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Effect of high temperature deposition on $CoSi_2$ phase formation

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This paper discusses the nucleation behaviour of the CoSi to $CoSi_2$ transformation from cobalt silicide thin films grown by deposition at elevated substrate temperatures ranging from 375 °C to 600 °C. A combination of channelling, real-time Rutherford backscattering spectrometry, real-time x-ray diffraction, and transmission electron microscopy was used to investigate the effect of the deposition temperature on the subsequent formation temperature of $CoSi_2$, its growth behaviour, and the epitaxial quality of the $CoSi_2$ thus formed. The temperature at which deposition took place was observed to exert a significant and systematic influence on both the formation temperature of $CoSi_2$ and its growth mechanism. CoSi films grown at the lowest temperatures were found to increase the $CoSi_2$ nucleation temperature above that of $CoSi_2$ grown by conventional solid phase reaction, whereas the higher deposition temperatures reduced the nucleation temperature significantly. In addition, a systematic change in growth mechanism of the subsequent $CoSi_2$ growth occurs as a function of deposition temperature. First, the $CoSi_2$ growth rate from films grown at the lower reactive deposition temperatures is substantially lower than that grown at higher reactive deposition temperatures, even though the onset of growth occurs at a higher temperature, Second, for deposition temperatures below 450 °C, the growth appears columnar, indicating nucleation controlled growth. Elevated deposition temperatures, on the other hand, render the $CoSi_2$ formation process layer-by-layer which indicates enhanced nucleation of the $CoSi_2$ and diffusion controlled growth. Our results further indicate that this observed trend is most likely related to stress and changes in microstructure introduced during reactive deposition of the CoSi film. The deposition temperature therefore provides a handle to tune the $CoSi_2$ growth mechanism.
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INTRODUCTION

If a thin layer of Co deposited on a single crystal Si substrate is heated, Co_2Si begins to form around 350 °C, and this is closely followed by the formation of CoSi.[1] The final phase, $CoSi_2$, does, however, not begin to form until the temperature is raised above around 550 °C.[2] Cobalt disilicide has received a great deal of attention over the past decade or two, much of this due to its implementation as a contact material for microelectronic devices.[3,4] However, apart from its technological applications, $CoSi_2$ growth is interesting from a fundamental point of view for understanding thin film growth, in general. For example, its formation appears to be nucleation controlled as the CoSi phase is normally completed around 450 °C, or earlier, while formation of the subsequent $CoSi_2$ phase only commences once a temperature of around 550 °C has been reached. It is generally accepted that the relatively high temperature required for the onset of $CoSi_2$ formation is due to its small heat of formation from CoSi which causes the initial disilicide formation to be nucleation controlled.[5] However, although the onset of growth is nucleation controlled, the subsequent growth of $CoSi_2$ is layer-by-layer, indicative of diffusion controlled growth.[6] While the formation temperature for binary $CoSi_2$ is reasonably well defined, it has been shown that the onset temperature can be raised or lowered by alloying Co with elements such as Ni, Fe, Ti, and W (Refs. 7–9) or by the insertion of an Au or Ti layer.[10–12]

Another interesting feature of $CoSi_2$ is its cubic CaF_2 structure with a lattice constant which differs from that of Si by only −1.2% making is possible, in principle, for $CoSi_2$ to grow epitaxially on silicon single crystal substrates. Intriguingly, while it is relatively easy to grow $CoSi_2$ films with a high epitaxial quality on Si(111) substrates it is difficult to grow good quality epitaxial films on Si(100) substrates despite the cubic symmetry.[13]

As the Si(100) substrate is of technological importance a variety of techniques have been developed to achieve epitaxial $CoSi_2$ formation on this substrate. One of the best known methods is that reported by Dass *et al.*[14,15] where an interlayer of Ti is deposited between the Si(100) substrate and the Co film, a technique now known as Titanium Interlayer Mediated Epitaxy (TIME). Although this system has been extensively studied, the growth mechanism of the epitaxial $CoSi_2$ layer remains unclear. It was originally believed that the role of the Ti was to reduce the native oxide

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which prevented epitaxial growth,[15] but subsequent explanations suggest that the Ti interlayer acts a barrier, thereby reducing the supply of Co to the Si and raising the $CoSi_2$ formation temperature.[12] Another explanation[16] was that epitaxy was achieved because a reduced Co supply and higher formation temperature resulted in the Co_2Si and CoSi phases being skipped and the $CoSi_2$ formed directly. It was, however, subsequently shown[12,17,18] that CoSi can form prior to epitaxial $CoSi_2$ growth, which suggests that only the Co_2Si phase needs to be skipped in order to produce epitaxy. Other proposals are that epitaxy occurs via the formation of CoSi with (311) preferred orientation[18] or that Ti present on the CoSi grain boundaries influences the nucleation of $CoSi_2$ thereby resulting in a preferential orientation of the disilicide.[8]

Another method of achieving good epitaxy on Si(100) is to grow the disilicide film by a technique referred to as reactive deposition, i.e., deposition carried out with the substrate temperature maintained high enough to ensure that the silicide is formed directly throughout the deposition process. In the case of $CoSi_{2,}$ Vantomme *et al.* have shown[19,20] that disilicide films of good epitaxial quality could be achieved with deposition rates of around 0.14 Å/s for a 600 °C substrate temperature. The quality of the epitaxy, however, deteriorated if the deposition rate was raised too high or if the substrate temperature lowered much lower than 600 °C.

Given that reactive deposition can produce $CoSi_2$ films of superior quality it is only natural to question how CoSi films grown by reactive deposition differ from those grown by conventional solid phase reaction. In particular, given that the Co_2Si phase was skipped in the formation of the CoSi film by reactive deposition, the question that arises is how the epitaxial quality of $CoSi_2$ grown from CoSi prepared in this way compares with that grown directly at 600 °C by reactive deposition epitaxy? Furthermore, as one of the most distinctive features of the Co/Si system is the nucleation controlled onset of $CoSi_2$ formation this investigation also examined the $CoSi_2$ formation temperature from reactively deposited CoSi films to establish if reactive deposition had had any effect on the formation temperature.

EXPERIMENTAL TECHNIQUES

Wafers of Si(100) were given an RCA etch, dipped in 2% HF for two minutes and then rinsed in deionised water before being loaded into an MBE system. No further *in situ* cleaning was performed, and all evaporations were carried out at pressures of $<2 \times 10^{-10}$ Torr. For CoSi films prepared by reactive deposition, 250 Å of Co were deposited at a rate of 0.12 Å/s while the silicon substrates were held at a temperature in the range 375–525 °C using intervals of 25 °C (i.e., temperatures high enough to form the monosilicide directly, but not so high that it would induce complete disilicide formation). For comparison Co was deposited on a Si wafer at room temperature and subsequently annealed at 450 °C for 30 min to convert the film to "conventional" CoSi. An epitaxial $CoSi_2$ film was also grown directly by reactive deposition at 600 °C to enable one to assess the quality of the $CoSi_2$ grown from the reactive deposited CoSi films.

Real-time X-ray diffraction (XRD) was used to carry out the initial stage of the investigation as it was able to rapidly and reliably establish the onset of $CoSi_2$ formation. The measurements were performed with a Bruker D8 diffractometer equipped with a custom built heating stage. Cu K_α X-rays at an incident angle of $\theta = 24°$ were used together with a linear detector placed at 51°, which covered a window range from 41.5° to 60.5° and allowed for fast acquisition of the XRD spectra during the reaction. The window range selected incorporated (210) and (211) diffraction peaks of CoSi at 45.6° and 51.2°, respectively, and $CoSi_2$(220) at 47.9°. The ramped thermal anneals from room temperature to 900 °C were performed at a linear heating rate of 1 °C/s under flowing He.

Real-time Rutherford backscattering spectrometry (RBS) was used to probe the reaction rate and growth mechanism as a function of thermal annealing. Real-time RBS analysis was carried out at pressures of around 2×10^{-5} Pa using 2 MeV alpha particles at an angle of incidence of 60° with respect to the sample normal and a scattering angle of 165°. During the *in situ* analysis the samples were continuously analysed by RBS while being subjected to a linear ramped anneal at a rate of 2 °C/min. During this period the sample temperature, chamber pressure and beam current were measured every 3 s, and a RBS spectrum was recorded every 30 s. This resulted in several hundred 30-s RBS spectra being captured during the anneal, but to improve statistics four such spectra were combined with each of the resulting 2-min spectra being thus representative of the sample over a temperature range of 4 °C. With any real-time analysis of a growth process it is natural to be concerned whether the analysing beam can have an effect the growth rate. This issue has been extensively studies by Theron *et al.*[21,22] using intermittent beams and analysing beam with currents varying from 30–500 nA. No noticeable effect on silicide growth rate could be detected, presumably because the number of vacancy/interstitial defects injected by the reaction at the growth interface far exceeds that induced by the beam.

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) experiments were carried out on a Philips CM30 microscope operated at 300 kV and a JEOL 3000F microscope, also operated at 300 kV. TEM samples were prepared in cross-section as follows; the samples were cut using a diamond wire, stuck together head-on and hand polished down to micrometer thickness. To thin the samples down to electron transparency, the samples were polished by ion-milling in a Balzers ion mill starting with a 8 kV beam until film perforation, continuing with a 5 kV beam for thinning and a 2 kV beam for final polishing.

RESULTS

Figure 1 shows the results of a (room temperature) XRD analysis of samples prepared by reactive deposition at temperatures ranging from 375 to 525 °C. The XRD spectra indicate that films prepared by reactive deposition at temperatures of 475 °C and below consisted entirely of CoSi, while those prepared at 500 °C and 525 °C consisted of a mixture of CoSi and $CoSi_2$. RBS analysis of the as-prepared samples

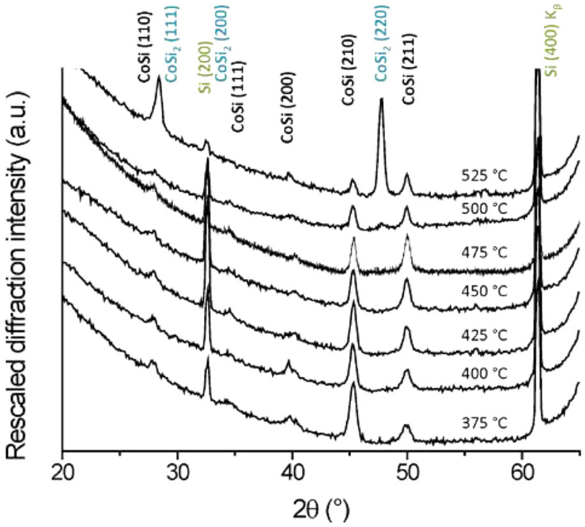

FIG. 1. X-ray diffraction spectra from cobalt silicide thin films deposited by reactive deposition at temperatures ranging from 375 °C to 525 °C.

was also performed, and the results were consistent with the XRD analysis, indicating that the 500 °C sample consisted of about 10% $CoSi_2$ and the 525 °C sample of about 70% $CoSi_2$.

Portions of the CoSi samples were then annealed at 600 °C for 60 min to convert the reactively deposited films to $CoSi_2$. These were then subjected to RBS channelling to determine the epitaxial quality of the $CoSi_2$ prepared in this manner. The result from a $CoSi_2$ film grown from CoSi produced by reactive deposition at 400 °C is shown in Fig. 2. Also shown, for comparison, is the channelled spectrum for $CoSi_2$ prepared by reactive deposition epitaxy at 600 °C. Clearly the film prepared by thermal annealing of reactively deposited CoSi is of very poor epitaxial quality; in fact, no better than $CoSi_2$ produced by conventional solid phase reaction of room-temperature deposited Co films. Similar results were obtained from other reactive-deposited CoSi films, even from those deposited at 525 °C which contained a significant quantity of $CoSi_2$ seed which had been formed earlier during the reactive deposition. This was, however, not completely unexpected as the XRD spectra from 500 and 525 °C showed that the $CoSi_2$ formed during reactive deposition at these temperatures was randomly orientated with a substantial contribution from (111) and (220) XRD reflections.

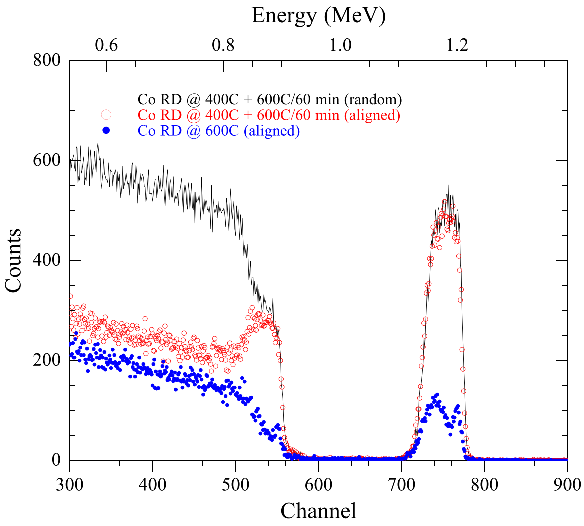

FIG. 2. Aligned and random spectra from a CoSi sample deposited by reactive deposition at 400 °C and subsequently annealed at 600 °C to form $CoSi_2$. For comparison an aligned spectrum from an epitaxial $CoSi_2$ sample formed directly by reactive deposition at 600 °C.

Next the effect that the reactive deposition temperature had on the onset temperature of $CoSi_2$ formation was investigated. In order to provide a reference for the study a Co film deposited at room temperature was annealed at 450 °C for 30 min to produce a conventional CoSi film. The "conventional" CoSi film was then subjected to real-time RBS analysis using a ramp rate of 2 °C/min. A 3D plot of 2-min RBS spectra obtained over the range 450–700 °C is presented in Fig. 3(a), in which the onset of reaction between the CoSi film and the underlying silicon substrate to form $CoSi_2$ is clearly visible. The real-time RBS data are generally best presented in the form of contour plots as shown in Fig. 3(b), with grey-scale representing different levels of backscattering yield. In the figure the RBS cobalt signal falls between channels 320 and 380, and the silicon signal in channels below 280. To interpret the contour plots one needs only to recall that when CoSi transforms to the disilicide the Co RBS signal will broaden and its height will decrease. Contours that run parallel in a vertical direction therefore indicate no change in thickness of the layer, while a broadening or narrowing of the contours (e.g., diagonal contours) indicate that a change in elemental composition has occurred as a consequence of phases growing or shrinking. The "broadening" of the lower energy Co contours around

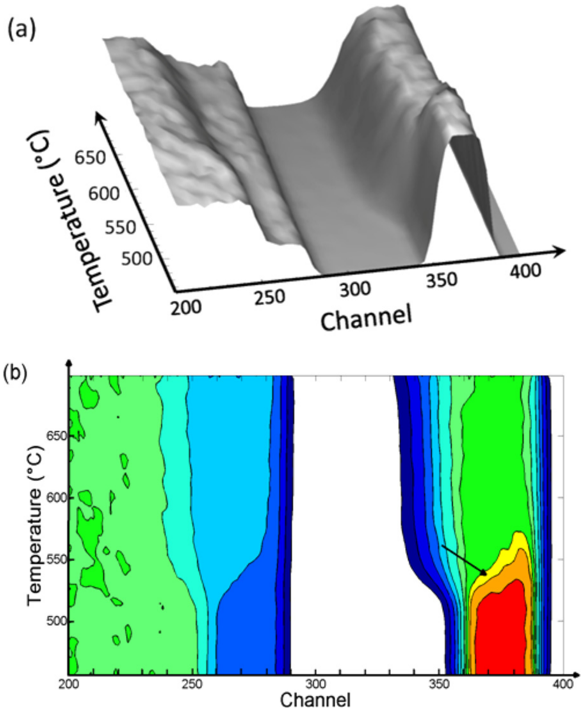

FIG. 3. (a) 3D plot of real-time RBS spectra obtained during a 2 °C/min ramped thermal anneal. The CoSi sample used in this investigation has been prepared by annealing a room temperature deposited Co film at 450 °C for 30 min. (b) RBS contour plot constructed from the real-time RBS spectra with the grey scale representing different levels of backscattering yield.

520 °C therefore indicates the onset of $CoSi_2$ formation. At the same time the high-yield Co contours (indicated by an arrow in Fig. 3(b)) move off diagonally to the right, consistent with a CoSi film that is shrinking as a consequence of layer-by-layer $CoSi_2$ growth. From Fig. 3(b) it can be seen that around 580 °C the contours return vertical again, thereby indicating that the reaction is over and the CoSi film has been completely transformed to $CoSi_2$.

The CoSi film formed by conventional solid phase reaction was also subjected to real-time XRD analysis. The result showed the onset of the $CoSi_2$ phase occurring at a temperature of around 560 °C, the higher onset temperature observed during real-time XRD being not unexpected, given the faster ramp rate used in the XRD analysis (i.e., 1 °C/s for real-time XRD compared to the 2 °C/min for real-time RBS). All the CoSi films produced by reactive deposition were then subjected to real-time XRD analysis to compare their behaviour to those grown by conventional solid phase reaction. The XRD spectra obtained during ramped anneals of samples produced at reactive deposition temperatures of 400 °C and 500 °C are presented in Figs. 4(a) and 4(b), respectively. At low temperatures only two intense CoSi peaks are visible at 45.6° and 51.2°, while at higher temperature an intense $CoSi_2$ peak appears at 47.9° (the less intense $CoSi_2$ peak at 56.9° is also visible at high temperatures in Fig. 4(b)). From the figures it is easy to identify the onset of the formation of the $CoSi_2$ phase, as well as disappearance of the CoSi phase (which occurs when all the CoSi is converted to $CoSi_2$). One of the most striking features observed from a comparison between the two sets of results is the significant difference in the onset temperature of the $CoSi_2$ phase, occurring around 610 °C for CoSi prepared by reactive deposition at 400 °C, compared to about 510 °C for that prepared at 500 °C. Analysis of the remaining samples confirmed the trend; the lower the reactive deposition temperature at which the CoSi film was prepared, the higher the subsequent formation temperature of the $CoSi_2$ phase during the ramped anneal.

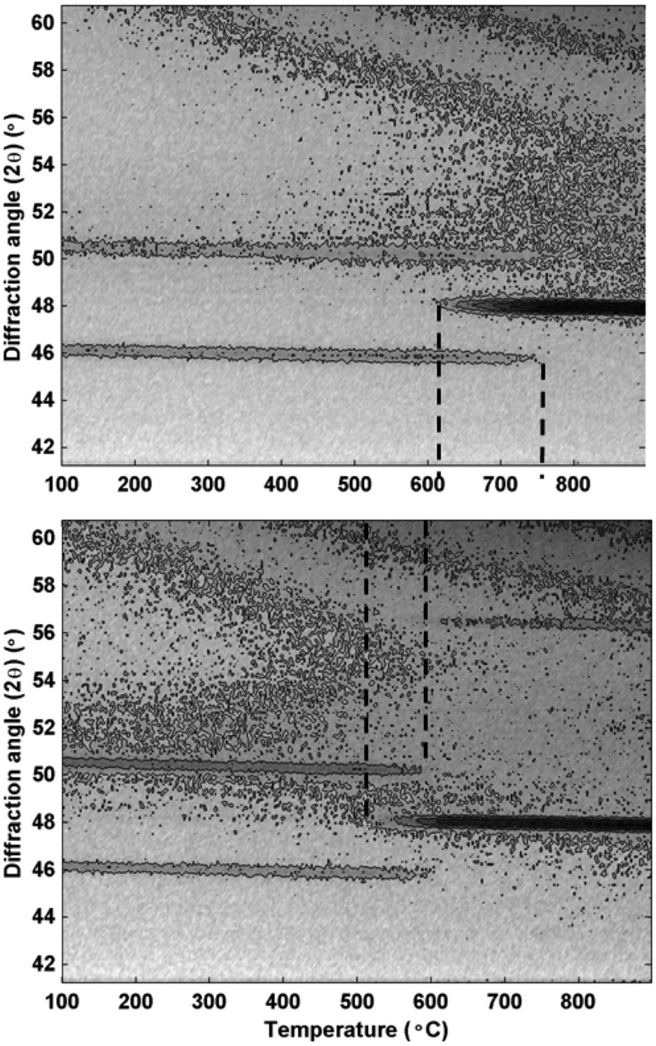

FIG. 4. Contour plots from real-time XRD spectra obtained during a 1 °C/s ramped thermal anneal of a CoSi sample prepared by reactive deposition at (a) 400 °C and (b) 500 °C.

A second noticeable feature is the temperature duration over which both the CoSi and the $CoSi_2$ phases are present. For the sample prepared at 400 °C the CoSi phase begins to transform to $CoSi_2$ at around 610 °C and the reaction is completed by 740 °C, while for that prepared at 500 °C disilicide formation begins around 510 °C and is completed before the temperature reaches 590 °C. Therefore, not only is the onset of the $CoSi_2$ phase at a lower temperature for the sample prepared by reactive deposition at 500 °C, but the rate at which the CoSi phase is converted to $CoSi_2$ is significantly faster, even though the reaction takes place at a lower temperature.

The reactively deposited samples were also subjected to real-time RBS analysis over the temperature range 425–700 °C at a ramp rate of 2 °C/min. For direct comparison with the XRD results presented above the real-time RBS results from the two CoSi films prepared by reactive deposition at 400 °C and 500 °C are presented in the form of contour plots in Fig. 5. By comparing the two plots it can be seen that the CoSi sample prepared by reactive deposition at 400 °C begins to transform to $CoSi_2$ at 575 °C (Fig. 5(a)) while that prepared at 500 °C begins to transform at around 470 °C (Fig. 5(b)). The RBS contour plots also confirm that the 400 °C sample exhibits a slower rate of reaction, given that the transformation to $CoSi_2$ is completed in about 100 °C compared to 50 °C.

A summary of real-time XRD and real-time RBS results for the onset temperature of $CoSi_2$ are shown in Fig. 6 (for comparison the onset temperature for $CoSi_2$ formation from conventional CoSi prepared by room temperature deposition is indicated by a dashed line for real-time RBS and a dotted line for real-time XRD). The results from the two techniques are clearly in general agreement as the trend is essentially the same in both sets, while the average difference between the onset temperature measured by the two techniques can largely be ascribed to the higher heating rate used in the real-time XRD analysis.

A indication of what might be behind this behaviour can be gleaned by noting that the shape of the cobalt contours appear different in the two RBS contour plots presented. In the case of the sample prepared by reactive deposition at 500 °C (Fig. 5(b)) the highest cobalt contours again glide off diagonally to the right as the CoSi film transforms to $CoSi_2$ (i.e., similar in behaviour to that found for CoSi prepared by solid phase reaction see Fig. 3). The 500 °C contours are

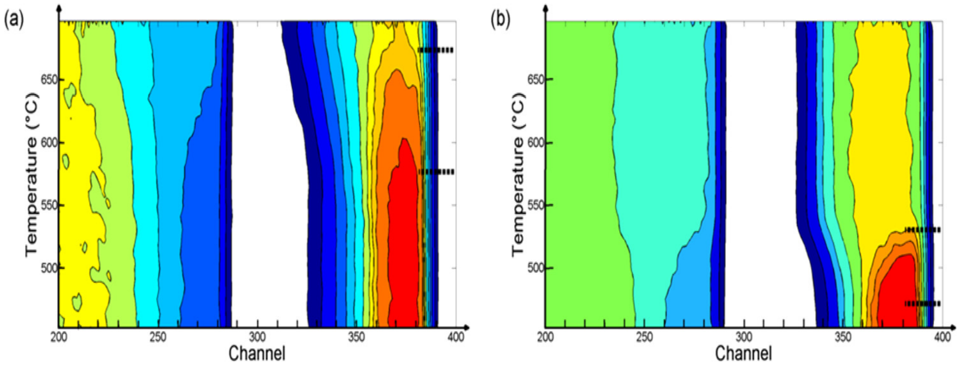

FIG. 5. RBS contour plot constructed from real-time RBS spectra obtained during a 2 °C/min ramped thermal anneal of a CoSi sample prepared by reactive deposition at (a) 400 °C, and (b) 500 °C.

therefore consistent with a Si(100)/$CoSi_2$/CoSi configuration, with the $CoSi_2$ layer growing at the expense of the CoSi by layer-by-layer growth. On the other hand, with the sample prepared at 400 °C the contours no longer glide off diagonally to the right indicating that the transformation from CoSi to $CoSi_2$ is no longer layer-by-layer. When it came to the analysis of individual real-time RBS spectra using the RUMP[23] code it was found that while spectra obtained from samples prepared by reactive deposition at temperatures of 450 °C and above could be analysed assuming a Si(100)/$CoSi_2$/CoSi configuration and layer-by-layer growth, those prepared at 425 °C and below could only be analysed in terms of a Si(100)/$CoSi_{1+x}$ configuration, with x changing from 0 to 1 as the film transformed from CoSi to $CoSi_2$. This therefore suggests that for samples prepared at lower deposition temperatures the CoSi to $CoSi_2$ transformation takes place by columnar growth, as one would expect for nucleation controlled growth.

The result of the detailed RBS analysis from reactively deposited CoSi is shown in Figure 7. For comparison the growth of $CoSi_2$ from CoSi prepared by conventional solid phase reaction is also shown in the figure (open triangles). Although this conventional prepared CoSi layer is slightly thinner than those prepared by reactive deposition the trend is nevertheless clear. The variation of the onset temperature of $CoSi_2$ with reactive deposition temperature is clearly visible. (As there was already about 8 nm of $CoSi_2$ present in the film prepared at a reactive deposition temperature of 500 °C, the onset temperature of $CoSi_2$ formation is taken as the temperature at which the remaining disilicide phase began to grow during the ramped thermal anneal.) From the slope of the curves one can also see that there is a significant difference in the growth rate between the various samples, with those samples which exhibited layer-by-layer growth (450–500 °C) having a significantly higher growth rate than those which exhibited columnar growth (400–425 °C), even though their growth was taking place at a lower temperature. The growth pattern of $CoSi_2$ from conventionally grown CoSi is similar to that for CoSi prepared by reactive deposition at temperatures ranging from 450–500 °C, but with a higher $CoSi_2$ onset temperature.

Clearly the lower $CoSi_2$ onset temperature from CoSi prepared by reactive deposition at 500 °C could be explained by the small amount of $CoSi_2$ in the as-prepared sample circumventing any problem associated the nucleation of the disilicide phase during conventional growth. It is not clear if the same explanation could be used for films prepared by reactive deposition at 475 °C and 450 °C which also exhibit a reduced $CoSi_2$ onset temperature as neither XRD nor RBS detected the presence of $CoSi_2$ in these films but it is just possible it could have been below their detection limit. To test the $CoSi_2$ seed hypothesis a sample was prepared by first depositing 50 Å of cobalt at a reaction deposition temperature of 500 °C (i.e., at a temperature which would produce a $CoSi_2$ seed),

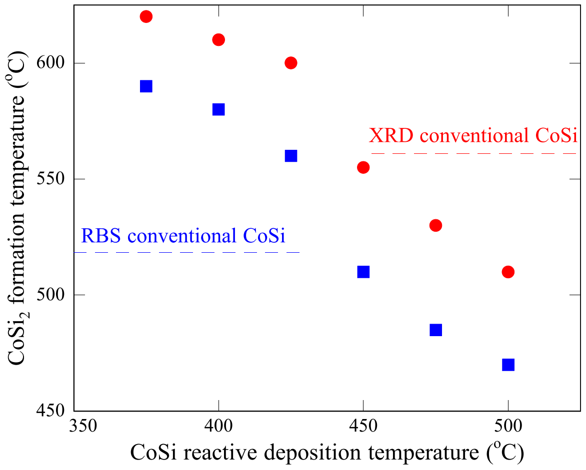

FIG. 6. Plot showing how the onset temperature of $CoSi_2$ formation varies as a function of reactive deposition temperature.

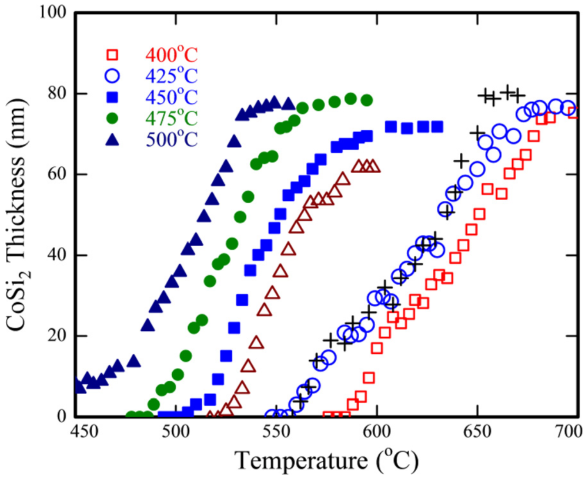

FIG. 7. Plot of thickness of $CoSi_2$ layer as a function of temperature, for cobalt disilicide grown from CoSi prepared at different reactive deposition temperatures. For comparison the growth rate of $CoSi_2$ from conventional, solid phase grown CoSi is also shown.

followed by the remaining 200 Å of cobalt at a reactive deposition temperature of 400 °C. The real-time RBS data obtained from the composite sample (shown by a + symbol in Fig. 7, indicate that the $CoSi_2$ onset temperature and growth pattern is similar to that of the 425 °C sample; in other words, its behaviour is closer to that of the 400 °C sample than the 500 °C. It would therefore appear that the difference in behaviour between the various samples cannot be ascribed to the presence of a $CoSi_2$ seed between the CoSi film and silicon substrate but appears more to be a property of the reactively deposited CoSi film itself.

Cross sectional TEM was carried out on CoSi films prepared by reactive deposition at 400, 450, and 500 °C to ascertain if there were any physical differences in the nature of the films (the samples selected therefore contained those with $CoSi_2$ onset temperatures which were higher and lower than convention films, and also those with and without $CoSi_2$ present in the films). TEM micrographs from the 400 °C sample (Fig. 8(a)) indicate that the CoSi grains vary in width between 15 and 35 nm, with most grains extending across the whole thickness of the CoSi film. Although the CoSi layer is of relatively uniform thickness it is, however, not flat and appears to be bent or buckled. Another significant feature is that the CoSi layer was broken in several places, as shown in Fig. 8(b) for the 450 °C sample. Similar micrographs were obtained from the 400 °C sample, and in neither of these samples was there any evidence of the presence of $CoSi_2$. In the case of the 500 °C sample the CoSi layer appeared to be almost fully intact. A thin, non-continuous layer with a thickness of up to 10 nm, situated between the CoSi layer and the silicon substrate, was observed in one of the 500 °C micrographs (Fig. 9); likely to be a layer of $CoSi_2$ whose presence was indicated in the earlier XRD and RBS analysis. However, the $CoSi_2$ phase was mostly found to be present as inclusions below the CoSi film, as evidenced by the HRTEM image and corresponding Fourier Transform (FT) of a single $CoSi_2$ inclusion imaged along the [110] zone axis orientation, inset to Figure 9(a). The crystalline nature of the CoSi grains is evidenced by the HRTEM image of a single CoSi grain imaged along the [110] zone axis orientation in Figure 9(b).

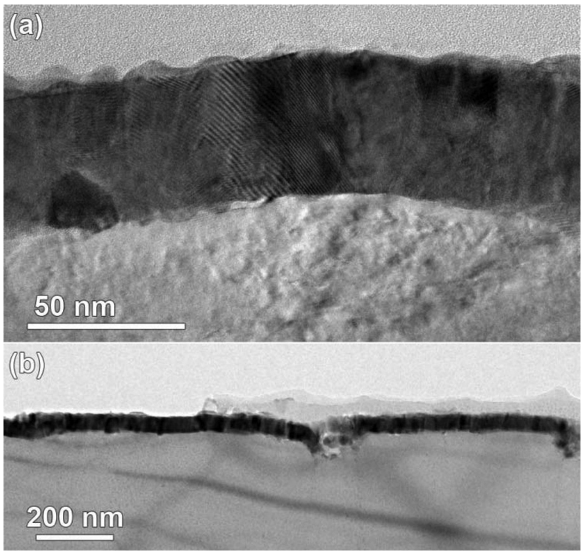

FIG. 8. (a) Cross-sectional TEM micrograph of a CoSi film grown by reactive deposition at 400 °C. (b) Cross-sectional TEM micrograph of the CoSi film grown by reactive deposition at 450 °C showing a crack in the CoSi film.

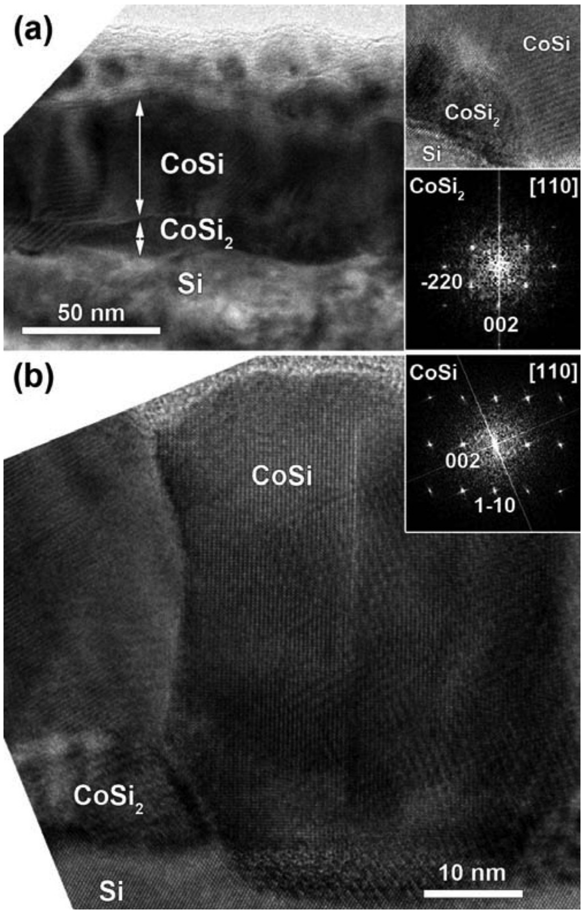

FIG. 9. (a) Cross-sectional TEM micrograph of CoSi film grown by reactive deposition at 500 °C, showing a $CoSi_2$ layer situated between the CoSi film and the Si(100) substrate. The inset shows a $CoSi_2$ seed, imaged along the [110] zone axis orientation as evidenced by the inset FT. (b) HRTEM image showing the Si substrate, a CoSi grain, and a $CoSi_2$ seed. The inset FT evidences the CoSi grain is imaged along the [110] zone axis orientation.

DISCUSSION

The XRD spectra taken of as-deposited samples prepared by reactive deposition indicated that those samples prepared at temperatures of 475 °C and below consisted entirely of CoSi, those at 550 °C and above of $CoSi_2$, and at temperatures in between of a mixture of CoSi and $CoSi_2$. The finding that CoSi films could be prepared over a wide range of temperatures suggests that the CoSi formed directly on deposition, skipping the metal rich, Co_2Si phase. The $CoSi_2$ produced when these samples were transformed to the disilicide during a subsequent anneal was of poor epitaxial quality, and implies that skipping the metal rich phase is not, in itself, a sufficient requirement for the production of epitaxial $CoSi_2$ on Si(100) substrates. This lends support to those who argue that the orientation of the CoSi produced by the TIME process, or the need for Ti to be present in the grain boundaries, is key to determining the quality of the final $CoSi_2$ film.

The finding that the temperature at which the reactive deposition was performed had such a significant effect on the $CoSi_2$ formation temperature and on its growth rate was completely unanticipated. As conventionally grown CoSi forms at a temperature around 400 °C one would expect CoSi produced at 400 °C by reactive deposition would behave similar to conventionally grown CoSi. One finds, however, that the onset temperature of $CoSi_2$ formation is raised by some 60 °C and the reaction rate so reduced that even at elevated temperatures the time taken completely transform the film to $CoSi_2$ is approximately doubled.

It would appear that the effect on the reaction rate is in some way related to the growth mechanism. In Fig. 7 one can see that rate of $CoSi_2$ formation for the 400 °C and 425 °C samples are significantly different in behaviour from those samples deposited at higher temperatures, and the real-time RBS spectra obtained from both samples exhibit columnar growth while the rest exhibit layer-by-layer growth. Columnar growth arises when the nucleation sites of the growing phase are sparse and well separated causing columns of the new phase form initially, and the column then broadens laterally until all the original phase has been converted to the new phase.[5] The formation of $CoSi_2$ by conventional means is nucleation controlled with a substantial delay between the completion of the CoSi phase and the onset of the formation of the disilicide phase. Unlike many other nucleation controlled reactions, $CoSi_2$ growth is found to be layer-by-layer, which suggests that the nucleation sites are sufficiently densely packed to cause the growing region to rapidly coalesce into a continuous layer, and the subsequent growth then becomes layer-by-layer. Reactive deposition at temperatures of 425 °C and below appears to substantially suppress the number of nucleation sites thereby forcing growth to become columnar, which would explain the slower growth rate.

The results presented above indicate that at lower reactive deposition temperatures the thermal stability of the CoSi phase increases, while at the higher reactive deposition temperatures the stability of the CoSi phase was reduced. A similar effect was observed by Van Bockstael *et al.*[24] in their study of silicide phase formation from amorphous Co-Si mixed layers. There they found that when the Si composition of the Co-Si mixed layer approached 50% there was a substantial decrease in the formation temperature of the CoSi phase, and this was accompanied by a substantial increase in the formation temperature of the $CoSi_2$ phase. In their work Van Bockstael *et al.* noted that the lower CoSi formation temperature was accompanied by a significantly larger CoSi grain size which led them to suggest that the increase in size of the grains would have reduced the number of triple points between the heterogeneous grain boundaries required for $CoSi_2$ nucleation. Our TEM micrographs however showed that the grain size remained relatively constant at 15–35 nm in the three samples covering a deposition temperatures range from 400 to 500 °C (precisely the range over which a substantial variation in behaviour was observed) thus indicating that a variation in grain size is unlikely to be an explanation for the behaviour observed in this investigation.

As pointed out earlier, one possible explanation for the decrease in CoSi thermal stability in some of the films deposited at higher temperatures could be that the presence of a $CoSi_2$ seed in the as-deposited sample reduced the need for nucleation. It was to test this hypothesis that the composite 500 °C/400 °C sample was prepared, as any $CoSi_2$ seed in the portion of the film deposited at 500 °C should drastically lower the formation temperature of the remaining portion of CoSi deposited at 400 °C. As shown in Fig. 7 the resultant behaviour was not that different from the 400 °C results, but it is substantially different from the behaviour of the film grown at 500 °C which one might have expected. At first sight this result appears to rule out the presence of a $CoSi_2$ seed as an explanation of the decreased CoSi stability. One must recognise, however, that it is most probable that the subsequent reactive deposition at 400 °C could transformed any $CoSi_2$ seed in the initial layer as it has been shown[25] that $CoSi_2$ in the presence of Co will transform to CoSi when annealed at 400 °C. Nevertheless, while one can accept that the presence of a disilicide seed in those CoSi samples deposited at the high temperatures could give rise to a decreased thermal stability of the CoSi film, it is difficult to see how the *absence* of a $CoSi_2$ seed could give rise to the significant *increase* in the thermal stability observed in those CoSi layer prepared at the lower deposition temperatures. If there was no $CoSi_2$ seed present in these reactively deposited films then they should behave like conventional CoSi film, which they do not.

Finally, turning to the TEM results which show the CoSi layer deposited at 400 and 450 °C as being bent, or corrugated, and broken in places. It is not certain when the breaks in the film occurred, but it is unlikely to be during the deposition as there would then be signs of material being deposited on top of the breaks. The breaks are therefore more likely to have occurred either as the samples cooled after reactive deposition, or subsequently during the TEM preparation. As the silicon substrate was reported to thin faster than the CoSi film during TEM preparation the most likely explanation is that the film broke when the silicon substrate became too weak to support the film. The bending in the CoSi film, and the manner in which they broke, strongly suggests that the reactive deposited films were under considerable compressive stress. As most breaks were observed in the 400 °C sample, while the 500 °C was reported to be almost fully intact, it would appear that the stress was greatest in the films deposited at the lowest temperature.

Compressive stress has been shown to significantly retard the formation of Ni_2Si, NiSi, and $NiSi_2$ on Si(100) substrates,[26] while tensile stress was found to enhance silicide formation. The formation of $NiSi_2$ is nucleation controlled, similar to that of $CoSi_2$. The finding that stress influences $NiSi_2$ formation suggests that it can also influence the formation temperature of other nucleation controlled phases, such as $CoSi_2$. Compressive stress introduced by the low temperature reactive deposition would explain why a lower reactive deposition temperature results in greater CoSi thermal stability. If the stress also reduces the number of nucleation sites then a point will arise where the subsequent growth switches from the diffusion controlled growth observed in samples prepared at 450 °C and above, to the columnar growth observed for temperatures of 425 °C and below. Clearly if tensile stress were present in CoSi films produced at the higher reactive deposition temperatures it would also explain the decreased thermal CoSi stability of those films.

As pointed out earlier, CoSi grown in thin films by conventional solid phase reaction often takes place around 400 °C so the high level of stress in the CoSi film grown by reactive deposition at 400 °C cannot merely be ascribed to thermal stress arising from differences in thermal expansion between CoSi and Si, and more likely to be of an intrinsic nature[27] that is induced during reactive deposition since it takes place far from thermal equilibrium. Clearly the mechanism of CoSi growth by solid phase reaction is also very different to that by reactive deposition. With the former CoSi grows at the interface between Si and Co_2Si and since Si is the diffusing species the growth occurs at the CoSi/Co_2Si interface. In reactive deposition the CoSi grows directly on the Si substrate, but as the diffusing species during reactive deposition of CoSi is unknown it is not clear whether the growth interface is at the surface of the sample or at the Si(100)/CoSi interface. Nevertheless, the different growth environment of reactive deposition could give rise different levels of stress and/or microstructure which may explain the observed behaviour.

Although the exact mechanism is not fully understood the present investigation clearly demonstrates that the formation temperature and growth mechanism of $CoSi_2$ can be substantially altered by varying the reactive deposition temperature at which the CoSi is produced. Reactive deposition therefore provides an alternative method for controlling $CoSi_2$ formation, and it may well be applicable to other nucleation controlled systems.

CONCLUSION

CoSi films have been produced by reactive deposition over a range of temperatures. The epitaxial quality of $CoSi_2$ produced when these samples were subsequently annealed at 600 °C is rather poor, indicating that merely growing CoSi directly and skipping formation of the Co_2Si phase was not sufficient to enhance epitaxial disilicide formation on Si(100) substrates. On the other hand, the temperature at which the reactive deposition took place was found to have a significant influence on the stability of the CoSi phase with those produced at the lowest reactive deposition temperature being the most stable. Those deposited below 450 °C not only had their stability increased but also the growth mechanism of $CoSi_2$ from these films appeared columnar rather than the layer-by-layer growth normally observed. Reactive deposition at temperatures of 450 °C and above produced CoSi which was less stable than that grown conventionally by solid phase growth, with the nucleation of the $CoSi_2$ phase being reduced by up to 50 °C. We have put forward a physical model in which stress and changes in microstructure introduced during reactive deposition of the CoSi films played a major part in the observed behaviour, particularly at the lower deposition temperatures. Reactive deposition has thus been shown to have a major effect on the nucleation of $CoSi_2$ and on its subsequent growth rate, and it would be of interest to establish if similar behaviour is observed with other silicide phases that are nucleation controlled.

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[1] S. S. Lau, J. W. Mayer, and K. N. Tu, J. Appl. Phys. **49**, 4005 (1978).
[2] G. J. van Gurp and G. Lagnereis, J. Appl. Phys. **46**, 4301 (1975).
[3] S.-L. Zhang and M. Östling, Crit. Rev. Solid State Mater. Sci. **28**, 1 (2003).
[4] S.-L. Zang and U. Smith, J. Vac. Sci. Technol. A **22**, 1361 (2004).
[5] F. M. d'Heurle, J. Mater. Res. **3**, 167 (1988).
[6] R. Pretorius, M.-C. Chen, and H. A. Ras, Mater. Lett. **3**, 282 (1985).
[7] C. Detavernier, R. L. Van Meirhaeghe, F. Cardon, and K. Maex, Phys. Rev. B **62**, 12045 (2000).
[8] C. Detavernier, C. Lavoie, and R. L. Van Meirhaeghe, Thin Solid Films **468**, 174 (2004).
[9] D. Smeets, J. Demeulemeester, K. De Keyser, D. Deduytsche, C. Detavernier, C. M. Comrie, C. C. Theron, C. Lavoie, and A. Vantomme, J. Appl. Phys. **104**, 093533 (2008).
[10] C.-A. Chang and J.-S. Song, Appl. Phys. Lett. **51**, 572 (1987).
[11] C. Detavernier, C. Lavoie, F. D'Heurle, H. Bender, and R. L. Van Meirhaeghe, J. Appl. Phys. **95**, 5340 (2004).
[12] A. Vantomme, M.-A. Nicolet, and N. D. Theodore, J. Appl. Phys. **75**, 3882 (1994).
[13] S. M. Yalisove, R. T. Tung, and D. Loretto, J. Vac. Sci. Technol. A **7**, 1472 (1989).
[14] C.-S. Wei, D. B. Fraser, M. L. A. Dass, and T. Bratt, in *Proceedings of the VII International IEEE VLSI Multilevel Interconnection Conference* (Santa Clara, CA, 1990), p. 233.
[15] M. L. A. Dass, D. B. Fraser, and C.-S. Wei, Appl. Phys. Lett. **58**, 1308 (1991).
[16] S. L. Hsia, T. Y. Tan, P. Smith, and G. E. McGuire, J. Appl. Phys. **70**, 7579 (1991).
[17] J. Cardenas, S. Hatzikonstantinidou, S.-L. Zhang, B. G. Svensson, and C. S. Petersson, Phys. Scr., T **54**, 198 (1994).
[18] M. Falke, B. Gebhardt, G. Beddies, S. Teichert, and H.-J. Hinneberg, Thin Solid Films **336**, 201 (1998).
[19] A. Vantomme, S. Degroote, J. Dekoster, and G. Langouche, Appl. Surf. Sci. **91**, 24 (1995).
[20] A. Vantomme, S. Degroote, J. Dekoster, G. Langouche, and R. Pretorius, Appl. Phys. Lett. **74**, 3137 (1999).
[21] C. C. Theron, Ph.D. dissertation, University of Stellenbosch, 1997.
[22] C. C. Theron, J. A. Mars, C. L. Churms, J. Farmer, and R. Pretorius, Nucl. Instrum. Methods Phys. Res. B **139**, 213 (1998).
[23] L. R. Doolittle, Nucl. Instrum. Methods Phys. Res. B **9**, 344 (1985).
[24] C. Van Bockstael, K. De Keyser, J. Demeulemeester, A. Vantomme, R. L. Van Meirhaeghe, C. Detavernier, J. L. Jordan-Sweet, and C. Lavoie, Microelectron. Eng. **87**, 282 (2010).
[25] E. C. Cahoon, C. M. Comrie, and R. Pretorius, Appl. Phys. Lett. **44**, 511 (1984).
[26] L. W. Cheng, H. M. Lo, S. L. Cheng, L. J. Chen, and C. J. Tsai, Mater. Sci. Eng., A **409**, 217 (2005).
[27] A. Steegen and K. Maex, Mater. Sci. Eng. R **38**, 1 (2002).