Cobalt silicide formation on a Si(100) substrate in the presence of an interfacial (Fe$_{90}$Zr$_{10}$) interlayer

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Abstract: The reaction between a thin film (126 nm) of Co and Si has been studied at 450 °C for 24 h under high vacuum conditions, in the presence of a FeZr barrier layer. Without a diffusion barrier layer between Co and Si, Co$_2$Si forms at 350 °C as the initial phase while CoSi$_2$ forms at 550 °C. The FeZr barrier layer changed the flux of atoms arriving at the reaction interface. Co reacted with the Si from the substrate and formed a mixed layer of CoSi and CoSi$_2$ in the interlayer region. The use of the FeZr diffusion barrier has been demonstrated to lower the temperature formation of CoSi$_2$ to 450 °C. The reactions were characterized by Rutherford backscattering spectrometry, Auger electron spectroscopy depth profiling, X-ray diffraction using CoK$_\alpha$ radiation and scanning electron microscopy.

Keywords: Co, Si, FeZr, diffusion barrier, reactions, cobalt silicide.

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1. Introduction

Cobalt silicides have proven to be very useful for application in microelectronic devices as contact materials, interconnects, gate electrodes and have a wide range of applications in the semiconductor industry [1-7]. Among the silicides, $CoSi_2$ is of special interest due to favourable properties such as low resistivity (15 $\mu\Omega$-cm compared to 147 and 110 $\mu\Omega$-cm for CoSi and Co_2Si respectively) [8], high thermal stability and low lattice mismatch with Si (approximately 1.2%) [9].

Of interest is the addition of an alloying element to the metal so that the silicidation reaction is offered additional degrees of freedom (choice of the element and its concentration) that may be used to tailor the properties of the resultant silicide (texture, grain size) and/or to engineer the reaction path through which the phase of interest is formed. Several authors have studied the effect of alloying elements on the formation and properties of $CoSi_2$ [10-16]. Other work has focussed on the use of barrier layers to influence the phase formation sequence. The formation of $CoSi_2$ has been reported by applying a Ti barrier layer at temperatures of 550 to 900 ºC [17]. When using a Ta barrier layer between Co and Si the formation of $CoSi_2$ at 560 ºC and CoSi at 850 ºC was observed [18]. There have been some efforts to grow crystalline $CoSi_2$ above 600 ºC by making use of an Fe layer as a barrier placed between cobalt and a Si-substrate [13]. Zr has also been used as a diffusion barrier between Si-substrate and Co, here the formation of $CoSi_2$ above 600 ºC was found to occur [19, 20].

Amorphous diffusion barrier layers are usually preferred due to the absence of grain boundaries which are channels for atomic diffusion. The Fe-Zr system is known to have a good amorphous alloy in the Fe rich side of the Fe-Zr phase diagram with a composition of $Fe_{90}Zr_{10}$ [21]. This alloy has been observed by Osamura [22] not to form crystalline phases in Fe-Zr system such as $FeZr_3$, Fe_2Zr and $FeZr_2$ after thermal annealing. In this study, we investigated the effect of a co-deposited $Fe_{90}Zr_{10}$

barrier layer on Co-silicide formation in the Co-Si system with the view to alter the phase formation sequence.

2. Experimental Method

A 50 mm diameter Si(100) single crystalline p-type substrate was cleaned in solvents and etched in a 4% HF solution prior to being mounted in a molecular beam epitaxy (MBE) chamber. A wedge of $Fe_{90}Zr_{10}$ was co-deposited onto the Si by slowly moving the shutter over the sample during growth. This resulted in a film varying in thickness over the wafer from zero thickness to a total nominal $Fe_{90}Zr_{10}$ thickness of 100 nm at the other end of the wedge. The geometry of the e-guns in the MBE was such that Fe was deposited perpendicular to the main shutter before the substrate, while the Zr e-gun was at a slight angle. This resulted in an enrichment of Zr at the top of this wedge layer. On top of the wedge a uniform 126 nm Co film was deposited. The base pressure of the deposition system chamber was less than 2×10^{-11} Torr and never exceeded 2×10^{-9} Torr during growth. Following deposition, the samples were cleaved into approximately 5×5 mm pieces using a diamond scriber and placed in a desiccator when not being analysed.

In this work we report on the results obtained from the 63 nm FeZr layers and studies on other thickness of barrier layer is being performed. These samples were annealed under high vacuum conditions in a quartz tube furnace at a temperature of 450 °C for 24 h. In order to minimize subsequent delamination of the films, it was discovered that it was necessary to anneal the samples in a two stage process. This consisted of an initial anneal for 3 h at 450 °C followed by a natural cooling to room temperature, after which it was possible to anneal the samples for longer durations without the layers delaminating. The reported annealing times include this initial step and therefore represent the total time spent at a temperature of 450 °C.

The samples were analysed by Rutherford backscattering spectrometry (RBS) before and

after annealing, using 1.6 MeV He$^+$ ions. The detector was at a backscattering angle of 165°

and the sample was tilted by a goniometer to minimize channelling effects. The annealed

samples were characterized by X-ray diffraction (XRD) using CoK$_\alpha$ radiation and scanning

electron microscopy (SEM). The cross-sectional SEM samples were prepared by a fracture

technique. The sample was rested on a pin lying on a brass block. The sample, pin and block

were submersed in LN$_2$ until most of the boiling stopped. Then one side of the sample was

kept in contact with the block, while pressure was applied at the free end, causing the sample

to fracture at the location of the pin. The Auger electron spectroscopy (AES) analysis was

performed using a PHI 600 spectroscope with electron beam energy of 10 keV and 2.6 µA

current with dual gun Ar$^+$ ion sputtering for concentration depth profile analysis in order to

obtain information on the solid-state reactions. The peak to peak heights were converted to

concentrations without the use of specific standards.

3. Results and Discussion

The RBS spectrum of the unannealed sample is shown in **Fig. 1.** RBS analysis using RUMP

[23] found the Co layer to be 1130×10^{15} at/cm^2 thick. Assuming an atomic density of

9.00×10^{22} at/cm^3 this yields a thickness of 126 nm. This is of course a lower limit of the Co

layer thickness as the actual density of the layer may well be less than the standard density.

The peak observed at about 1.15 MeV is from the enriched Zr part of the FeZr layer and is

superimposed on the Co-signal. The corresponding Fe signal is visible between channels 300-

340. The narrowness of the Zr peak is due to the overgrowth of a thin Zr layer due to the

asymmetric e-gun geometry the rest of the Zr peak overlaps with Co, up to an energy of 1.08

MeV. The FeZr layer was found to be 490×10^{15} at/cm^2 thick and assuming that the density of

$Fe_{90}Zr_{10}$ can be estimated from the elemental densities, this equals 63 nm. All the RBS
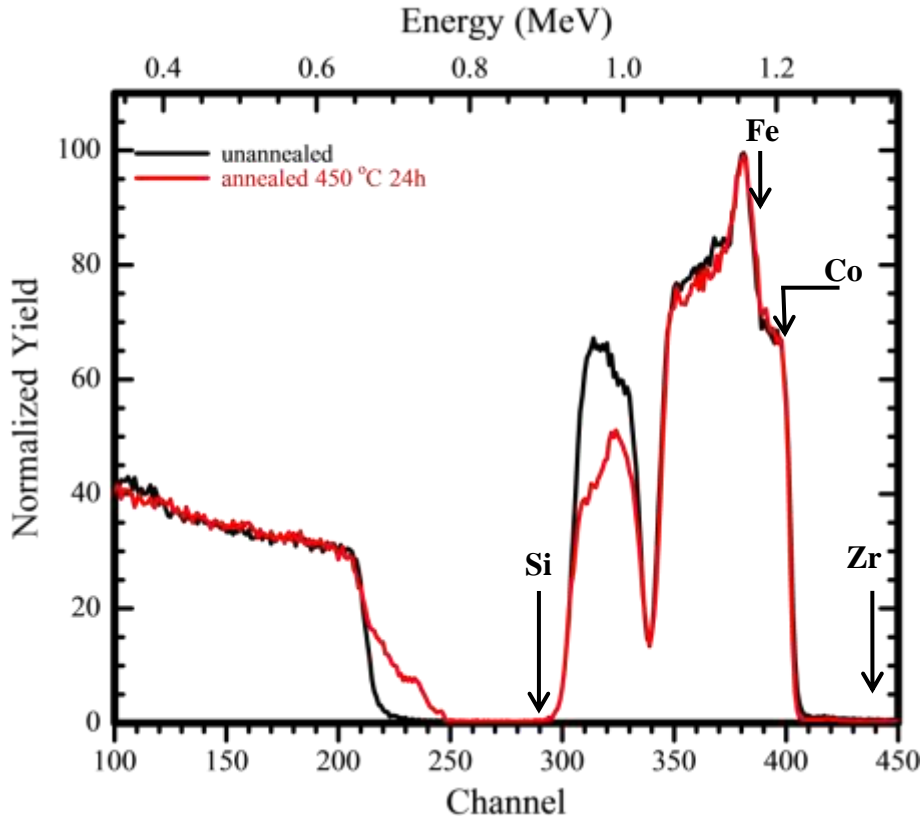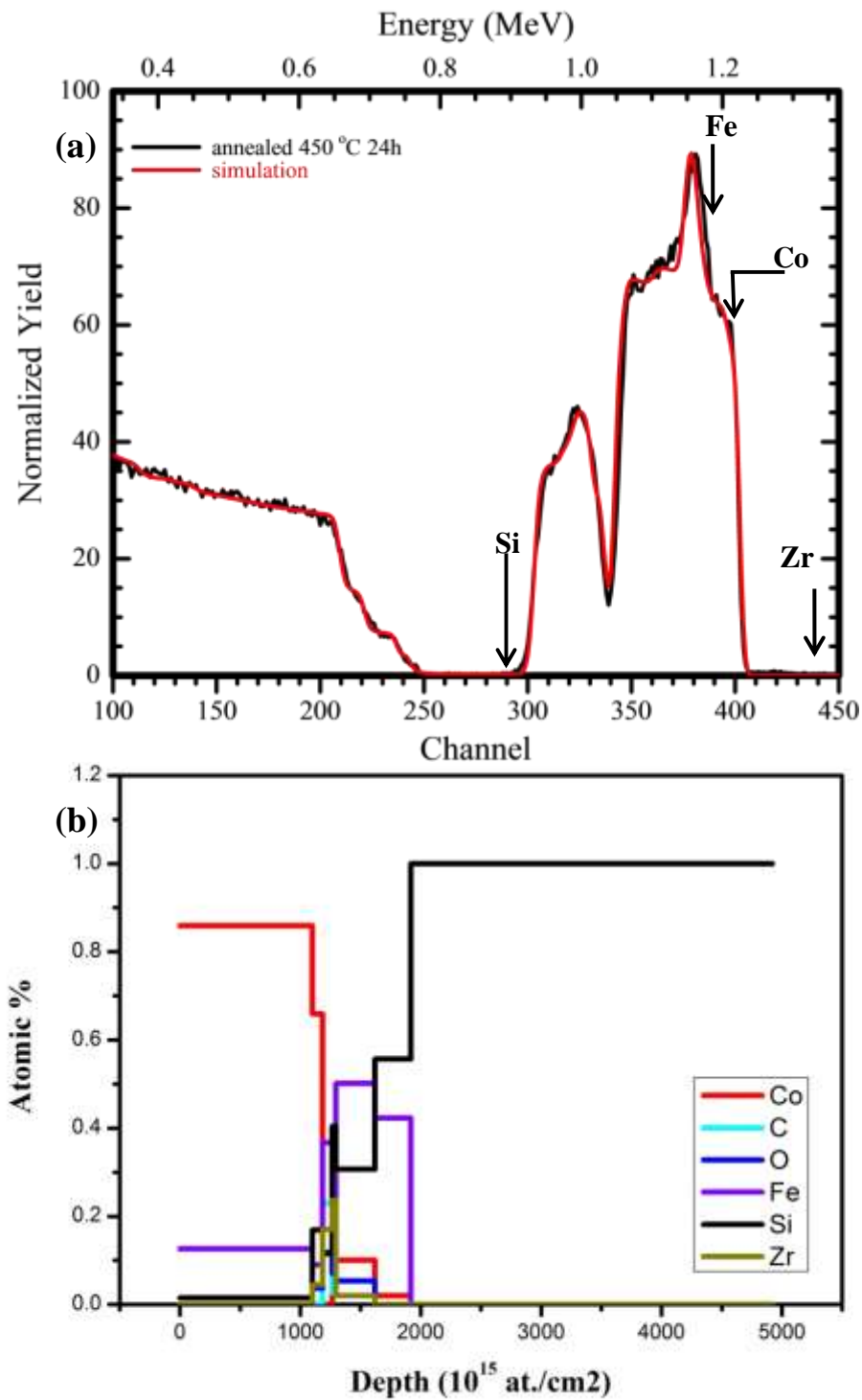
Fig. 1 RBS spectra comparing the sample annealed at 450 °C for 24 h, with its unannealed state. The arrows indicate the surface channel positions for the respective elements.

spectra of samples annealed up to 350 °C were found to perfectly overlay with the unannealed samples and hence are not reported here as there was no visible reaction, even after annealing for 7 days. Also shown in **Fig. 1** is the spectrum obtained after annealing for 24 h at 450 °C. The following qualitative information can be derived by comparing these spectra. The Si signal shifted to higher channels, indicating movement towards the surface but not mixing with the original Co layer to any significant extent. The front most part of the Si signal shows a region of constant Si composition, while the deeper region shows a graded composition profile. Substantial changes in the Fe distribution can be noted (channels 300-340), while the Zr enrichment layer appears to be unchanged. Since the mass resolution between Co and Fe is problematic for RBS the samples were analysed by AES after all XRD and SEM measurements were performed.
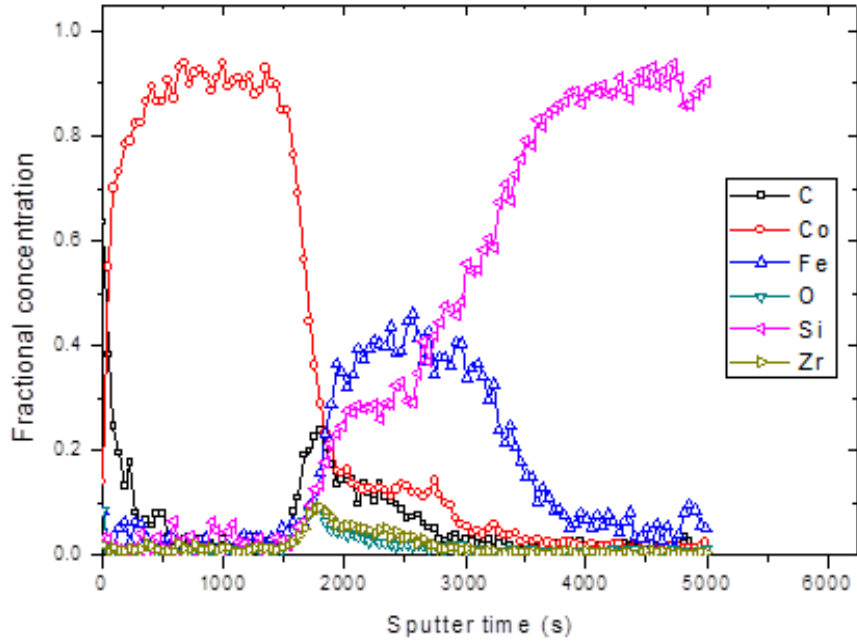
Fig. 2 The AES depth profile after annealing at 450 °C for 24 h.

The depth profiles obtained by AES analysis in **Fig. 2** show Co, Fe, Zr and Si peaks and the presence of carbon at the surface and at the Co/FeZr interface. Oxygen was also picked up by AES analysis and it is striking that its variation in concentration follows that of Zr. This could be due to Zr's affinity for oxygen linking the two elements strongly together. The AES results indicate that a complex mixed phase region with up to six elements could be identified. In this region (sputtering time between 2000-2500 s) it is interesting to note that the Si and Co concentrations are constant and in a 2 to 1 ratio, while the Fe concentration steadily increases. This suggests that the Co and Si are in a phase with a narrow composition range. Fe was also found to be uniformly distributed in the Co layer with a concentration of approximately about 5-10%. According to the Co-Fe phase diagram [24] as much as 10% of Fe can dissolve into Co. The AES results confirmed our RBS simulations and the resulting depth profiles determined from the RBS simulations are shown in **Fig. 3(b)**. The Co and Si profiles

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Fig. 3 (a) Comparison between the RBS spectrum and a simulation of the annealed sample, the arrows indicate the surface channel positions for the respective elements, and **(b)** a representative composition profile obtained from RUMP simulations.

obtained from RUMP simulations indicate the formation of Co-silicides. These depth profiles are similar and consistent with the AES profiles illustrated in **Fig. 2**. The simulation of the RBS spectra of the samples annealed at 450 °C for 24 h was done with five layers (excluding the surface Co and the Si substrate layers) as shown in **Table. 1**. The first three of these layers were used to model the Zr enrichment layer. A reduction in height at the low energy edge of the Fe peak was observed as seen in **Fig. 3(a)**. This was consistent with the AES results as shown in **Fig. 2** and the peak height reduction was due to the solution of Fe atoms into Co forming a Co(Fe) alloy. Therefore, after annealing at 450 °C, the RBS spectrum corresponding to the original Co layer seems unchanged.

Table 1 Results of the RBS simulations of the annealed sample.

| Layer	Thickness (at. /cm^2)	Composition (%)					
		Co	Fe	Zr	Si	O	C
1	1100	86	13	-	1	-	-
2	85	66	10	4	17	3	-
3	80	-	37	17	11	12	23
4	30	13	13	24	40	7	3
5	325	11	50	-	31	6	2
6	300	2	42	-	56	-	-
7	3000	-	-	-	100	-	-
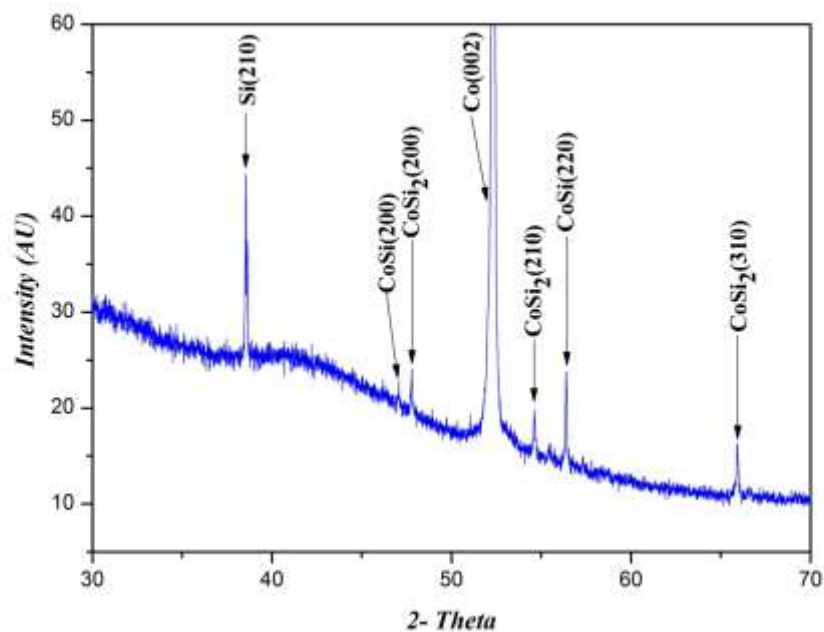
Fig. 4 XRD pattern of the annealed sample.

The XRD scan of the 450 °C (24 h) annealed sample contains peaks corresponding to diffraction from the (200) and (210) planes of the CoSi phase respectively (see **Fig. 4)**. Other peaks of Co silicides are indexed as $CoSi_2$ from the (200), (210) and (310) planes. At the same time the diffraction pattern showed Si(210), as well as cubic Co(002) and possibly cubic Fe(110). However, the cubic Fe phase is only stable above 900 °C, while the Co(002) phase is stable at 450 °C. We therefore index this peak as only Co(002). The $FeSi_2(040)$ and $CoSi_2(210)$, as well as the $FeSi_2(041)$ and CoSi(220) reflections are close (d spacing within 0.003-0.005 Å). We make use of the fact that $FeSi_2$ is a high-temperature phase usually formed at 700 to 950 °C [25-27], with the lowest reported temperature of 550 °C [28] to exclude the possibility of $FeSi_2$ formation and we therefore positively identify the peaks at 54.7 and 56.3° 2-theta positions as $CoSi_2$ (210) and CoSi (220) respectively. While FeSi exists at 450 °C [28] its interplanar lattice spacing is very far from all the Co-Si interplanar spacings that are indicated on the XRD results shown in **Fig. 4**. The FeZr was found to be a barrier to the reaction between Co and Si therefore significantly increasing the reaction times. We find no evidence for any silicide formation at 350 °C for 7 days and no XRD trace of Co_2Si could be found even at an intermediate annealing temperature of 400 °C. Only CoSi and $CoSi_2$ were observed to have formed. The formation temperature of $CoSi_2$ was effectively reduced to 450 °C, compared to 700 °C reported when Ta was used as a diffusion barrier between Co and Si [29].

In **Fig. 5** a cross-sectional SEM image of the sample prepared by LN2 fracture is shown and three different layers can be observed. At the top is the Co(Fe) layer that has formed with large grains. These grains as well as some darker spots (identified to be surface carbon contamination and also observed by the carbon surface peak observed in the AES measurements) were clearly visible on plane-view SEM micrographs (not shown). Below this layer, the columnar microstructure of the reaction zone containing FeZr and a mixture of
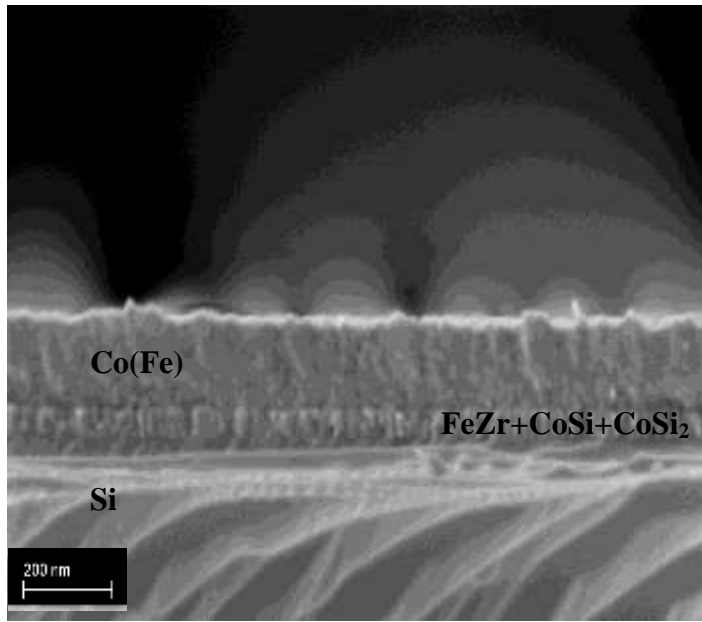
Fig. 5 Cross-sectional SEM image of the annealed sample, prepared by fracturing.

CoSi and CoSi$_2$ is clearly visible. The interface of the reaction zone and both the Si substrate and the Co layer seems quite laterally uniform, which is in good agreement with the sharpness of the back edges of this layer as observed in the RBS spectra. The thickness of the Co(Fe) is about 175 nm, while the reaction zone thickness is 70 nm, both in good agreement with the RBS simulations.

4. Conclusion

In the quartenary system where Co and Si are separated by an FeZr interlayer, the formation of both CoSi and CoSi$_2$ was observed. No evidence for the formation of Co$_2$Si and FeSi has been found and the possibility of FeSi$_2$ formation has been excluded. At the interface between Fe and Si, the AES results show intermixing which is typical of interdiffusion in the absence of phase formation. On the other hand, there is evidence (RBS and AES) that some of the Fe was dissolved in the Co layer within the limits as indicated by the equilibrium phase diagram. Both Co and Si were found in the FeZr interlayer, so that it must be concluded that

the interlayer was not a selective barrier, but rather impeded the diffusion of both Co and Si. Both Co and Si diffused into the reaction zone and formed CoSi and $CoSi_2$. Normally for the Co-Si system without a diffusion barrier layer, Co_2Si has been observed to be the initial phase to form at 350 °C while $CoSi_2$ forms at 550 °C [30, 31]. We found no evidence for any silicide reaction at 350 °C, even for annealing times as long as 7 days. The FeZr interlayer retarded the Co-Si reaction, skipping the formation of Co_2Si, while CoSi and $CoSi_2$ are formed at a lower temperature (450 °C) than normal.

Acknowledgements

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