Pulsed laser deposition of Co and growth of CoSi$_2$ on Si(111)

M. Löffler$^{1,2}$
J. Córdon$^{2,3}$
M. Weinelt$^{1,4}$
J.E. Ortega$^{2,3}$
T. Fauster$^{1,5}$

1 Lehrstuhl für Festkörperphysik, Staudtstraße 7, 91058 Erlangen, Germany
2 Donostia International Physics Center (DIPC), Paseo de Manuel Lardizabal 4, 20018 San Sebastián/Donostia, Spain
3 Departamento de Física Aplicada I, Universidad del País Vasco, Plaza Oñati 2, 20018 San Sebastián/Donostia, Spain
4 Max-Born-Institut, Max-Born-Straße 2A, 12489 Berlin-Adlershof, Germany

Our aim was to apply PLD to a system where the deposited material reacts with the substrate material to form the desired surface phase. The interesting question is whether after the reaction induced by annealing the sample, the system still has a memory of the deposition method. We have chosen the growth of CoSi$_2$ on the Si(111) surface, because of the technological interest in films of improved quality. This system has been studied using thermal deposition with a wide variety of surface-science techniques under ultra-high-vacuum conditions [10–16]. As experimental methods we used scanning tunneling microscopy (STM) to study the local morphology and surface structure as well as low-energy electron diffraction (LEED) to study the structure and quality of the films averaged over a larger surface area. After a short account of the experimental details, we describe the growth phases and their evolution as a function of the annealing temperature in the monolayer regime (Sect. 3). Sections 4 and 5 present the results for the growth at higher annealing temperatures and higher coverages, respectively. Section 6 summarizes the results and the consequences for the growth of improved CoSi$_2$(111) films by PLD.

1 Introduction

Due to the great interest of the microelectronics industry, transition-metal silicides have been widely studied in recent years [1, 2]. CoSi$_2$ films seem to be an ideal candidate for contacting Si devices because of their low resistivity of $16 \mu\Omega \cdot \text{cm}$ and very small lattice mismatch of $-1.2\%$ [2]. The Si(111) surface provides a good substrate for the growth of flat, ultra-thin cobalt silicide films by depositing Co at room temperature and subsequent annealing at higher temperatures. However, at the required annealing temperature of $550 \degree\text{C}$ for the reaction to CoSi$_2$, pinholes appear after annealing the deposited Co films [3–5].

Usually metals are deposited by evaporation of a heated wire (thermal deposition, TD). An alternative method is laser ablation of the material from a metal target (pulsed laser deposition, PLD) [6, 7]. PLD has following the laser pulse a deposition rate of $4–5$ orders of magnitude larger than the continuous deposition from a thermal source. For metal-on-metal epitaxy a higher density of nucleation centers and an improved layer-by-layer growth have been observed for PLD compared to TD [8, 9]. The higher kinetic energy of the ablated atoms and ions [7] might also influence the growth.

$\infty$ Fax: +49-9131-852-8400,
E-mail: thomas.fauster@physik.uni-erlangen.de

1 One Co monolayer (ML) equals one Co atom for each surface atom of the unreconstructed Si(111) surface.
400 °C overnight by direct current, then degassed for several hours at 700 °C and flashed to 1260 °C for at least 20 s, not allowing the pressure to rise to more than 5 × 10⁻¹⁰ mbar during the flash. The samples were then rapidly cooled to 920 °C (< 5 s). The (1 × 1) to (7 × 7) transition at about 870 °C was passed very slowly (< 1 °C/s) [21] and the cooling proceeded slowly down to 700 °C. The samples were held at 700 °C for 10 min and then cooled to room temperature (< 10 s).

The temperatures were monitored by infrared pyrometers, with the emissivity set to 0.4 [22]. Before any evaporation, the surface quality was controlled by STM to avoid contaminated samples, so the evaporation was performed after more than 1 h of cooling time, at sample temperatures below 30 °C. The deposited films were annealed at the given temperatures for 5 min and the heating current was immediately turned off after annealing. All STM images shown were taken in constant-current mode at 0.05 nA and a tunneling voltage of 2 V. The LEED intensity spectra were measured as described in Ref. [23] and the average intensity for the individual spots was evaluated in the energy range from 55 eV to 188 eV.

3 Surface structures at low Co coverage

LEED measurements average over a macroscopic surface area and show a single surface structure for most annealing temperatures and Co coverages [13]. With the atomic resolution of STM we always see a mixture of different surface structures on the substrate terraces. Figure 1 shows an example for 0.5 ML Co deposited from a thermal evaporator and annealed to 520 °C. From a detailed study of the various structures at different coverages and annealing temperatures [24], we can identify areas with characteristic local order by their appearance and voltage dependence in STM. Unreconstructed (1 × 1) areas are known to exist in Co- or Si-rich phases depending on the annealing temperature [10,25,26]. The ring-cluster phase (indicated in Fig. 1 with rc) exists in areas of low Co coverage [27]. Densely packed ring clusters exhibit a (√7 × √7)R19.1° structure at a coverage of 1/7 ML [27,28]. The ring clusters develop mainly at higher annealing temperatures on the substrate when compact, higher CoSi₂ islands form [29]. A structure with higher Co coverage is the (√13 × √13)R13.9° reconstruction marked R13 in Fig. 1, which was observed before by Dolbak et al. [13]. This phase as well as the (√19 × √19)R23.4° reconstruction (R19) is found only for well-cleaned substrates [24]. The (√19 × √19)R23.4° phase has been observed before for Ni on Si(111) [30].

From atomically resolved and overview images for every coverage and annealing temperature we can determine the fraction of the surface covered with a certain surface structure. In addition to the structures shown in Fig. 1, we find surface areas covered by islands, and very small areas of a (2 × 2) structure. Areas without a specific surface structure are called ‘disordered’. For a certain Co coverage and annealing temperature we plot the fractions of the different surface structures in structure diagrams shown in Fig. 2. These show the evolution of the different surface phases for one initial Co coverage deposited at room temperature as a function of the annealing temperature.

On the basis of Fig. 2 we first introduce some general features of all structure diagrams for Co coverages below 1.5 ML on Si(111). At annealing temperatures below 300 °C most of the surface is disordered. For a coverage below 1.0 ML some areas with low local Co coverage are visible, which are described by the ring-cluster phase. With increasing annealing temperature, up to 500 °C, most of the surface is covered by ordered surface phases, and the disordered areas are disappearing. Starting at 400 °C compact islands of several monolayers height are forming, which have CoSi₂ stoichiom-

![FIGURE 1](image1.png)

**FIGURE 1** STM image (50 × 50 nm) for 0.5 ML Co thermally deposited on Si(111) and annealed to 520 °C. Representative areas of different surface structures are marked.

![FIGURE 2](image2.png)

**FIGURE 2** Structure diagrams for Co on Si(111). The fraction of the (1 × 1)-structured areas is marked by horizontal shading, of the (√19 × √19)R23.4°-structured areas by vertical shading and of the (√13 × √13)R13.9°-structured areas by diagonal shading.
etry [11, 31, 32]. The growth of islands leads to a Co depletion around the islands and an increase of surface areas covered by ring clusters at low Co concentration [29]. At a certain temperature, which depends on the initial Co coverage, the conversion from two-dimensional to three-dimensional growth is completed. At even higher temperatures only the ring-cluster phase can be found on the terraces between the islands.

We now focus on the coverage-dependent changes in the structure diagrams. At first, we mention the lower transition temperature to the three-dimensional growth for higher initial Co coverage, easily seen in the structure diagrams for 1.0 ML Co (Fig. 2, top) at ∼600 °C compared to ∼700 °C for 0.5 ML Co TD (Fig. 2, bottom). In addition to the transition temperature, the predominant structure formed on the terraces changes with the initial Co coverage. For 0.5 ML Co TD the (√19×√19)R23.4° reconstruction (vertical shading) is the prevailing structure on the surface, while the (√13×√13)R13.9° phase (diagonal shading) covers only a small fraction of the surface. For 1.0 ML Co the situation is reversed: while the (√19×√19)R23.4°-reconstructed area is very small, the (√13×√13)R13.9° reconstruction covers most of the terrace area. The initial Co coverage on the surface determines the ratio of the fractions of the (√13×√13)R13.9°- and the (√19×√19)R23.4°-reconstructed areas, because the (√19×√19)R23.4° structure has a lower Co content compared to the (√13×√13)R13.9° structure [24].

For deposition of 1 ML Co by PLD (Fig. 2, center) most of the ordered areas show the (√19×√19)R23.4° reconstruction for annealing temperatures below 500 °C, while only a small area is covered by the (√13×√13)R13.9° structure. This implies a lower Co concentration at the surface as compared to TD at 500 °C. However, the transition temperature to the three-dimensional growth at ∼600 °C and the Co coverage calculated from the island volume (assuming CoSi2 islands for T > 600 °C [11]) indicate a total Co coverage of the film of ∼1.0 ML.

These findings are consistent with a partial implantation of Co during PLD due to the deposition of energetic ions and atoms. One monolayer deposited by PLD gives a Co coverage in the surface layer of ∼0.5 ML; the rest is incorporated in subsurface layers. At higher annealing temperatures the implanted Co diffuses to the surface and the deposited Co goes almost completely into the islands. Implantation of Co even at low kinetic energies has been shown by hyperthermal Co deposition on Si(001) [33]. From these data an implanted amount in the range of 0.37–0.67 ML can be estimated. This is in good agreement with our results considering that the kinetic energy of the deposited particles was not measured in our experiment.

4 Island growth at low Co coverages

The implantation of Co by PLD influences not only the relative fraction of the surface structures but also the island growth and morphology. For annealing temperatures up to 300 °C no islands appear for PLD and TD (Fig. 3, top row); the morphology of the surface is governed by the step structure of the Si(111) substrate. For temperatures in the range of 350 °C to 400 °C we observe the growth of first islands. For an annealing temperature of 440 °C (Fig. 3, bottom row) irregularly shaped 1.5-Å-high islands evolve near the 3.1-Å-high step edges for TD, while for PLD compact islands of more than 3-Å height grow equally distributed over the terraces.

Because of the preferential growth of islands at step edges for TD we assume the growth of islands to start at defect sites. For TD the mean energy of the deposited atoms is below 0.25 eV, so no defects are generated in the substrate during deposition. The only morphological defects are substrate steps, and so during annealing nucleation takes place at the step edges. As mentioned, the Co ions have an energy of 50 eV for PLD. This energy is sufficient to produce surface or bulk defects and a significant number of defects in the subsurface layers is created by PLD [34]. These PLD-induced defects act as nucleation centers for the silicide islands, and the influence of the substrate steps on island nucleation becomes negligible.

5 Films at higher Co coverages

Because of the intermixing of the deposited Co with the Si substrate during PLD, differences in the film growth compared to TD can be expected also for initial Co coverages of several monolayers. However, we find the same structures on the films for the same Co coverage and annealing temperature. For 7 ML Co we observe the Co-rich (1×1) phase for annealing below 500 °C and the Si-rich phase for higher annealing temperatures up to ∼700 °C. The (01) LEED beams show distinct differences for the two phases [10, 26] and are used to compare different sample preparations. The agreement of the LEED spectra for different
deposition methods but otherwise identical preparation parameters is measured by a Pendry $R$-factor $R_P$ [23] of less than 0.15. The same agreement is obtained with published reference spectra for samples produced by simultaneous deposition of Co and Si [26]. The Co- and Si-rich phases are found to be independent of the deposition method for all annealing temperatures. However, the Pendry $R$-factor $R_P$ is sensitive mainly to the surface structure. In order to obtain a measure of the film quality we have to look at the averaged LEED intensity, which is proportional to the area covered by the ordered structure.

In Fig. 4 the averaged intensity of the (01) LEED beam for the 7 ML film (top panel) at low annealing temperatures is higher for the PLD film than for the TD film. This indicates a better-ordered film, which can be understood as follows. For the TD film a higher rate of diffusion is necessary to obtain a well-ordered film, because all the Si for the silicide film has to diffuse through the Co layers. For PLD an intermixing of Co and Si after deposition takes place, and so less diffusion is necessary. For annealing temperatures above 500 °C the averaged intensity is similar, and so under these conditions PLD and TD films are of comparable quality.

For 14 ML Co (bottom panel of Fig. 4) the findings are different. For annealing temperatures above 530 °C we find for TD and PLD the Si-rich (1 x 1) phase, with a good agreement with the Si-rich (1 x 1) phase of [26] quantified by $R_P < 0.2$. Comparing the averaged beam intensities in Fig. 4, a significantly better order of the surface for the PLD-prepared films is obvious.

For annealing temperatures below 500 °C only the PLD film shows the Co-rich phase ($R_P \leq 0.2$ compared to the reference data [26]). For the TD film we obtain $R_P \geq 0.5$ by comparing our LEED spectra to PLD or the reference spectra [26]. This is in contrast to reports by Nagashima et al. who prepared the Co-rich phase by annealing 14 ML TD films to 450 °C [35]. The structural disorder can be caused by the existence of domains of cobalt silicides with higher Co content than CoSi$_2$ [36]. Because of the structural difference of the PLD and TD films for 14 ML Co at annealing temperatures below 530 °C, the comparison by the averaged intensity of a single beam is questionable. Without doubt the PLD films are of better quality compared to the TD films, because of the high structural conformity with the simultaneously deposited films, which are known to show an excellent film quality.

6 Conclusions

For submonolayers of Co prepared by PLD on Si(111) we find an implantation of Co into the substrate and an intermixing at the surface. After moderate annealing this intermixing leads to silicide structures containing less Co on the terraces, compared to TD. Because of the high energy of the Co ions in PLD defects are generated on the terraces, leading to an isotropic island nucleation, in contrast to island nucleation at substrate steps for TD. Because of the higher intermixing we have found an improved growth on ultra-thin cobalt silicide films for several ML Co, especially at annealing temperatures below 500 °C. The annealed PLD films are comparable to films produced by simultaneous deposition of Co and Si with TD. Further improvement can be expected by simultaneous stoichiometric PLD from a CoSi$_2$ target.

REFERENCES