Characterization of codeposited Co-Si layers on Si(100)

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Cobalt disilicide is a promising material for conductive layers in the microelectronics industry due to its low resistivity. The small lattice mismatch to Si (−1.2%) opens prospects for three-dimensional chip architecture. The properties of the interface between Si and CoSi$_2$ are of crucial importance for the Schottky barrier height of the contact. The production of low-defect layers on the technologically relevant Si(100) surface is difficult, due to the higher surface energy of the CoSi$_2$(100) surface. Films obtained by solid phase epitaxy (SPE) after Co deposition and annealing contain a lot of defects and Si pinholes. The best films are prepared by the template method. At room temperature (RT) a 5−7 Å thick amorphous layer with CoSi$_2$ stoichiometry is deposited on top of 2.6−3 monolayers (ML) Co on the Si(100) substrate [1]. Thicker CoSi$_2$(100) films can be obtained by further CoSi$_2$ deposition on the template layer held at 460°C. However, the role of the predeposited Co layer for the epitaxial disilicide growth [1] and the chemical state of the ultrathin amorphous film are not well understood. We studied the temperature-induced evolution of template and SPE layers using the high-resolution spectroscopy of Si 2p photoelectrons, which gives information about the chemical environment of the Si atoms.

The experiments were performed with the display-type electron energy spectrometer [2] at the TGM-3 beamline at the BESSY storage ring. The overall resolution was ∼ 0.35 eV for the measurements of the Si 2p core levels. Co and Si were evaporated from electron-beam evaporators with integrated flux monitors (Focus EFM3) at a rate of 0.01 ML per second onto Ar sputtered and annealed Si(100) surfaces at a pressure of < 2·10$^{-10}$ mbar. The amorphous CoSi$_2$ layers of the template were prepared at RT by simultaneous (codeposition) or alternating (sandwich) evaporation of Si and Co in stoichiometric ratio. The RT-deposited films were further annealed in steps up to 650°C for 2 min at each temperature.

Spectra for a predeposited Co SPE film and several codeposited template films on a Si(100) substrate are presented as a function of the annealing temperature in Fig. 1. The spectra show only the 3/2 components of the Si 2p core-level and are normalized to maximum height. For a detailed analysis of the Si 2p spectra we performed line fits following the procedure described previously [2]. The fit functions are shown as solid lines in Fig. 1. Only two main components with 99.20 ± 0.05 eV and 98.92 ± 0.05 eV binding energy (BE) are needed for a good fit of the RT films. Bulk-sensitive measurements with 115 eV photon energy demonstrate that peaks B and A have bulk and surface character, respectively. The BE of the component B corresponds to the position known from bulk silicon. Taking into account, however, that the mean free path of 30 eV electrons in Si is ∼ 3.3 Å, it is surprising that after ∼ 10 Å deposit (top spectrum), the Si bulk component dominates the spectrum. Therefore, one is led to assume that some Co-Si phase with similar BE forms on the surface after the template preparation procedure. We tentatively attribute this component to Si in an amorphous silicide. For thinner films some contribution from the substrate can not be excluded. The BE of the component A corresponds either to lower-coordinated Si atoms on the surface of the amorphous layer or to some other Co-Si phase [2]. The similarity of the Si 2p spectra of the SPE and template films suggests that they have similar stoichiometry and chemical state.
The annealing at 450°C leads to a broadening of the Si 2p spectra. Now up to four main components, labeled in Fig. 1b and c are needed for a good fit. The binding energies of the four components are averaged from all experiments with different preparation procedures (template and SPE) and are indicated in Fig. 1 by vertical lines. Experiments with 115 eV photon energy show that components B and C have bulk, and components A and S have surface character. Peak B is at 99.20 ± 0.05 eV which allows us to interpret this component as due to Si atoms in a Si bulk environment and/or to unreacted RT amorphous silicide. It is most intensive for template films. Peak B persists even for the thickest film measured (∼ 14 Å continuous CoSi$_2$ film). If this component originates from bulk Si, the obtained films either have Si pinholes or inhomogeneous thickness which is rather surprising for the presumably best preparation procedure.

The peak C is at 99.45 ± 0.05 eV BE. This corresponds to the Si binding energy in CoSi$_2$ in CaF$_2$ structure as observed earlier [2]. The component C does not appear for RT films. Therefore, even the stoichiometric codeposited films are not reacted to CoSi$_2$ and annealing is needed for the reaction. The disilicide (C) component is not observed for the 1 ML codeposition and sandwich films. The low intensity of the component C is surprising taking into account the LEED experiments [3] which show that identically prepared films annealed at 450°C consist of Si terminated disilicide(C). A possible explanation is that the disilicide(C) film does not cover the whole surface or is hidden below a thick Si overlayer.

The component S has a BE of 98.55 ± 0.05 eV and was attributed earlier to emission from lower-coordinated Si surface atoms of the disilicide [2]. The intensity of this component is higher for 1 ML films. Peak A has a BE of 98.97 ± 0.05 eV, very close to the the
component A of the RT spectrum. No such component exists for disilicide films on the Si(111) surface, regardless of the preparation procedure. The intensity of this component is similar to the disilicide for the 3 ML template film but dominates the SPE spectrum.

After annealing to 650°C the component C disappears and the Si 2p spectra of the four preparations are quite similar. The relative intensity of the component B decreases slightly for the template films, but increases for the SPE film. It is well known, that pinholes form after annealing above 500°C [4] and one should expect an intensity increase of the Si bulk component. Therefore, this component should have another origin for temperatures below the critical temperature for pinhole formation. Above this temperature, peak B could have a bulk Si contribution from the pinholes. The behavior of component B shows that the area covered by pinholes is higher for the SPE film. The relative intensity of the surface contribution increases in all spectra and is close to the intensity of a single dangling-bond component of the clean Si(100)(2×1) surface which corresponds to half a monolayer [2].

At 650°C a pronounced increase of peak A occurs and it dominates the Si 2p spectra in the case of the template films. Using valence-band photoemission data [5], we attribute this component to another disilicide crystal structure, the adamantane structure, which was proposed by Tu [6]. One is led to conclude that the component with the same BE at lower temperature is due to adamantane disilicide as well, and both disilicides coexist on the surface. The high intensity of the adamantane component at 650°C excludes its origin from the topmost layer only. This and the observed surface character imply that it originates from a subsurface region which is 3 – 5 mean free path lengths thick. This suggests that adamantane disilicide occupies the topmost surface layers with disilicide (C) underneath. Coexistence of domains of both structures can not be excluded.

We studied the temperature evolution of ultrathin films with CoSi2 stoichiometry prepared by a template procedure using Si 2p core-level spectroscopy. The codeposited Co and Si atoms react in the film at RT, but the layer does not have the electronic structure of CoSi2(C). The stoichiometry and chemical state of the amorphous silicide film are similar to those of the RT Co predeposited layer which could explain the importance of the latter for the quality of the disilicide film. Annealing of the surface is needed to produce CoSi2(C). Additional features of Si 2p spectra suggest, however, that another (adamantane) Co-Si phase coexists on the surface. Depending on the annealing temperature and the film thickness the C phase disappears from the probing depth of the electron spectroscopy. After annealing at 650°C the Si 2p core-level spectra of the films are qualitative identical. The template films are dominated by the adamantane phase.

References


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