***In situ* x-ray diffraction study of CoSi_2 formation
during annealing of a Co/Ti bilayer on $\text{Si}^*(100)^*$**

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***In situ* x-ray diffraction study of CoSi_2 formation during annealing of a Co/Ti bilayer on Si(100)**

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X-ray diffraction (XRD) was performed *in situ* during annealing of a Co/Ti/Si(001) multilayer, which produced an epitaxial CoSi_2 layer. The results indicate that the Ti layer did not stay intact during the reaction, and thus could not act like a membrane, moderating Co/Si interdiffusion. A strongly textured metastable phase (M) formed prior to CoSi_2 nucleation. This intermediary reaction product was unobservable upon completion of the anneal. We report that nucleation and growth of CoSi_2 on Si(100) took place in the presence of M, a new Co-Ti-Si-(O) phase, located at the metal/Si interface. M might play an important role in the perfection of the silicide. Ti and Co metals intermix already below 300°C, and there was evidence that metallic Ti precipitated at the surface, commencing at 550°C.

Formation of epitaxial CoSi_2 on $\text{Si}(100)$ by annealing of a Co/Ti/Si multilayer structure has been the focus of a number of recent publications.¹⁻⁶ This method has attracted special attention, due to superior quality of the final layer, and self-aligned processing compatibility. Moreover, the need for ultra high vacuum processing can be eliminated,¹ since both the metal deposition and the annealing step may be performed in a moderately clean environment. The Ti layer cleans the Si surface from any residual oxide, allowing CoSi_2 to nucleate and to form a homogeneous epitaxial layer by a solid state interdiffusion and metal layer inversion reaction.² It has been established that the Ti is prevented from forming stable ternary silicides by processing in nitrogen gas, rather than in vacuum or in an inert gas.³

The knowledge is limited, however, about the details of the nucleation of CoSi_2 , and the reaction paths followed using the described method. Nevertheless, a recent study showed that the CoSi_2 could form directly,⁴ without going through intermediary formation of Co_2Si and CoSi .⁵ Evidence has been presented for a diffusion-retarding amorphous layer at the metal/Si interface,⁶ allowing the desired silicide to grow at a controlled rate. To elucidate these issues we present in this letter *in situ* XRD data, acquired during annealing of a $300\text{\AA}$ $\text{Co}/50\text{\AA}$ Ti metal bilayers on $\text{Si}(100)$. Ti and Co intermixed already at temperatures below 300°C , indicating that an intact Ti layer did not play any active role in the CoSi_2 formation. Diffraction from a strongly textured phase (M) was present in the $450\text{--}700^\circ\text{C}$ temperature range, but was unobservable after the reaction was completed.

Metal bilayer samples were fabricated without breaking vacuum, both in a Varian M-2000 UHV sputtering system, and in a high vacuum (HV) chamber by sequential sputtering of first 50Å Ti, and then 300Å Co, onto Si(100) substrates. The silicon was cleaned, and stripped of the native oxide, and immediately thereafter inserted into the deposition chamber. The base pressure in the HV system was better than 8×10^{-6} Pa, the deposition was carried out in 1.30 Pa, 99.999% research grade Ar. There was no intentional substrate heating, therefore the substrate temperature remained below 70°C. This combined with high deposition rates, 3-5 Ås⁻¹, prevented oxygen contamination, caused little interdiffusion of the metals in the as-deposited samples, and gave small grain sizes. Results obtained from annealing of UHV, and HV grown samples were identical.

The *in situ* anneals were completed in a hot cell, which was mounted on a powder diffractometer. Samples, 6 X 8 mm, were mounted on a Ta strip heater within the furnace. A flow of 99.9995% research grade N₂ at ambient pressure was maintained throughout the process. The diffractometer featured a rotating anode source, a large flat graphite monochromator, and a position sensitive detector arrangement,⁷ which rendered the data acquisition very rapid. Each diffractogram ($2\theta=28-50^\circ$) took only six minutes to complete. Data was acquired concurrently as the temperature was ramped at a 5°Cmin⁻¹ rate, from ambient to 880°C, at which temperature the CoSi₂ formation was completed.

Identical films, to those annealed *in situ*, were annealed in a quartz tube diffusion furnace to different final temperatures in

flowing nitrogen. These reference samples were studied by *ex situ* XRD, and were useful in verifying the reactions observed *in situ*. The bilayer anneal was, furthermore, studied *in situ* by x-ray fluorescence (XRF) depth profiling, a technique particularly well suited to study the observed interdiffusion and metal layer inversion in this system.⁸

Fig. 1 shows a sequence of *in situ* XRD scans. The temperatures were recorded at the completion of each scan. The first scan represents the virgin sample at close to room temperature, with Ti(002), hcp Co(100), and fcc Co(111) diffraction peaks. The bump at around $2\theta=33^\circ$ is the shoulder of the single crystalline substrate Si(200) peak, which is only visible by coincidence using the present technique. With increasing temperature, the Ti(002) completely vanished at 300°C , indicating that Ti-Co intermixing had occurred, and that metal layer inversion had begun. In the scan at 547°C , two diffraction peaks appeared close to the anticipated positions of the Ti(100) and (002), and consequently, at least some of the Ti had started to precipitate, forming a cap layer at the surface. From this point on, diffraction that could be attributed to metallic Ti was visible until the completion of the anneal. Above 666°C , the two peaks assigned to hcp Ti were replaced by a single peak at app. $2\theta=39^\circ$. This was most likely due to the formation of a bcc Ti(Co) solid solution at the eutectoid temperature 686°C .⁹ Hcp Ti(100), and (002) peaks then reappeared towards the end of the reaction, when all Co metal had been consumed. The *in situ* XRF depth profiling supported the XRD results, inasmuch extensive diffusion of Ti towards the surface was detected at temperatures around and above 550°C .

Except for the Ti interdiffusion, the Co layer seemingly stays intact until the very final stage of the anneal. Diffraction from the hcp-Co allotrope disappeared as the temperature was ramped up, consistent with the fact that hcp Co is unstable above 442°C.⁹ Up to around 700°C, the fcc Co(111) peak sharpened and increased in intensity, most likely due to Co grain growth, and the annealing of defects. At temperatures higher than that, the Co intensity dropped, because the metal was gradually used up by the growing CoSi₂ layer.

The CoSi₂(200) peak emerged above 577°C, showing that nucleation of the desired phase had taken place. There was no sign of neither intermediate CoSi, nor Co₂Si formation. Below app. 800°C, the growth of the CoSi₂ peak proceeded at a limited rate. Towards the end, however, the CoSi₂(200) intensity soared, as the Co(111) peak waned: the Co supply was exhausted, and the silicide formation was brought to completion. The post-annealed film consisted of mainly (100) oriented CoSi₂, with a (400) peak rocking curve full width at half maximum (FWHM) of 0.5°.

Weak diffraction from a new metastable phase (M) was discernible in the scans at 607°C, and 636°C of Fig. 1 (dashed line). Fig. 2 shows details of XRD data obtained from another run, during which the presence of M was especially obvious. Starting at 449°C, the peak marked M_I grew, and was later joined by M_{II} at a slightly higher temperature. In the 721°C scan and above, both peaks were gone. It was also noted that the Co(111) intensity dropped substantially, as the M formed.

In order to better analyze the M phase, one *in situ* anneal was interrupted at the point where strong M intensity was observed. The

sample was quenched to room temperature and further analyzed, primarily by XRD, but unambiguous phase identification using transmission electron microscopy (TEM) is under way. Fig. 3 shows a post annealing diffractogram from this film. Filled diamonds denotes M diffraction peaks. Strong texture was demonstrated by the rocking curve for $2\theta=36.5^\circ$, which had a FWHM of less than 2° . Although the M peaks were not readily identifiable with known phases, preliminary TEM and nano-probe analyses suggested that M is a ternary, possibly oxygen stabilized Co-Ti-Si-(O) phase, located at the metal/Si interface. The diffractogram in Fig. 3 also exhibits a number of unidentified peaks, which were due to W contamination of the Cu X-ray anode. There was neither diffraction from Ti-Co intermetallic phases, nor other silicides than CoSi_2 .

The reactions occurring during the complete annealing cycle, as suggested mainly by the *in situ* XRD results above, are summarized in the schematic drawing in Fig. 4. Note that the layer thicknesses are not drawn to scale. The as-deposited bilayer structure is shown to the left, and the final structure^{4,8} is depicted to the right in the diagram, showing the CoSi_2 layer with a cap layer of expelled Ti. The disappearance of a well defined Ti layer below 300°C is due to Ti-Co interdiffusion. At 550°C , Ti reappears, symbolizing that metallic Ti has started to precipitate at the surface, *de facto* an inversion of the metal layers. This conclusion was also supported by XRF depth profiling. The nucleation of CoSi_2 is preceded by formation of a metastable or intermediary reaction product, a ternary Co-Ti-Si-(O) phase M, present at the Co/Si interface. CoSi_2 nucleates at the M/Si interface, and subsequently grows by Co diffusing into the Si

substrate. This is not only supported by our preliminary TEM studies, but also consistent with earlier results that indicated that an interface compound prevented extensive diffusion of Si into the metal layer.⁶

The maximum intensities of the twin M peaks varied significantly between different runs, and this could not easily be coupled to changes in any specific annealing conditions. If the peaks were due to, e.g., oxygen contamination, a varying degree of oxygen during annealing should result in different amount of M. Indeed, by microprobe analysis a detectable oxygen signal was observed in samples annealed *in situ*. However, even a contamination-free separately annealed sample exhibited strong M diffraction. A plausible explanation is that small amounts of remaining and dissolving native silicon oxide in the virgin samples released enough oxygen during anneal to stabilize, for example, a ternary Co-Ti-Si(O) phase at the metal/Si interface.

As the intensity of the diffraction peaks corresponding to M disappeared slightly above 700°C, we conclude that the Co-Ti-Si(O) phase mainly influences the nucleation stage of CoSi₂, which is likely to be a major factor in determining the quality of the silicide. We suggest that M acted as a diffusion membrane that enabled CoSi₂ to nucleate and grow epitaxially at a controlled rate. As such, it also prevented Si from diffusing out into the metal layers, where other silicides might form. It should be pointed out, however, that the role of annealing ambient, N₂, and temperature ramp rate is not yet completely revealed, and will have to be the subject of future *in situ* XRD studies. These and further TEM analyses will be essential to

firmly assess the role of both the M phase, as well as the role of the N₂ annealing ambient, in epitaxial CoSi₂ formation.

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Fig. 1. *In situ* XRD data showing a sequence of scans, obtained during ramping at $5^{\circ}\text{Cmin}^{-1}$ from room temperature to 880°C .

Fig. 2. *In situ* XRD showing the development of peaks, M_I , and M_{II} , from a metastable intermediary reaction product (M).

Fig. 3. Post-annealed X-ray diffractogram from a quenched film containing mainly the M phase, and remaining Co metal.

Figure 4. A schematic drawing, tentatively showing the annealing process of a Co/Ti/Si multilayer structure as a function of temperature. Layer thicknesses are not drawn to scale.