å for the film and 2.35 Å for the bulk sample. A slight cobalt enrichment in the first full Si layer reduces the R-factor from 0.27 to 0.25 for the bulk sample. All interlayer spacings \(d_{nm}\) and a lateral displacement parameter \(dS\) of the first substrate Si layer (\(dS > 0\) for positions closer to the Si adatom) are listed in Table 1 here without stoichiometry optimization. Further details of the analysis are discussed in Ref. [9]. Fig. 3 shows the agreement between experimental and calculated data for two selected beams. Note also the

![Best-fit model for the CoSi₂(100)-c(2×2) phase of film and bulk sample in side and top view.](image)

Table 1

<table>
<thead>
<tr>
<th></th>
<th>CoSi₂(100) film</th>
<th>CoSi₂(100) bulk</th>
</tr>
</thead>
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<tr>
<td>(dS)</td>
<td>(-0.12 \pm 0.10 ) Å</td>
<td>(0.05 \pm 0.08 ) Å</td>
</tr>
<tr>
<td>(d_{01})</td>
<td>(1.365 \pm 0.05 ) Å</td>
<td>(1.454 \pm 0.038 ) Å</td>
</tr>
<tr>
<td>(d_{12})</td>
<td>(1.256 \pm 0.05 ) Å</td>
<td>(1.252 \pm 0.036 ) Å</td>
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<tr>
<td>(d_{23})</td>
<td>(1.386 \pm 0.04 ) Å</td>
<td>(1.426 \pm 0.025 ) Å</td>
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<tr>
<td>(d_{34})</td>
<td>(1.306 \pm 0.06 ) Å</td>
<td>(1.279 \pm 0.028 ) Å</td>
</tr>
<tr>
<td>(d_{45})</td>
<td>(1.334 \pm 0.07 ) Å</td>
<td>(1.378 \pm 0.034 ) Å</td>
</tr>
<tr>
<td>(d_{56})</td>
<td>(1.334 ) Å (fixed)</td>
<td>(1.264 \pm 0.058 ) Å</td>
</tr>
<tr>
<td>(R_p)</td>
<td>0.33</td>
<td>0.27</td>
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</table>
Fig. 3. Experimental and best-fit for film and bulk CoSi$_2$(100)-c(2×2).

The similarity between experimental data for film and bulk samples.

4. The (2√2 × √2)-R45° with Si(100)-(2 × 1) patches—a “c(4×4)” LEED pattern

The LEED pattern of the film phase developing after annealing to 600°C consists of two classes of fractional-order spots. Bright quarter-order spots form a (2√2 × √2)-R45°, i.e. appear at positions (1 1 1), (1 1 2), (3 3 2), (1 1 2), and so forth. A class of weaker spots corresponds to a (2×1) periodicity. I(E) spectra of these “2×1” spots appear to be very similar to spectra taken from the clean Si(100)-(2×1) surface. This is demonstrated in Fig. 4a where the (1/0), (1 1 0) and (1/0) spectra are displayed for the CoSi$_2$ film and the clean Si surface on a normalized scale. Obviously the film structure is cranked through the annealing process and clean Si(100) patches large enough to form the (2×1) reconstruction are present on the surface. Correspondingly, the decreased Co/Si AES ratio of 0.08 does not necessarily indicate a cobalt depletion in the film. The remaining (2√2 × √2)-R45° pattern contains all spots of a c(2×2) phase. So, the possible presence of both phases on the surface can only be judged using their I(E) spectra. In Fig. 4b the respective (1 1 2) and (10) spectra are compared on an absolute scale: The (1 1 2) intensity more or less vanishes for the (2√2 × √2)-R45° phase at energies where the c(2×2) phase displays a maximum (e.g. 70, 170 eV). Therefore, phase mixing appears to be negligible. In the (10) spectra significant differences appear especially at higher energies, which indicates differences in the substrate structure rather than only a different adlayer. So, the (2√2 × √2)-R45° phase is not mixed with and probably considerably different from the c(2×2) phase and not just an adatom structure of lower density. For example a shifted adlayer row model as proposed by the STM work [10] would involve different adatom sites and could

Fig. 4. Comparison of experimental I(E) spectra for CoSi$_2$(100)-(2√2 × √2)-R45° with data of the (a) clean Si(100)-(2×1) structure and (b) CoSi$_2$(100)-c(2×2) film phase.
lead to the observed differences in the \(I(E)\) spectra. However, it should be noted that without a detailed LEED structure analysis this discussion cannot go beyond qualitative arguments.

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**References**


