Growth of ultrathin Si films on fcc Co(100) surfaces

G. Rangelov, U. Thomann, Th. Fauster

Sektion Physik, Universität München, Schellingstrasse 4, D-80799 München, Germany

Received 1 August 1994; accepted for publication 25 November 1994

Abstract

Ultrathin Si layers were deposited at room temperature on fcc Co(100) films grown epitaxially on Cu(100). The surfaces were studied by low-energy electron diffraction (LEED), Auger electron, and photoelectron spectroscopy using synchrotron radiation. The growth mode was studied by Auger uptake curves. From the Si 2p core-level shifts the existence of a unique adsorption site is inferred at low coverages. Photoelectron forward-scattering experiments revealed no pronounced binding directions, whereas LEED patterns were observed at all coverages. This is compatible with the growth of an ordered layer of Si on top of the Co(100) substrate at low coverages followed by the growth of a disordered Si layer with holes.

Keywords: Auger electron spectroscopy; Chemisorption; Cobalt; Growth; Silicon; Soft X-ray photoelectron spectroscopy

1. Introduction

The epitaxial growth and structure of CoSi$_2$ on Si surfaces has been intensively studied during the past years due to its importance for the microelectronics industry [1]. Cobalt atoms are found to form a silicide when deposited at room temperature on Si surfaces [2]. Very little is known about the reaction between Co and Si at surfaces at the opposite extreme of the concentration limit: deposition of Si on a transition metal surface. This problem is interesting for applications of Schottky barriers [3–6] and bears some relevance for the development of novel catalysts [7–9].

We studied the adsorption behavior of Si on Co and were interested in particular in a possible silicide formation on the surface. As a substrate we chose thin face-centered cubic Co films of (100)-orientation grown epitaxially on a Cu(100) bulk crystal [10]. This provides a well-ordered and clean Co substrate with a lattice constant of 3.61 Å. Because the lattice constant of Si is approximately $\sqrt{2}$ larger, there exists the possibility for the growth of epitaxial Si(100) films with the in-plane axes rotated 45° relative to the Co(100) substrate and a lattice mismatch of 6%.

The main experimental technique was the high-resolution spectroscopy of Si 2p photoelectrons, which gives information about the chemical environment of the Si atoms. In addition, the Co 3p core levels and the valence bands were measured. Information about the geometrical structure was obtained from low-energy electron diffraction (LEED) and forward-scattering of photoelectrons.
2. Experiment

Sample preparation, Auger electron spectroscopy (AES), and LEED measurements were performed in a separate ultra-high vacuum chamber. The Cu(100) crystal was cleaned by sputtering and annealing. The surface cleanliness and crystallographic order were verified with AES, LEED, and photoelectron forward scattering. Cobalt (∼8 ML) and silicon were evaporated from electron-beam evaporators with integrated flux monitors (Focus EFM3) at a rate of 0.01 monolayers (ML) per second onto the substrate at room temperature and at a pressure of <2 × 10\(^{-10}\) mbar. The photoemission experiments have been performed at the TGM-3 and HE-TGM-1 beamlines at the BESSY storage ring. The emitted electrons were detected by means of a display-type electron-energy spectrometer [11] housed in the analyzer chamber which is connected to the preparation chamber by a transfer system. The overall resolution of the analyzer at 30 eV kinetic energy and the TGM-3 monochromator at 130 eV photon energy was ∼0.35 eV for the measurements of the Si2p core levels. The large acceptance angle of the spectrometer (∼88°) allowed for true angular integration and for fast data accumulation with good statistics. The typical measuring times were ∼10 min at a base pressure of ∼4 × 10\(^{-11}\) mbar. The measured counting rates were normalized to the photon flux, so an absolute comparison between the intensities of different spectra is possible. For the forward-scattering experiments synchrotron radiation with an energy of ∼650 eV from the HE-TGM-1 beam line was employed to excite the Si2p and Co3p core levels. The angular distribution patterns of the photoelectrons were recorded in the angle-resolving mode of the display analyzer [11]. The data processing and the normalization with respect to the spatial analyzer efficiency has been described previously [12–14].

3. Results

The ratio of the Si LVV AES intensity normalized to the sum of the Si LVV and Co MVV AES intensity is shown in the top part of Fig. 1 as a function of deposition time. From the initial slope of the data at the top of Fig. 1 we estimate a mean free path of 3.7 ± 0.5 Å for electrons in Si with 53 eV kinetic energy in agreement with previous reports [15]. The breakpoint given by the intersection of the straight line fits has been used to convert the deposition time into a coverage scale. The breakpoint is characterized by a c(2 × 2) LEED pattern compatible with an adsorption of 0.5 ML of Si with a lattice constant close to the one of a Si(100) layer. The (1 × 1) spots of the LEED pattern can be recognized for coverages up to 7 ML. The coverage calibration agrees with deposition experiments on a Co-rich CoSi\(_2\)(111)–C surface which converts to a Si-rich CoSi\(_2\)(111)–S surface after adsorption of 2 ML Si [2,16].

Forward-scattering experiments with photoelectrons of ∼500 eV kinetic energy show an enhanced intensity along the directions of the internuclear axes [12,14,17]. For coverages below 0.5 ML we did not observe any anisotropies in the angular distributions of the Si2p photoelectrons. This is compatible with
an adsorption of a smooth one-atom Si layer as inferred from the AES uptake curve. Even at higher coverages no forward-scattering directions could be identified and, therefore, we do not present any angular distribution patterns. The observations indicate a disordered growth of the Si film in the form of three-dimensional islands.

Valence-band photoemission spectra (not shown) taken at 115 eV photon energy are mostly sensitive to the Co 3d bands. The Co signal decreases in intensity with increasing Si coverage. The maximum shifts from an energy close to the Fermi energy down and a broad peak \( \sim 1.5 \) eV below the Fermi energy develops. This is neither characteristic for bulk Si nor for CoSi\(_2\) valence bands, but typical for a Co-rich silicide [2].

The Si \( \sim 2p \) core-level spectra taken at 130 eV photon energy are shown in Fig. 2 for Si coverages up to 7 ML on Co(100). The two lowest spectra show a larger slope of the background due to the two times higher sensitivity. For coverages below \( \sim 0.5 \) ML the doubled structure can be clearly resolved. This excludes contributions from many overlapping lines as expected for the simultaneous occurrence of different binding configurations or adsorption sites. It also proves that the lineshape observed in our experiments on the clean Si surfaces [2,18] is not limited by experimental resolution, but is due to intrinsic properties of the surfaces. For higher Si coverages the peak becomes broader and shifts to higher binding energy.

For the detailed analysis of the Si \( \sim 2p \) spectra we performed line fits following the procedure described previously [18]. The fit functions are shown as solid lines in Fig. 2. Up to four components of the signal were included. A broad peak with a binding energy around 100 eV has little intensity and might be due to an energy loss process [15,18] or to an inadequate description of the background by a polynomial. The \( 2p_{3/2} \) peak with 99.25 \( \pm 0.05 \) eV binding energy corresponds to the position known from bulk silicon. The binding energy of another \( 2p_{3/2} \) component shifts with coverage from 98.82 \( \pm 0.05 \) eV (\( \leq 0.5 \) ML) to 98.89 \( \pm 0.05 \) eV (\( \geq 2.0 \) ML). The latter value is close to the value known for the surface atoms on Si(100) surfaces [18,2]. For coverages below 0.5 ML an additional component was necessary to obtain a satisfying fit to the data. Its binding energy is 98.46 \( \pm 0.10 \) eV. It can be recognized from a careful inspection of Fig. 2 which shows an extension of the main peak at low binding energies and it is seen more clearly in spectra taken at 115 eV photon energy with better resolution.

The relative intensities of the various peaks normalized to the total Si 2p intensity are shown at the bottom of Fig. 1 as a function of coverage. The main feature is that the bulk line (open squares) is not observed for coverages below 0.5 ML. The component attributed to surface atoms (filled circles) makes up \( \sim 90\% \) of the intensity in this coverage range, whereas the extra component with low binding energy (filled diamonds) contributes \( \sim 10\% \). The surface component approaches for higher coverages a value of \( \sim 30\% \) of the total intensity similar to the percentage observed on the clean Si surfaces [15].

The appearance of the bulk component for coverages above 0.5 ML only can be easily understood
with the initial adsorption of a single Si layer on Co(100). The binding energy of atoms in this layer is 98.82 eV: a value close to the one found for Si in a Co-rich Co–Si solid solution [2,16]. The character of the component at low binding energy is not clear, but its energy indicates undercoordinated Si atoms which might occupy step edges or constitute other defects. For higher coverages the Si bulk line gains intensity and the surface component looses weight. Due to the small energy shift we cannot separate the contribution of the Si atoms at the Co surface from the Si surface atoms. The observed intensity as a function of coverage is compatible with a Stranski–Krastanov growth mode where the area covered by a single layer of Si atoms decreases. Using only these data we cannot exclude a simple attenuation of the interface signal by the Si layer with increasing thickness. The latter interpretation, however, is based on the assumption of an unchanged binding energy of the interface atoms upon adsorption of the next Si layer.

We have also measured the Co 3p core levels at 130 and 170 eV photon energy. There is a reduction of the Co 3p peak intensity and a shift in binding energy from the bulk value of 59.4 to 60.0 eV at high coverages. The latter value is similar to the one found for CoSi₂. The fact that the Co signal has not disappeared at 7 ML is compatible with the Stranski–Krastanov growth mode or with some Co diffusion into the Si layer forming a silicide. In the former case we can understand the binding-energy shift as due to a relative increase of the contribution from the top Co layers which have reacted with Si. This statement is supported by the binding energy of Si “surface” atoms in the first layer, found to be close to the binding energy of Si in a Co-rich silicide.

4. Conclusions

Our results show that a single atomic layer of Si can be deposited in an ordered fashion on Co(100) at room temperature. For Si on Ni(100) annealing to 500°C was necessary to obtain an ordered c(2 × 2) surface [5,7]. The further growth is disordered in agreement with findings for Si on Ni(100) [7]. There is no indication for a CoSi₂ formation at room temperature. It would be interesting to study the growth of Si on the hexagonal close-packed (0001) surface of a bulk Co crystal which might lead to the growth of Si(111). The bulk substrate could be annealed to induce a silicide formation. Such experiments are difficult in our case because of interdiffusion between the Co layer and the Cu substrate above 100°C.

Acknowledgement

This work was supported in part by the Bundesminister für Forschung und Technologie (BMFT 05 5WMABB 2).

References