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# Titanium Interlayer Mediated Epitaxy of $CoSi_2$ on $Si_{1-x}Ge_x$

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## Abstract

Titanium Interlayer Mediated Epitaxy (TIME) has been shown to promote the formation of epitaxial  $CoSi_2$  on Si (100). Similarities between Si and  $Si_{1-x}Ge_x$  alloys have motivated a study of whether the TIME process could be successful in forming epitaxial  $CoSi_2$  on  $Si_{1-x}Ge_x$ . Titanium layers of varying thickness were deposited as interlayers between a Co layer and c-Si/Si<sub>0.8</sub>Ge<sub>0.2</sub> grown epitaxially onto Si (100) to investigate their role in the formation of epitaxial  $CoSi_2$  on  $Si_{1-x}Ge_x$  alloys. The effect of Ti interlayer thickness on the orientation of  $CoSi_2$  to the  $Si_{1-x}Ge_x$  substrate, and the conditions under which a polycrystalline  $CoSi_2$  film has been formed have been studied. It was found that Ti was beneficial in promoting epitaxial  $CoSi_2$  adjacent to the substrate was achieved, and pinhole formation was minimized. It was also observed that for increased interlayer thickness, Ti reacted with Si to form a titanium silicide.

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## 1. Introduction

Integrated circuit fabrication processes have employed the formation of metal silicide source/drain contacts to Si, where the C54 phase of TiSi<sub>2</sub> has been preferred due to its low resistivity. However, complementary metal-oxide-semiconductor (CMOS) devices employing TiSi2 as the electrical contact material suffer from structural instabilities at the source and drain regions, due to the lateral growth of the silicide over the oxide spacer. These instabilities lead to leakage currents in the device [1]. The formation of CoSi2 contacts to Si is now preferred for implementation into existing self-aligned silicide (SALICIDE) processing schemes [2]. The SALICIDE process with CoSi<sub>2</sub> is more desirable as a CMOS device contact because its resistivity  $(\sim 15 \ \mu\Omega \ cm)$  is comparable to that of TiSi<sub>2</sub>, yet it has a higher thermal stability on Si and SiO<sub>2</sub>, and its cubic CaF<sub>2</sub> structure has a smaller lattice mismatch with Si. On the basis of this small lattice mismatch it might be expected that epitaxial CoSi<sub>2</sub> on Si (100) would form relatively easily. However, this is not the case.

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The formation of epitaxial CoSi2 on Si (111) has been reported in the literature and is well documented [3-6]. However, the formation of epitaxial CoSi<sub>2</sub> on Si (100) by the co-sputtering of Co and Si on Si (100) [7,8], or by the deposition of Co on Si (100) [9,10] has been found to lead to the formation of a poly-crystalline CoSi2 film. Other methods, such as template approaches, have also been used to achieve CoSi2 epitaxy to Si (100) with two epitaxial orientations [11,12]. Templating to Si (100) requires that the ratio of the Co and Si atoms needed to form the initial template to be carefully controlled to avoid the formation of a poly-crystalline silicide film [11,12]. The concept of templating to form epitaxial CoSi<sub>2</sub> has been extended to strained Si-Ge substrates by Boyanov, et al. [13], where they established the formation of epitaxial CoSi<sub>2</sub> using a conventional Co/Si template and a modified template method.

One of the more successful means of promoting  $CoSi_2$  epitaxy on Si has been by the use of what has been called Titanium Interlayer Mediated Epitaxy (TIME) [14–23]. In the TIME process a Co/Ti/Si structure is employed, and Ti assists in the formation of epitaxial  $CoSi_2$  by acting as an oxygen getter, cleaning the surface of the Si substrate, and by affecting the diffusion of Co atoms, thereby controlling the formation of the

successive cobalt silicide phases that eventually lead to the formation of  $CoSi_2$ . Although the role Ti plays in the formation of epitaxial  $CoSi_2$  remains unclear, its relative success with Si (100) has motivated this study of whether the TIME process can be used to form epitaxial  $CoSi_2$  on  $Si_{1-x}Ge_x$  grown to Si (100).

The formation of  $CoSi_2$  on Si–Ge was studied using the following general scheme: where  $Co/Ti/Si/Si_{1-x}Ge_x$  layers, with Ti layers 10, 30, 50, 70, and 100 Å thick, were sequentially deposited on Si (100) substrates. To initiate phase formation, all samples were then annealed in UHV at 700 °C. The films were grown on Si<sub>0.8</sub>Ge<sub>0.2</sub> substrates, since this composition is close to that which is considered to be stable with CoSi<sub>2</sub>, according to the Co–Si–Ge ternary phase diagram [24,25]. The samples were characterized by Auger electron spectroscopy (AES), X-ray diffraction (XRD), scanning electron microscopy (XTEM), and X-ray absorption near-edge structure (XANES) measurements.

#### 2. Experiment

The p-type Si (100) wafers were prepared for deposition by spinetching using an HF:H<sub>2</sub>O:ethanol (1:1:10) solution. The cleaned wafers were quickly loaded into a UHV Integrated Process and Analysis System, consisting of a linear transfer line coupled to various processing and analysis chambers, where the sample fabrication and in-situ characterization was performed. The samples were transferred to a solid-source  $Si_{1-x}Ge_x$  molecular beam epitaxy (MBE) chamber (base pressure  $< 3.2 \times 10^{-8}$  Pa) and thermally desorbed at 900 °C for 10 min to remove surface oxides and contaminants [13]. Prior to MBE growth of the strained  $Si_{1-r}Ge_r$ layer, a silicon buffer layer of 200 Å thickness was grown at 550 °C at a rate of 0.2 Å/s. Strained Si<sub>1-x</sub>Ge<sub>x</sub> layers with x=0.2 were grown approximately 500 Å thick onto the buffer layer at a temperature of 550 °C. The silicon and germanium were deposited at rates of 0.4 Å/s and 0.1 Å/s, respectively. The deposition thickness of the layers was established by an oscillating quartz crystal deposition monitor.

Immediately after the Si<sub>0.8</sub>Ge<sub>0.2</sub> layer had been formed, an epitaxial Si layer was deposited at a temperature of 550 °C and a rate of 0.2 Å/s, and grown to a target thickness of 728 Å. This corresponds to the stoichiometric amount of Si needed to form CoSi<sub>2</sub> by reaction with a Co layer of 200 Å thickness and should minimize the consumption of the underlying Si<sub>1-x</sub>Ge<sub>x</sub> layer through reaction with either Co or Ti.

Following the growth of the epitaxial Si layer, the samples were allowed to cool to near ambient temperature and were transferred in UHV to an e-beam metallization chamber (base pressure  $<4 \times 10^{-8}$  Pa) where layers of Ti and Co were deposited at a rate of 1 Å/s using an oscillating quartz crystal deposition monitor. Ti thicknesses of 10, 30, 50, 70, and 100 Å, were employed to study the effects of the diffusion barrier layer thickness upon phase formation. Co layers were deposited to a thickness of 200 Å. All samples were then annealed in UHV at 700 °C for 15 min.

The films were studied *in situ* using Auger electron spectroscopy (AES) to determine the surface chemistry. After removal from the UHV system the films were studied by X-ray

diffraction (XRD) using a Rigaku Geigerflex diffractometer with Cu K<sub> $\alpha$ </sub> radiation, at a 27 kV tube voltage and 20 mA tube current. Data was collected in a  $\theta$ -2 $\theta$  mode, where 2 $\theta$  ranged between 25–75°, with 1° diffraction and scattering slits, and a detector energy resolution of 42–45%. The surface morphology of the films was recorded using a Joel Scientific model 6400 field emission scanning electron microscope.

The juxtaposition of the individual layers of material which comprise the samples was examined using cross-sectional transmission electron microscopy (XTEM), and the composition of the layers was analyzed using electron energy loss spectroscopy (EELS). The sample preparation process involved sectioning, sandwiching, polishing, placing the sample on a copper TEM ring, dimpling and ion milling. Two pieces of the material of interest were cut into 0.1-0.15 cm×0.29-0.38 cm pieces, with an average thickness of less than 1 mm, and were sandwiched together, facing each other, with two similar sized pieces of general silicon subsequently glued on the outside faces of the sandwich for support. Between each of these layers was a 10:1 resin and hardener epoxy mixture from Gatan (part number 601.07270). The sandwich was heated to 130 °C for 30 min to cure the epoxy mixture and cooled to room temperature. Each sample was polished with a rough grit paper to flatten all four material phases. The samples were then sequentially polished using 30 micron, 15 micron, 6 micron, 3 micron and 1 micron diamond papers and a colloidal silica slurry on a Buehler Microcloth paper. Each sample was then inverted with the polished side down and attached to a copper ring with the 10:1 resin and hardener epoxy mixture. The samples were again cured at 130 °C for 30 min and flattened with either a rough grit paper or 30 micron diamond paper to a thickness of 70-100 µm. Each sample was then dimpled using a Model 656 Gatan Dimple Grinder, 3 micron diamond paste and a starting weight on the samples of 20 grams. The approximate thickness of each sample was monitored on a dial indicator, however, the actual thickness of the material was determined using an Olympus BX60 light microscope. When backlighting on the microscope showed a red color the sample in question was polished on the dimpler to eliminate as many scratches possible, cleaned with acetone and methanol and placed in the ion milling. A Gatan Dual Ion Mill set at 4 kV, 1 mA and at an angle of 13° was employed until a hole was produced near the interface. The JEOL 2010F TEM operating at 200 kV along with an EELS system at the North Carolina State University was used to analyze the samples.

The near-edge X-ray absorption (XANES) features at the Co and Ti K-edges were used to determine the relative amounts of the various silicide phases present in the films. The XANES measurements were conducted at the National Synchrotron Light Source on beamline X-11A at Brookhaven National Laboratory.

#### 3. Results

The AES of the samples after annealing and an AES analysis of a 50 Å sample before and after UHV annealing at 700 °C for 15 min are shown in Figs. 1 and 2. As displayed in Fig. 1, Si, Ti, and Co LMM peaks indicate the presence of these elements at or near the surface of the film ( $\sim 2$  nm). Small differences in the



Fig. 1. AES scans of the 10 (a), 30 (b), 50 (c), 70 (d), and 100 Å (e) inter-layered samples after annealing at 700  $^\circ$ C for 15 min.

peak-to-peak heights from the Si, Ti, and Co signals are detected, which reflect the trends in the film composition, but do not suggest that all of the Ti inverts during the annealing process. Other studies have shown that residual amounts of Ti are found in CoSi2 thin films formed during the interlayer mediated epitaxy process [15,16]. Shown in Fig. 2 is a comparison of the AES spectra for the 50 Å diffusion barrier sample before and after annealing. Fig. 2 indicates the development of a small peak due to oxygen ( $\sim$  510 eV) which represents submonolayer coverage presumably at the surface. We do not anticipate that this contamination affects the process or the analysis. After annealing, a decrease in the Co signal is observed. A Ti peak is not present before annealing since the interlayer is covered by a thick layer of Co. Its emergence after annealing suggests the presence of Ti or a Ti compound on or near the surface of the film, which would attenuate the signal from the underlying layers containing Co and Si atoms.



Fig. 2. AES spectra of a 50 Å diffusion barrier sample before and after annealing at 700  $^{\circ}\mathrm{C}$  for 15 min.

The long-range crystalline order was determined from the  $\theta$ -2 $\theta$  X-ray diffraction scans, as shown in Figs. 3 and 4. Each sample was marked by the appearance of the Si (200) peak at 32.91°, shown in Fig. 3, as well as peaks corresponding to diffraction from the CoSi<sub>2</sub> (400) planes at ~70.80° as shown in Fig. 4.

As shown in Figs. 3 and 4, relatively intense  $CoSi_2$  (200) and (400) peaks and a well-defined (220) peak of low intensity were present in the scan for the 10 Å diffusion barrier sample, whereas the  $CoSi_2$  (200), (400), and (220) peaks, in addition to a peak from a  $Ti_5Si_3$  phase with (202) orientation, were present in the 30 Å diffusion barrier sample. Aside from peaks associated with the substrate, only the  $CoSi_2$  (200) and (400) peaks were present in the 50 Å diffusion barrier sample. For the 50, 70 and 100 Å samples the absence of additional  $CoSi_2$  peaks is consistent with the formation of an epitaxial layer.

The change in Ti interlayer thickness from 50 to 70 Å and 100 Å was marked by a transition from the exclusive presence of cobalt silicide phases, to the re-emergence of peaks from Ti silicide phases. These peaks increased in intensity with the diffusion barrier thickness. The presence of C54 TiSi<sub>2</sub> was indicated by the weak (311) and (004) peaks. In addition, a weak peak corresponding to Ti<sub>5</sub>Si<sub>3</sub> was found in the 100 Å sample. The range was enlarged by extending the 2 $\theta$  scan to 150° for all of the samples; no other peaks were observed, which indicates the absence of any additional ordered phases.

The degree to which the  $\text{CoSi}_2$  films were strained to the substrate was determined using the X-ray diffraction results. The out-of-plane lattice constants for the  $\text{CoSi}_2$  films were calculated from XRD, using the (200) and (400) peaks. The in-plane lattice constants of the  $\text{CoSi}_2$  film were obtained using classical elasticity theory [26] and the  $\text{CoSi}_2$  elastic constants [27]. Using the (200) peaks, the out-of-plane lattice constant ranged from



Fig. 3. X-ray diffraction data for the Ti interlayered samples, in a  $2\theta$  scan range between 25–75°. Diffraction results indicate the formation of CoSi<sub>2</sub> (200), (400), and (220) for 10 (a) and 30 Å (b) Ti inter-layered samples, Ti<sub>5</sub>Si<sub>3</sub> (202) for the 30 Å interlayered sample, CoSi<sub>2</sub> (200) and (400) for the 50 Å (c) inter-layered sample, and CoSi<sub>2</sub> (200) and (400), Ti<sub>5</sub>Si<sub>3</sub> (102), TiSi<sub>2</sub> (311) and (004), and Ti<sub>5</sub>Si<sub>3</sub> (202) for the 70 (d) and 100 Å (e) inter-layered samples.

5.301±0.001 Å to  $5.315\pm0.001$  Å. Using the (400) peaks, the lattice constants ranged from  $5.310\pm0.001$  Å to  $5.320\pm0.001$  Å. The CoSi<sub>2</sub> (200) and (400) diffraction peak positions and perpendicular lattice spacing determined from XRD measurements, as well as the diffraction peak positions and perpendicular lattice spacing assuming both a fully strained and fully relaxed Si<sub>1-x</sub>Ge<sub>x</sub> layer are shown in Table 1. Using the (200) peak, it was found that the in-plane lattice constant of CoSi<sub>2</sub> ranged from  $5.407\pm0.002$  Å to  $5.415\pm0.002$  Å. Using the (400) peak, the in-plane lattice constant ranged from  $5.4028\pm0.001$  Å to  $5.4074\pm0.001$  Å. The in-plane lattice constant of the CoSi<sub>2</sub> films is close to that of bulk Si, with a value of 5.431 Å. The bulk CoSi<sub>2</sub> lattice constant is 5.364 Å [24], suggesting that the CoSi<sub>2</sub> films are partially relaxed but still under tensile stress in the plane of the interface.

The  $Si_{1-x}Ge_x$  (400) diffraction peak was examined to explore the strain relaxation and the relative Si and Ge concentration in the films. It is not possible to separately determine both properties from the single diffraction peak. From the peak positions the lattice constant of the  $Si_{1-x}Ge_x$  films were determined. The deviations of the lattice constants from that of unstrained  $Si_{0.8}Ge_{0.2}$  indicates that all the films were partially relaxed. The  $Si_{1-x}Ge_x$  (400) and diffraction peak positions and lattice spacing determined from XRD measurements, as well as the  $Si_{1-x}Ge_x$ (400) diffraction peak positions and perpendicular lattice spacing for a fully strained and fully relaxed  $Si_{1-x}Ge_x$  layer are shown in Table 1. Variations in peak positions of the different layers indicated that the  $Si_{1-r}Ge_r$  concentration deviated somewhat (by  $\sim \pm 2\%$ ) from the target of 80% Si and 20% Ge, with the exception of the 10 Å sample which showed a larger deviation of  $\sim 4\%$ . These variations were attributed to slight changes in the calibration of the deposition rates. Based on this analysis it appears that all of the samples were partially relaxed.



Fig. 4. X-ray diffraction data in a  $2\theta$  scan range from  $66-72^{\circ}$ , indicating the formation of epitaxial CoSi<sub>2</sub> (400) for the 10 Å (a), 30 Å (b), 50 Å (c), 70 Å (d), and 100 Å (e) inter-layered samples. The peaks corresponding to the formation of epitaxial CoSi<sub>2</sub> (400) are located at ~ 70.80°. Diffraction peaks from the Si<sub>1-x</sub>Ge<sub>x</sub> layer are located at ~ 68°, while peaks from the Si (400) substrate are located at ~ 69.13°.

| Table 1 |
|---------|
|---------|

The Si<sub>1-x</sub>Ge<sub>x</sub> (400) and CoSi<sub>2</sub> (200) and (400) diffraction peak positions and perpendicular lattice constant obtained from the XRD measurements, and calculated diffraction peak positions and lattice spacing for Si<sub>1-x</sub>Ge<sub>x</sub> (400) and CoSi<sub>2</sub> (200) and (400) for a fully strained and fully relaxed Si<sub>1-x</sub>Ge<sub>x</sub> (400) layer

| Interlayer<br>thickness<br>(Å) | $Si_{1-x}Ge_x$ (400)                 |                                      | CoSi <sub>2</sub> (200)              |                            | CoSi <sub>2</sub> (400)              |                            |
|--------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|----------------------------|--------------------------------------|----------------------------|
|                                | 2θ<br>(degrees)                      | Lattice<br>constant<br>(Å)           | 2θ<br>(degrees)                      | Lattice<br>constant<br>(Å) | 2θ<br>(degrees)                      | Lattice<br>constant<br>(Å) |
| 10                             | 68.259<br>±0.013                     | $5.4931 \pm 0.001$                   | $33.688 \pm 0.002$                   | 5.3109<br>±0.001           | $70.862 \pm 0.011$                   | $5.3162 \pm 0.001$         |
| 30                             | $68.107 \pm 0.030$                   | $5.5038 \pm 0.002$                   | $33.663 \pm 0.003$                   | $5.3147 \pm 0.001$         | $70.797 \pm 0.010$                   | $5.3205 \pm 0.001$         |
| 50                             | 68.024 + 0.020                       | 5.5098<br>+0.002                     | $33.750 \pm 0.004$                   | 5.3014 + 0.002             | 70.920 + 0.025                       | 5.3125 + 0.002             |
| 70                             | 68.109                               | 5.5037                               | 33.719                               | 5.3062                     | 70.950                               | 5.3106                     |
| 100                            | $\pm 0.021$<br>68.159<br>$\pm 0.043$ | $\pm 0.002$<br>5.5002<br>$\pm 0.003$ | $\pm 0.003$<br>33.710<br>$\pm 0.003$ | $\pm 0.002$<br>5.3075      | $\pm 0.011$<br>70.919<br>$\pm 0.000$ | $\pm 0.001$<br>5.3126      |
| Fully<br>strained<br>layer     | £0.043<br>68.005                     | ±0.003<br>5.5111                     | ±0.003<br>33.926                     | ±0.001<br>5.2817           | ±0.009<br>71.397                     | ±0.001<br>5.2817           |
| Fully<br>relaxed<br>layer      | 68.497                               | 5.4763                               | 34.299                               | 5.3640                     | 72.105                               | 5.3640                     |

SEM micrographs of the Ti diffusion barrier samples are shown in Fig. 5(a)–(e). The surface features of the micrographs of the 10, 30, and 100 Å samples indicate the existence of pinholes of varying dimensions. In the 10 and 30 Å samples, the pinholes had an aerial density of  $\sim 1.68 \times 10^8$  cm<sup>-2</sup>. The formation of pinholes was not observed in significant numbers in the 50 and 70 Å samples. However, the formation of pinholes is again observed in the 100 Å sample, but with a smaller aerial density than that of the 10 and 30 Å samples. The penetration depth of the pinholes found in these samples has not been determined. Small compact islands are also found on the surface of the CoSi<sub>2</sub> film with a 10 Å interlayer (Fig. 5(a)), with similar results observed for the 30 and 50 Å samples (Fig. 5(b) and (c)). The islands on the surface of the 50 Å sample are about a factor of 2 larger than those found on the surface of the 10 and 30 Å samples. Elongated island structures, which appear to be oriented along preferential directions, are found on the surface of the 70 Å sample as shown in Fig. 5(d). The SEM micrograph of the 100 Å sample indicates the formation of a somewhat agglomerated surface layer which also appears to be preferentially oriented, just as in the case of the 70 Å sample. As shown in Fig. 5(e), the agglomerated islands appear to have a size distribution that ranges on the order of  $1-10 \ \mu m$ .

An XTEM bright-field image of a 50 Å interlayer sample is shown in Fig. 6, and information from the EELS measurements indicated that the points labeled 1, 2, and 3 in the figure correspond to the  $Si_{0.8}Ge_{0.2}$  layer, the  $CoSi_2$  layer, and a mixed Co/Ti layer, respectively. A high resolution XTEM image of the  $CoSi_2-Si_{0.8}Ge_{0.2}$  interface is shown in Fig. 7. The [011] selective area (SAD) zone axis diffraction pattern shown in Fig. 8 of the image in Fig. 7 displays  $CoSi_2$  {200}, {311}, {111}, and {022} spots. This pattern is similar to that obtained by Hsia, et al. [1], in their study of the formation of epitaxial

(a) (b)(c) islands islands islands um um (d)elongated islands lum

Fig. 5. (a)-(e): SEM micrographs of 10 Å (a), 30 Å (b), 50 Å (c), 70 Å (d) and 100 Å (e) diffusion barrier samples.

CoSi<sub>2</sub> on Si (100) using Ti-Co alloy and bimetal source materials, and Byun, et al. [28], in their study of the epitaxial growth of CoSi<sub>2</sub> on Si (100) using a Co/Ta bi-layer, where XTEM and SAD was used to confirm epitaxy to the substrate.

The X-ray absorption near-edge structure (XANES) scans for both Co and Ti K-edge absorption are shown in Figs. 9-12. All of the XANES data were pre-processed by background removal and edge energy calibration using the Athena EXAFS Data Processing program, and the data were fit to reference compound standards using the principle component analysis and least squares fitting routines found in Six PACK. Both Athena and Six PACK are graphical user interfaces to the IFEFFIT XAFS analysis numerical library [29].

In Fig. 9, the Co K edge spectra for the samples and Co, CoSi, and CoSi2 reference standards are shown. A principle component analysis of the samples with respect to the reference standards indicates that the Co in the films is predominately CoSi<sub>2</sub>. Leastsquares analysis fits of the Co K edge spectra with the Co, CoSi, and CoSi<sub>2</sub> reference standards are shown in Fig. 10, and substantiate the principle component analysis information. The fits were performed within an energy range 50 eV below and 50 eV above the Co K absorption edge of 7709 eV, assuming that the obtained spectra can be expressed as a linear combination of spectra from Co, CoSi, and CoSi<sub>2</sub>.

An examination of the Ti K edge X-ray absorption data shown in Fig. 11 indicates the presence of TiO<sub>2</sub>/TiSi<sub>2</sub>/Ti<sub>5</sub>Si<sub>3</sub> phases in the 10, 30, and 50 Å samples, whereas mostly TiSi<sub>2</sub> and Ti<sub>5</sub>Si<sub>3</sub> was found in the 70 and 100 Å samples. Graphs of the data and associated fits are shown in Fig. 12. The fits were





Fig. 7. Cross-sectional TEM image of the 50 Å interlayered sample, indicating the CoSi<sub>2</sub>/ Si<sub>0.8</sub>Ge<sub>0.2</sub> interface.





Fig. 8. Selected area zone axis diffraction pattern of the 50 Å interlayered sample shown in Fig. 5, along the [011] zone axis. The diffraction pattern for the  $Si_{0.8}Ge_{0.2}$  layer is on the left, while that for the  $CoSi_2$  layer is to the right.

performed in an energy range of 50 eV above and below the absorption edge and assumed that the signals from the nearedge data could be expressed as linear combinations of anatase  $TiO_2$ ,  $Ti_5Si_3$ , and C54  $TiSi_2$ . The appearance of the Ti-oxide in the XANES data and the absence of O peaks from the AES data suggest that while under vacuum the island structures are mainly composed of un-reacted Ti or Ti silicides, which are present on the surface of the cobalt disilicide layer after inversion and  $CoSi_2$  formation, and that the Ti or  $TiSi_2$  was oxidized after removal from the UHV environment.

Shown in Fig. 13 is a graph, depicting the fraction of the initial Ti layer converted into a silicide or oxide as a function of diffusion barrier thickness, determined from the Ti K-edge XANES data. The results from the fits shown in Table 2 give the fraction of the interlayer that was converted to a silicide or oxide and the associated uncertainty, and were used to generate Fig. 13. With low initial interlayer coverage an oxide is formed. However, note that there is a significant increase in the amount of the interlayer converted into a silicide in the thickness range of 50–70 Å, and that a majority of the interlayer is converted into a silicide in the 70–100 Å thickness range.



Fig. 9. Co K-edge XANES spectra for the 10 (a), 30 (b), 50 (c), 70 (d), and 100 Å (e) inter-layered samples, along with XANES spectra from Co, CoSi, and  $CoSi_2$  reference standards.

This crossover point, characterized first by the onset of significant epitaxial Co silicide formation, and then by the onset of significant  $TiSi_2$  and  $Ti_5Si_3$  formation, can also be correlated with the information from XRD, as the diffraction pattern from the 50 Å interlayer sample indicates the absence of any other long-range ordered phases besides  $CoSi_2$  and the substrate, while that of the 70 Å and 100 Å samples indicate the formation of  $TiSi_2$  and  $Ti_5Si_3$  phases.

## 4. Discussion

#### 4.1. Reaction

The experimental observations are generally consistent with the results reported in the literature for the Co/Ti/Si solid phase reaction. The existence of  $Ti_5Si_3$  and  $TiSi_2$  phases has been confirmed, but the ternary Co–Ti–Si phase reported in Refs. [17,19] and from other studies was not observed in our films.



Fig. 10. Comparison of XANES data from X-ray absorption at the Co K edge and fits to the data of the 10 (a), 30 (b), 50 (c), 70 (d), and 100 Å (e) samples, assuming that the signal from each sample is a linear combination of signals from Co, CoSi, and  $CoSi_2$  reference standards. The actual data for each sample is indicated by the solid line, while the fit to the data is indicated by the dots (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 11. Ti K-edge XANES spectra for the 10 (a), 30 (b), 50 (c), 70 (d), and 100 Å (e) inter-layered samples, along with XANES spectra from  $TiO_2$  (anatase),  $Ti_5Si_3$ , and  $TiSi_2$  reference standards.

According to the ternary phase diagram for the Co–Ti–Si system [19,30], stability can exist between  $Co_{0.25}Ti_{0.75}Si_2$ ,  $CoSi_2$ , and  $TiSi_2$  phases at high temperature and under Si-rich conditions. It was conjectured [17,19] that under Si-rich conditions, the ternary phase and at least one of the two silicide phases should form, as was confirmed experimentally in these studies by Rutherford back scattering, XRD, and both plainview and cross-sectional TEM. The ternary phase was found to form at a temperature of 900 °C, therefore, the absence of the ternary phase in our experiments is most likely attributable to the lower growth temperatures.

Both  $\rm Ti_5Si_3$  and C49  $\rm TiSi_2$  have been postulated to be the first silicide phases to form in investigations concerning the



Fig. 12. Comparison of XANES data from X-ray absorption at the Ti K edge and fits to the data of the 10 (a), 30 (b), 50 (c), 70 (d), and 100 Å (e) samples, assuming that the signal from each sample is a linear combination of signals from TiO<sub>2</sub>, Ti<sub>5</sub>Si<sub>3</sub>, and TiSi<sub>2</sub> reference standards. The actual data for each sample is indicated by the solid line, while the fit to the data is indicated by the dots (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 13. The fraction of the initial Ti interlayer which reacted to form a silicide compound as a function of the diffusion barrier thickness.

stages of solid state reaction at Ti/Si interfaces [31-37]. The transformation of the Ti<sub>5</sub>Si<sub>3</sub> compound into an Si-rich silicide can occur with the availability of Si, along with an increase in the annealing temperature. Although the annealing temperature in these experiments was high enough to induce its transformation to an Si-rich silicide, the transformation was apparently affected by the availability of Si from the underlying substrate, due to its consumption by Co atoms in the formation of the CoSi<sub>2</sub> film.

As indicated by the XRD and XANES data, within certain regimes of interlayer thickness, it appears that both Co and Ti actively compete to form bonds with Si in the formation of their respective silicide. The competition between these phases has been examined by Alberti, et al. [38], and Hong and Rozgonyi [39] to qualitatively explain the experimental results observed in multi-layered Co/Ti/Si systems. This phenomenon was modeled by considering the rate dependent free energy change associated with the Co–Si and Ti–Si reactions. According to the model they proposed, an increase in the Ti interlayer thickness will lead to a decrease in the diffusion of Co through the barrier and a decrease in the CoSi<sub>2</sub> reaction rate [38,39].

#### 4.2. Surface morphology-pinhole formation

Pinhole formation in the Co/Si (100), Co/Si<sub>1-x</sub>Ge<sub>x</sub> (100), and Co/Ti/Si (100) systems has been examined by various groups. Reconstruction on the CoSi<sub>2</sub> (100) surface in the Co/Si (100) reaction has been studied by Kenny, et al. [40] and Hayashi, et al.

Table 2

Comparison of the initial Ti interlayer thickness and the fraction of the interlayer converted into a Ti silicide or oxide phase

| Initial interlayer thickness (Å) | TiO <sub>2</sub>  | Ti <sub>5</sub> Si <sub>3</sub> | TiSi <sub>2</sub> |
|----------------------------------|-------------------|---------------------------------|-------------------|
| 10                               | $0.84 \pm 0.03$   | $0.16 {\pm} 0.03$               | $0.00 \pm 0.03$   |
| 30                               | $0.89 \pm 0.03$   | $0.055 \pm 0.03$                | $0.055 \pm 0.03$  |
| 50                               | $0.97 \pm 0.03$   | $0.015 \pm 0.03$                | $0.015 \pm 0.03$  |
| 70                               | $0.04 \pm 0.03$   | $0.27 {\pm} 0.03$               | $0.69 \pm 0.03$   |
| 100                              | $0.03\!\pm\!0.03$ | $0.30 \!\pm\! 0.03$             | $0.68 {\pm} 0.03$ |

[41]. The formation of pinholes has been associated with the transformation of the CoSi2 film from a Co-terminated surface to an Si-terminated surface. It has been suggested that the pinholes are formed in order to permit diffusion of Si from within the layer to form the lower energy Si-terminated structure. This phenomenon has also been studied in the Co/Ti/Si (100) system by Cardenas, et al. [16]. It was speculated that a reaction between the CoSi<sub>2</sub> and Ti silicide layers was the main thermodynamic mechanism generating the pinholes. In addition, Boyanov, et al. [13] examined pinhole formation in the  $CoSi_2/Si_{1-x}Ge_x$  system during the reaction between thin Co films and an  $Si_{1-x}Ge_x$  film which had been pseudomorphically strained to Si (100). The stronger preference for Co-Si bonding as opposed to Co-Ge bonding at the  $CoSi_2/Si_{1-x}Ge_x$  interface was proposed to lead to an increase in the interfacial energy which would generate the formation of pinholes [13].

When a relatively thin Ti interlayer is present (10-30 Å), the diffusion of Co towards the substrate is retarded, but not to the extent that the Si-terminated  $\text{CoSi}_2$  film is allowed to nucleate and grow first. It is less probable that the Co atoms are able to react with the Si<sub>0.8</sub>Ge<sub>0.2</sub> layer to generate the morphological instability generated by preferential Co–Si bonding discussed in Ref. [13]. Also, the XRD and XANES results indicate the absence of significant Ti silicide formation in this regime, implying that the morphological instability of Ref. [16] does not occur.

In the cases where the pinhole formation is not observed (>50 Å), the thickness of the interlayer is such that the amount of reactants in the region adjacent to the substrate are controlled by the presence of the interlayer to the extent that when the CoSi2 film eventually nucleates and grows, the Si-terminated structure is the one that initially forms and the previously mentioned Coterminated 
ightarrow Si terminated surface transformation does not occur [42-44]. In addition, the presence of the c-Si layer serves to prevent contact between the Si<sub>0.8</sub>Ge<sub>0.2</sub> layer and Co atoms diffusing towards it, until the CoSi2 phase is able to nucleate and grow, and the further consumption of the c-Si leads to the positioning of the CoSi<sub>2</sub> layer adjacent to the substrate. In this manner, direct contact between the two layers can be minimized until the Co silicide forms, and the problem with preferential Co-Si bonding discussed in Ref. [13] could be eliminated. The XRD and XANES results indicate the absence of any significant Ti silicide formation in the 50 Å sample, implying that this phenomenon is not a factor in generating a morphological instability as reported in Ref. [16].

When a relatively thick interlayer is present (70–100 Å), the diffusion of Co towards the substrate is retarded to the extent that the initial nucleation and growth of a Ti silicide is most probable. The experimental results indicate that epitaxial  $CoSi_2$  is allowed to form in spite of this. Given the thickness of the c-Si interlayer and Co/Ti bilayer, it is expected that the c-Si layer is totally consumed along with a portion of the  $Si_{0.8}Ge_{0.2}$  layer. With this approach the preferential Co–Si bonding is the most likely candidate in generating the morphological instabilities in this case.

#### 4.3. Nucleation

By controlling the flux of Co atoms toward the substrate, the interlayer assists in the formation of substrate matched nuclei

[45]. It is conjectured that as the diffusion barrier thickness is increased from 10 to 50 Å, and as both Ti and Si react, Co is able to diffuse through the diffusion barrier at a sufficient rate for epitaxial nucleation. As the interlayer thickness is increased to 70 and 100 Å, the diffusion of Co decreases, and more of the Ti interlayer interacts with available Si to form its own compounds. This in turn will decrease the amount of Si available to form CoSi<sub>2</sub>. Previous studies have also shown that the presence of the Ti interlayer exerts an influence on the nucleation barrier to  $CoSi_2$  formation. In studies by Detavernier, et al. [43–45], the role of refractory metal interlayers in the nucleation of epitaxial CoSi<sub>2</sub> on Si (100) was examined. It was suggested that refractory compounds which are not miscible in CoSi<sub>2</sub> or CoSi, such as Ti, could alter the nucleation barrier by lowering the CoSi grain boundary and interfacial energies and by reducing CoSi grain boundary diffusion, leading to an increase in nucleation temperature and giving rise to preferential orientation of CoSi2 nuclei.

The possibility of the presence of Ti within the CoSi interfaces and grain boundaries, in addition to the fact that the diffusion barrier interlayer controls the flux of Co atoms towards the substrate, lends credence to the possibility that a templating mechanism is at work in forming epitaxial CoSi<sub>2</sub> adjacent to the substrate. However, previous studies which detail the templating mechanism involved in the formation of C54 TiSi<sub>2</sub> on Si substrates [46,47] and CoSi<sub>2</sub> on Si substrates [28] which employ Ta as an interlayer suggest that the ability of both Ti and Co to form solid solutions with Ta, in addition to the existence of in-plane crystal symmetries between CoSi2 or TiSi2 and their respective Ta solid solutions is the primary mechanism responsible for templating. This suggests that the Ti interlayer used in these experiments is not likely to lend itself to templating, due to the lack of in-plane symmetries between the terminal silicide phases.

### 5. Conclusion

The growth of epitaxial  $CoSi_2$  thin films on  $Si_{0.8}Ge_{0.2}$  utilizing a Ti interlayer has been demonstrated, and the various Ti and Co silicide phases formed after annealing have been characterized using AES, XAFS, XRD, XTEM, and SEM. Overall, the presence of a Ti interlayer has been found to be beneficial to the formation of  $CoSi_2$  on  $Si_{0.8}Ge_{0.2}$ , and an interlayer thickness of 50–60 Å was found to be optimal for the formation of  $CoSi_2$ , resulting in the consumption and transformation of CoSi<sub>2</sub>.

The final chemical state of the Ti interlayer was also observed, as the results from AES and an analysis of Ti–K edge absorption data suggests the formation of TiO<sub>2</sub>, Ti<sub>5</sub>Si<sub>3</sub>, and TiSi<sub>2</sub> compounds in the samples, indicating that in some cases titanium was able to bond with Si to form silicides, and in other cases Ti islands on the surface were oxidized after removal from the UHV environment. Additionally, the XRD scans do not indicate the presence of any long-range ordered TiO<sub>2</sub> phases for these interlayer thicknesses. The formation of the C54 TiSi<sub>2</sub> and Ti<sub>5</sub>Si<sub>3</sub> was confirmed by XAFS and X-ray diffraction. The XTEM measurements also confirm the formation of epitaxial CoSi<sub>2</sub> adjacent to the Si<sub>0.8</sub>Ge<sub>0.2</sub> layer, and substantiate the XRD measurements.

The effect of the diffusion barrier on the surface morphology of the  $CoSi_2$  film was explored. By effectively controlling the amount of reactants, the possibility exists that the low-energy Si-terminated  $CoSi_2$  surface was formed in the 50 and 70 Å samples as indicated by the absence of pinholes. However, further experimental evidence would be needed to support this claim. It was also conjectured that in some cases the presence of the c-Si layer would delay the interaction between the  $CoSi_2$ layer and the substrate, minimizing the increase in interfacial energy associated with preferential Co–Si bonding found in the  $Co/Si_{1-x}Ge_x$  system, which is thought to promote the formation of pinholes as well.

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