#### Help

# Germanium segregation in the Co/SiGe/Si(001) thin film system

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Cobalt disilicide contacts to silicon–germanium alloys were formed by direct deposition of pure cobalt metal onto silicon-germanium films on Si(001) substrates. Segregation of germanium was observed during the reaction of the cobalt with the silicon–germanium alloy. The nature of the Ge segregation was studied by transmission electron microscopy, energy dispersive spectroscopy, and x-ray diffraction. In the case of cobalt films deposited onto strained silicon-germanium films, the Ge segregation was discovered to be in the form of Ge-enriched  $Si_{1-x}Ge_x$ regions found at the surface of the film surrounding CoSi and CoSi<sub>2</sub> grains. In the case of cobalt films deposited onto relaxed silicon-germanium films, the Ge segregation was dependent on formation of CoSi<sub>2</sub>. In samples annealed below 800 °C, where CoSi was the dominant silicide phase, the Ge segregation was similar in form to the strained  $Si_{1-x}Ge_x$  case. In samples annealed above 800 °C, where  $CoSi_2$  was the dominant silicide phase, the Ge segregation was also in the form of tetrahedron-shaped, Ge-enriched, silicon-germanium precipitates, which formed at the substrate/silicongermanium film interface and grew into the Si substrate. A possible mechanism for the formation of these precipitates is presented based on vacancy generation during the silicidation reaction coupled with an increased driving force for Ge diffusion due to silicon depletion in the alloy layer.

### I. INTRODUCTION

Silicide/Si<sub>1-x</sub>Ge<sub>x</sub>/Si(001) heterostructures are promising for use in devices such as the heterojunction bipolar transistor and are interesting candidates for devices such as improved infrared detectors with high cutoff wavelengths.<sup>1</sup> Perhaps even more significant, Si<sub>1-x</sub>Ge<sub>x</sub>/Si heterostructures are being considered for raised source and drain structures in integrated circuits.<sup>2–5</sup> Many of these structures may require electrical contacts to the Si<sub>1-x</sub>Ge<sub>x</sub> layer. There have been several efforts to evaluate a number of metal silicide contact systems to Si<sub>1-x</sub>Ge<sub>x</sub> alloys by using metals such as Co,<sup>6–14</sup> Ni,<sup>15</sup> Pd,<sup>16,17</sup> Pt,<sup>16,18</sup> Ti,<sup>8–10,19–21</sup> W,<sup>22</sup> and Zr.<sup>23</sup>

Due to its high crystalline quality and structural perfection of the interface on silicon, as well as its low electrical resistivity and thermal stability,  $CoSi_2$  is one of the more promising candidates for contact to Si and by extension to SiGe layers. Direct deposition of pure cobalt onto Si<sub>1-x</sub>Ge<sub>x</sub> in a self-aligned silicide process would be an efficient technique and would take advantage of established technologies. Direct deposition methods, however, have been demonstrated to result in Ge segregation.<sup>8,9</sup> Furthermore, initial attempts at coevaporation of Co and Si have resulted in islanding and poor thermal stability of the silicide film.<sup>24</sup> Recently, a coevaporation technique coupled with the use of an interface template has resulted in high-quality epitaxial CoSi<sub>2</sub> films on Si<sub>1-x</sub>Ge<sub>x</sub>/Si(001) heterostructures.<sup>11,25</sup>

In this paper, the Ge segregation phenomenon that occurs with direct deposition of pure Co onto strained and relaxed  $Si_{0.80}Ge_{0.20}/Si(001)$  alloys was investigated. Previous work in our laboratories by Wang *et al.*<sup>8</sup> showed that Co directly deposited onto strained  $Si_{0.80}Ge_{0.20}/Si(001)$  films and annealed at temperatures in the range of 400–700 °C resulted in the formation of Ge-enriched clusters at the film surface and embedded at grain boundaries in the near-surface region of the film. It was observed that a Co(Si<sub>1-v</sub>Ge<sub>v</sub>) ternary phase initially

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formed at low annealing temperatures (400 °C), where the y indice was 0.12 at 400 °C and decreased to  $\approx 0$  at 700 °C. Thus, Ge segregation was observed to increase as the annealing temperature increased. Moreover, only after the Ge had completely segregated out from the ternary phase was the  $CoSi \rightarrow CoSi_2$  transition observed to commence. Qi et al.9 also observed Ge segregation when depositing Co onto strained Si<sub>0.80</sub>Ge<sub>0.20</sub> layers. In their case, the ternary  $Co(Si_{0.90}Ge_{0.10})$  phase was observed after annealing to 650 °C. A sample annealed to 900 °C exhibited only the CoSi<sub>2</sub> phase. No Co-Ge phases were observed in either prior study. Lin *et al.*,<sup>7</sup> using qualitative energy dispersive spectroscopy (EDS) and selected area diffraction, reported finding a  $Co(Si_{1-y}Ge_y)_2$  phase for Co (20 nm)/Si<sub>0.87</sub>Ge<sub>0.13</sub> (150 nm)/Si (001) samples annealed to 700 °C for 3 min. It has been pointed out, however, that there is no  $Co(Si_{1-\nu}Ge_{\nu})_2$  phase found in the Co-Si-Ge bulk ternary phase diagram.<sup>26</sup> Possibly, the expansion in the lattice constant of the CoSi<sub>2</sub> observed by Lin was due to strain and not Ge incorporation.

Understanding Ge segregation is critical in device fabrication as segregation effects lead to electrical nonuniformity<sup>16,27</sup> and chemically unstable interfaces.<sup>8,28</sup> In addition to contacts to strained alloy layers, silicide contacts to relaxed or partially strained Si<sub>1-x</sub>Ge<sub>x</sub>/Si heterostructures may be important in devices that make use of conduction band offsets.<sup>29,30</sup> Here we have focused on alloys of composition Si<sub>0.80</sub>Ge<sub>0.20</sub>, because this composition has been used in strained SiGe devices in both the channel<sup>31</sup> and source and drains regions<sup>3</sup> of short channel  $Si_{1-r}Ge_r$  p-metal-oxide-semiconductor field-effect transistors (p-MOSFETs) and is within the range of compositions used for SiGe buffer layers in field-effect transistor (FET) applications.<sup>29</sup> In the present work, the Ge segregation phenomenon was observed to be manifested in distinctly different ways depending on the strain state of the  $Si_{0.80}Ge_{0.20}$  alloy layer and whether  $CoSi_2$ was formed as opposed to only the monosilicide. The mechanism of Ge segregation observed in samples where CoSi<sub>2</sub> was formed on relaxed Si<sub>0.80</sub>Ge<sub>0.20</sub> layers was, in particular, unique and not previously reported.

### **II. EXPERIMENTAL**

The films used in this study were prepared in an ultrahigh vacuum (UHV) electron beam evaporation chamber equipped with three single pocket evaporators containing Si, Ge, and Co. The base pressure of the chamber was 27 nPa. All samples were prepared using 25-mm *n*-type Si  $\langle 001 \rangle \pm 0.5^{\circ}$  wafers, 0.5 mm thick, with a resistivity of 5–10  $\Omega$  cm (supplied by Virginia Semiconductor). Wafer cleaning was accomplished by spin etching<sup>32</sup> with a solution of HF/H<sub>2</sub>O/methanol (1:1:10) immediately before loading into the UHV system. After loading, the wafers were heated to >900 °C for 10 min to thermally desorb any remaining oxide. Samples were heated from the back side with a resistive heater that was calibrated with infrared pyrometry. For each wafer, a 20-nm Si buffer layer was then deposited at 550 °C, from which a sharp  $2 \times 1$  reactive high-energy electron diffraction (RHEED) pattern was observed along the [110] azimuth, indicating a well-ordered surface.

To prepare strained  $Si_{1-x}Ge_x$  films below the critical thickness,  $T_c$ , 64 nm of  $Si_{0.80}Ge_{0.20}$  was co-deposited onto the Si substrates at 550 °C. Relaxed  $Si_{1-x}Ge_x$  films were formed by co-depositing 240 nm of  $Si_{0.80}Ge_{0.20}$  at the same temperature. Subsequent  $CoSi_2$  formation was accomplished in all cases by allowing the samples to cool to room temperature and then depositing the appropriate amount of Co metal, depending on the required thickness of the  $CoSi_2$  layer. The samples were then annealed at the desired conditions. After annealing, the samples were removed from the UHV system.

To determine both the silicide phases present and the composition of the Si<sub>1-x</sub>Ge<sub>x</sub> alloy layers, x-ray diffraction (XRD) was performed with a Rigaku Geigerflex diffractometer with Cu K<sub> $\alpha$ </sub> radiation and a graphite (0001) monochromator. The data were collected in  $\theta$ -2 $\theta$  mode for 2 $\theta$  between 25° and 75°. The Cu anode was operated at 27.5 kV and 20 mA. Calibration of the goniometer was accomplished with the Si (400) substrate peak at 2 $\theta$  = 69.13°.

The composition of the relaxed SiGe layers can be determined directly from the 2 $\theta$  value of the SiGe (400) reflection by Vegard's Law. Although Si<sub>1-x</sub>Ge<sub>x</sub> alloys exhibit deviations from Vegard's Law, the difference at  $x_{Ge} = 0.30$  is only ~1% at 25 °C.<sup>33</sup> The composition of fully strained Si<sub>1-x</sub>Ge<sub>x</sub> layers can be determined by the following derivation. If the Si<sub>1-x</sub>Ge<sub>x</sub> film is fully strained, the in-plane lattice parameter of the alloy film  $a_{\parallel}$  will be constrained to match that of the Si substrate, and there will be a tetragonal distortion in the Si<sub>1-x</sub>Ge<sub>x</sub> unit cell. This distortion will result in expansion of the out-of-plane lattice parameter  $a_{\perp}$ , which is measured by XRD. From elasticity theory, the relationship between the out-of-plane and in-plane strains for cubic materials is

$$\boldsymbol{\epsilon}_{\perp} = -2 \left( \frac{c_{12}}{c_{11}} \right) \boldsymbol{\epsilon}_{\parallel} \quad , \tag{1}$$

where  $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$  are the perpendicular and parallel film strains and  $c_{12}$  and  $c_{11}$  are the elastic constants of the alloy. The film strains are defined as  $\epsilon_{\perp} = (a_{\perp} - a_0)/a_0$ and  $\epsilon_{\parallel} = (a_{\parallel} - a_0)/a_0$  where  $a_0$  is the lattice parameter of the unstrained (bulk) alloy. The rule of mixtures<sup>34</sup> can be used to calculate the  $c_{12}$  and  $c_{11}$  elastic constants for the alloy

$$c_{ij} = c_{ij}^{\text{Ge}} x_{\text{Ge}} + c_{ij}^{\text{Si}} (1 - x_{\text{Ge}}) \quad , \tag{2}$$

where  $c_{ij}$  is the elastic constant of the alloy;  $c_{ij}^{\text{Ge}}$  and  $c_{ij}^{\text{Si}}$  are the elastic constants of pure Ge ( $c_{11}^{\text{Ge}} = 128.5$ ,  $c_{12}^{\text{Ge}} = 48.3$  GPa) and pure Si ( $c_{11}^{\text{Si}} = 165.8$ ,  $c_{12}^{\text{Si}} = 63.9$  GPa), respectively, and  $x_{\text{Ge}}$  is the atomic fraction of Ge in the alloy.<sup>35</sup> The lattice parameter of the unstrained alloy,  $a_0$ , can be obtained from Vegard's Law

$$a_0 = a_{\rm Si}(1 - x_{\rm Ge}) + a_{\rm Ge}(x_{\rm Ge})$$
 , (3)

where  $a_{\rm Si}$  (=0.5431 nm) and  $a_{\rm Ge}$  (=0.56576 nm) are the lattice parameters of pure Si and pure Ge. By expressing the film strains  $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$ , in Eq. (1) in terms of the film lattice parameters and rearranging, the following relation between the film lattice parameters and elastic constants is obtained:

$$c_{11}(a_{\perp} - a_0) + 2c_{12}(a_{\parallel} - a_0) = 0 \quad . \tag{4}$$

By substitution of Eqs. (2) and (3) into Eq. (4) for the alloy elastic constants and  $a_0$ , respectively, a quadratic relation is obtained in which the unknown is the atomic concentration of Ge in the strained alloy film  $x_{Ge}$ . After substitution of numerical values for the elastic constants and lattice parameters, this quadratic takes the form

$$15.5x_{\rm Ge}^2 + [37.3a_{\perp} - 136.0]x_{\rm Ge} + 165.8a_{\perp} - 900.5 = 0 \quad ,$$
(5)

where  $x_{Ge}$  has units of atomic percent and  $a_{\perp}$  has units of nanometers. Equation (5) can thus be used to deduce the composition of fully strained Si<sub>1-x</sub>Ge<sub>x</sub> alloy films from the 2 $\theta$  value of the Si<sub>1-x</sub>Ge<sub>x</sub>(400) XRD peak.

To observe the morphology of the Ge segregation, transmission electron microscopy (TEM) was performed on the samples with a Topcon 002B instrument operated at 200 kV. Cross-sectional samples were prepared by mechanical grinding, dimpling, and Ar ion milling. Quantification of Si and Ge concentrations was performed with EDS on a Phillips CM300 FEG scanning transmission electron microscope (STEM) operated at 300 kV. An Oxford Link EDS detector was used to collect EDS spectra (probe size = 1.2 nm) and x-ray maps. The Desktop Spectrum Analyzer (DTSA) software<sup>36</sup> was used to analyze the EDS spectra. The Cliff-Lorimer ratio technique was used to perform the quantifications.<sup>37</sup> To determine the sensitivity factor,  $k_{SiGe}$ , a Si<sub>1-x</sub>Ge<sub>x</sub> standard was prepared by depositing 600 nm of alloy, with a nominal composition of Si<sub>0.50</sub>Ge<sub>0.50</sub>, onto a Si(001) wafer at 550 °C. The composition of the  $Si_{1-x}Ge_x$  layer was verified by XRD and was determined to be 50.0  $\pm$ 0.9 at.% Si and 49.0  $\pm$  0.9 at.% Ge. Using the standard, the  $k_{\text{SiGe}}$  factor was determined to be 1.91 ± 0.12. Care was taken to use the same microscope accelerating voltage, detector configuration, and peak-integration routines for the standard and all unknown spectra.

#### III. RESULTS

#### A. Co/relaxed SiGe layer

Reference to the samples in this study will be made with the following notation: Co thickness/SiGe thickness:(annealing temperature/annealing time). The Si<sub>0.80</sub>Ge<sub>0.20</sub> thickness for the relaxed samples (240 nm) was chosen to be above the metastable critical thickness,<sup>38</sup> and the Co thickness (25 nm) was chosen so that the Co layer would not react with the entire SiGe layer. Annealing temperatures in the range 700–800 °C were used because these were known to produce mixtures of CoSi and CoSi<sub>2</sub> in similarly prepared samples.<sup>39</sup>

XRD scans for the four samples prepared on relaxed  $Si_{1-x}Ge_x$  substrates (25 nm Co/240 nm  $Si_{0.80}Ge_{0.20}$ ), annealed at four different temperature/time conditions, are shown in Fig. 1. In the diffraction scan for each sample, two peaks associated with  $Si_{1-x}Ge_x(400)$  reflections are observed within the  $2\theta$  range of  $66-69^\circ$ . These peaks are labeled with the composition of the alloy, as determined by the  $2\theta$  position of the peak. The alloy peak nearest the Si(400) substrate reflection originates from the portion of the original Si<sub>0.80</sub>Ge<sub>0.20</sub> film, which remains unreacted with the Co layer after annealing-this peak is termed the  $Si_{1-x}Ge_x$  alloy peak. The  $Si_{0.80}Ge_{0.20}$  layer is assumed to relax when deposited to a thickness of 240 nm at 550 °C.<sup>38</sup> The other alloy peak in each scan, termed the Ge segregation peak, is presumed to originate from segregation of Ge caused by the reaction of the alloy layer with the deposited Co layer. Determination of the composition of the alloy in these Ge segregation regions, using the peak's  $2\theta$  position, is also made with the assumption that the alloy in these regions is relaxed.

For the Co(25 nm)/SiGe(240 nm):(700 °C/10 min) sample, the XRD scan [Fig. 1(a)] indicates that the dominant silicide phase present is CoSi, with a large CoSi(210) reflection and a weak CoSi(200) reflection. The presence of a small fraction of CoSi<sub>2</sub> is evidenced by a weak CoSi<sub>2</sub>(111) reflection. The positions of the CoSi and CoSi<sub>2</sub> peaks were within 0.05° of those listed in the JCPDS database,<sup>40</sup> indicating that less than 3% Ge incorporation was present in the CoSi structure after the annealing (in agreement with our prior results).<sup>8</sup> The Si<sub>1-x</sub>Ge<sub>x</sub> alloy peak corresponds to Si<sub>0.77</sub>Ge<sub>0.23</sub>, and the Ge segregation peak corresponds to Si<sub>0.50</sub>Ge<sub>0.50</sub>.

The beginning of a transition from CoSi to  $CoSi_2$  is indicated by the emergence of the  $CoSi_2(111)$  and  $CoSi_2(220)$  reflections in the XRD scan for the  $Co(25 \text{ nm})/\text{SiGe}(240 \text{ nm}):(700 \degree \text{C}/20 \text{ min})$  sample [Fig. 1(b)]. The silicide phase is still predominantly CoSi, as a strong CoSi(210) reflection dominates the scan. Weak CoSi(200) and CoSi(211) reflections are also observed. The Si<sub>1-x</sub>Ge<sub>x</sub> alloy peak corresponds to Si<sub>0.73</sub>Ge<sub>0.27</sub> and the Ge segregation peak corresponds to Si<sub>0.46</sub>Ge<sub>0.54</sub>.



FIG. 1. XRD scans for samples prepared on relaxed SiGe substrates: 25 nm Co/240 nm Si<sub>0.8</sub>Ge<sub>0.2</sub>/Si(001) annealed at (a) 700 °C/10 min, (b) 700 °C/20 min, (c) 800 °C/10 min, and (d) 800 °C/20 min.

The XRD scan for the Co(25 nm)/SiGe(240 nm): (800 °C/10 min) sample, shown in Fig. 1(c), indicates that the major silicide phase in this sample is CoSi<sub>2</sub>. A strong CoSi<sub>2</sub>(220) reflection is present, which is approximately 2.5 times more intense than the CoSi<sub>2</sub>(111) reflection. Because the Joint Committee for Powder Diffraction Standards (JCPDS) relative intensities of the (220) and (111) peaks in polycrystalline CoSi<sub>2</sub> are 100% and 90%,<sup>40</sup> respectively, the relative intensities of these two peaks in the scan for this sample indicate a (110) texturing of the CoSi<sub>2</sub>. The presence of CoSi is indicated by the weak CoSi(210) reflection. The Si<sub>1-x</sub>Ge<sub>x</sub> alloy peak and the Ge segregation peak correspond to Si<sub>0.78</sub>Ge<sub>0.22</sub> and Si<sub>0.60</sub>Ge<sub>0.40</sub>, respectively.

In the scan of the Co(25 nm)/SiGe(240 nm):(800 °C/20 min) sample [Fig. 1(d)], the appearance of CoSi<sub>2</sub> (200) and (400) peaks indicates the formation of predominantly (100)-oriented CoSi<sub>2</sub>. The reason for the development of the (100) orientation in this sample as opposed to the (110) orientation observed in the (800 °C/10 min) sample is not clear. The lower intensity of the CoSi(210) peak, relative to the same peak in the (800 °C/10 min) sample, indicates a higher CoSi<sub>2</sub>:CoSi ratio in the (800 °C/20 min) sample. The Si<sub>1-x</sub>Ge<sub>x</sub> alloy peak and Ge segregation peak correspond to the same compositions as in the (800 °C/10 min) sample.

The Ge segregation in the (700 °C/10 min) and (800 °C/20 min) samples was studied with EDS in the STEM. A dark-field STEM image of a cross section of the (700 °C/10 min) sample is shown in Fig. 2. In the corresponding x-ray map, shown below the STEM image, the presence of the CoSi grains can be observed at the film surface in between regions of Ge-enriched Si<sub>1-x</sub>Ge<sub>x</sub>. The Co-containing CoSi grains are clearly distinct from the Ge-enriched regions, as is evident from comparison of the Co and Ge x-ray maps. The EDS spectra obtained in spot mode (probe size = 1.2 nm) from the areas indicated by the letters a through f appear at the bottom of the figure. The spectrum for the grain labeled b indicates significant amounts of Si and Co and a barely detectable Ge peak. The spectra from the regions labeled a and c at the surface of the film indicate Si and Ge but no detectable Co. The spectra labeled d, e, and f were obtained from points within the  $Si_{1-x}Ge_x$  alloy film at approximately the same depth within the layer, separated by approximately 250 nm laterally. Quantitative EDS results for these spectra are listed in Table I. The regions a and c were determined to be Ge-enriched  $Si_{1-\nu}Ge_{\nu}$ . By Ge-enriched it is meant that the region has a  $Si_{1-\nu}Ge_{\nu}$  composition richer in Ge than the originally deposited alloy. The spectrum from the grain b contained a small Ge peak and the quantification result was Si<sub>0.95</sub>Ge<sub>0.05</sub>. However, the large Co peak present in the spectrum, together with the XRD results for this sample, indicate that the grain from which spectrum b was ob-

TABLE I. Quantitative EDS results.



FIG. 2. (a) Dark-field STEM image ([110] zone axis), (b) EDS map, and (c) EDS spectra from the Co(25 nm)/SiGe(240 nm):(700 °C/10 min) sample.

Probe location	$c_{Si}$ (at.%)	$c_{\rm Ge}$ (at.%)
Co(25 nm)/SiGe(240 nm)		
(700 °C/10 min)		
a	$34 \pm 1.6$	$66 \pm 1.6$
b	$95 \pm 0.4$	$5 \pm 0.4$
с	$42 \pm 1.6$	$58 \pm 1.6$
d	$78 \pm 1.2$	$22 \pm 1.2$
e	$76 \pm 1.2$	$24 \pm 1.2$
f	$78 \pm 1.2$	$22 \pm 1.2$
Co(25 nm)/SiGe(240 nm)		
(800 °C/20 min)		
g	$68 \pm 1.4$	$32 \pm 1.4$
h	$81 \pm 1.1$	$19 \pm 1.1$
i	$100 \pm 0.05$	$0 \pm 0.05$
Co(5 nm)/SiGe(64 nm)		
(750 °C/10 min)		
j	$78 \pm 1.1$	$22 \pm 1.1$
k	$98 \pm 0.2$	$2 \pm 0.2$
1	$77 \pm 1.2$	$23 \pm 1.2$
m	$77 \pm 1.2$	$23 \pm 1.2$
n	$55 \pm 1.6$	$45 \pm 1.6$
0	$89 \pm 0.6$	$11 \pm 0.6$
р	$77 \pm 1.2$	$23 \pm 1.2$
q	$70 \pm 1.4$	$30 \pm 1.4$

tained is undoubtedly a CoSi grain. The XRD results for this sample [Fig. 1(a)] indicated only the presence of pure CoSi; no shifting of the CoSi(210) peak to lower 20 was observed, which would have indicated incorporation of Ge in a Co(Si<sub>1-x</sub>Ge<sub>x</sub>) phase. A small part of the surrounding Si<sub>1-x</sub>Ge<sub>x</sub> layer is most likely overlapping the CoSi grain, and the EDS probe is interacting with both the CoSi grain and the overlapping Si<sub>1-x</sub>Ge<sub>x</sub>, which gives rise to the Ge signal in the EDS spectrum. The regions labeled d, e, and f were determined to have essentially the same composition as the Si<sub>1-x</sub>Ge<sub>x</sub> alloy peak, as determined by XRD [see Fig. 1(a)].

A dark-field STEM image of a cross section of the (800 °C/20 min) sample is shown in Fig. 3. The most outstanding feature is that of the large precipitates, triangular in cross section, penetrating deep into the Si substrate. An EDS x-ray map formed from the area around the largest precipitate is shown in the middle of Fig. 3. It is evident that the large precipitate is composed of Si and Ge with no detectable Co. The Co is in the form of CoSi and CoSi<sub>2</sub> grains, as detected by XRD, which lie at the surface of the film. Also shown in Fig. 3 are the EDS spectra obtained in spot mode from the areas labeled g, h, and i in the STEM image. The spectrum obtained from the center of the triangular precipitate (g) indicates only Si and Ge, whereas the spectrum of the grain at the film surface (i) indicates only Si and Co. The quantitative EDS results for this sample are listed in Table I. The spectrum from area i contained essentially no Ge, only Si and Co. The grain from which spectrum i was obtained is clearly a CoSi or CoSi<sub>2</sub> grain. The area





FIG. 3. (a) Dark-field STEM image ([110] zone axis); (b) EDS map, and (c) EDS spectra from the Co(25 nm)/SiGe(240 nm):(800 °C/20 min) sample.

labeled g was determined to be of composition  $Si_{0.68}Ge_{0.32}$ . The area labeled h, which is between Corich particles at the film surface, is found to be a slightly Ge-depleted alloy region of composition  $Si_{0.81}Ge_{0.19}$ .

One of the large, triangular precipitates in this sample was examined with strong beam centered dark-field (CDF) imaging in a 200-keV TEM using the  $g_{\overline{220}}$  reflection from a foil prepared in cross section. The dark-field image is on the left in Fig. 4, and the bright-field image is shown on the right. Dislocation lines are evident running through the precipitates in both images and moiré fringes are observed in the dark-field image. A plan-view foil was also prepared from this sample by first removing the silicide/Si<sub>1-x</sub>Ge<sub>x</sub> layer with a felt polishing wheel with 0.25-µm diamond paste for 1 min. The foil was then prepared in the usual manner by grinding, dimpling, and ion milling from the back side. Removal of the silicide/  $Si_{1-x}Ge_x$  layer was performed in order to image only the precipitates that grow into the Si substrate, without having the image confused by the silicide/Si<sub>1-x</sub>Ge<sub>x</sub> overlayer. Figure 5 displays a bright-field image indicating a tetrahedron-shaped precipitate (zone axis (z.a.) = [001]).

The (800 °C/10 min) sample was also examined with TEM. A bright-field TEM image of a cross section of this sample is shown in Fig. 6. The same triangular precipitates as in the (800 °C/20 min) sample are observable. Strong beam (CDF) images using the  $g_{\overline{220}}$  reflection are shown in Fig. 7. Dislocation lines and moiré fringes are observable in both images.

#### B. Co/strained SiGe layer

To compare Ge segregation on relaxed and strained SiGe layers, two samples were prepared with strained Si<sub>1-x</sub>Ge<sub>x</sub> layers by depositing 20 and 5 nm of Co, respectively, onto 64 nm of Si<sub>0.80</sub>Ge<sub>0.20</sub>. The 20-nm Co sample was annealed at 700 °C for 20 min and the 5-nm Co sample was annealed at 750 °C for 10 min. In previous work, similarly prepared samples exhibited a mixture of CoSi and CoSi<sub>2</sub> in the case of the 20-nm Co sample, and only CoSi in the case of the 5-nm sample.<sup>8,14</sup> Thus, Ge segregation on strained Si<sub>0.80</sub>Ge<sub>0.20</sub> layers, in cases in which only CoSi is formed and in cases in which a mixture of CoSi and CoSi<sub>2</sub> is formed, could be compared with Ge segregation on the relaxed SiGe samples.

The XRD scan for the Co(20 nm)/SiGe(64 nm): (700 °C/20 min) sample is shown in Fig. 8(a). A single  $Si_{1-x}Ge_x(400)$  reflection is observed, which corresponds to an alloy of composition  $Si_{0.59}Ge_{0.41}$ . The 20 nm of Co deposited on the 64 nm of  $Si_{0.80}Ge_{0.20}$  in this sample was sufficient to react with all the Si present in the alloy layer. Thus, none of the originally deposited  $Si_{0.80}Ge_{0.20}$  layer remains unreacted with Co. CoSi (210) and (211) reflections, as well as those due to  $CoSi_2$  (111), (200), (220), and (400), are present, indicating a mixture of polycrystalline CoSi and CoSi<sub>2</sub>.

The XRD scan for the Co(5 nm)/SiGe(64 nm): (750 °C/10 min) sample is shown in Fig. 4(b). The only silicide reflection in the scan is the CoSi(210). The



FIG. 4. Strong beam (CDF) images ([110] zone axis,  $\mathbf{g}_{\overline{220}}$ ) of the Co(25 nm)/SiGe(240 nm):(800 °C/20 min) sample: (a) dark-field image and (b) bright-field image.



FIG. 5. Bright-field TEM image ([001] z.a.) of the Co(25 nm)/ SiGe(240 nm):(800 °C/20 min) sample, showing tetrahedron-shaped precipitate.

Si<sub>1-x</sub>Ge<sub>x</sub> alloy peak is evident at  $2\theta = 68.15^{\circ}$ ; however, this peak is shifted to lower 2 $\theta$  because of the strain in the Si<sub>1-x</sub>Ge<sub>x</sub> film. In this sample, the 5 nm of Co deposited on the 64 nm of Si<sub>0.80</sub>Ge<sub>0.20</sub> will only react with ~9.1 nm of the alloy to form CoSi. Thus, most of the originally deposited alloy remains intact after the annealing. Using Eq. (5), the composition of the Si<sub>1-x</sub>Ge<sub>x</sub> alloy in this sample was determined to be Si<sub>0.83</sub>Ge<sub>0.17</sub>.

Quantitative EDS was performed on this sample. A bright-field STEM image of the sample is shown at the top of Fig. 9. A dark-field STEM image of the two middle grains is shown in the middle of the figure along with the corresponding x-ray maps for Si, Ge, and Co. It is evident that the two large grains contain Co and Si only and are therefore identified as the CoSi detected by XRD.



FIG. 6. Bright-field TEM image ([110] z.a.) of the Co(25 nm)/ SiGe(240 nm):(800  $^{\circ}$ C/10 min) sample.

The EDS spectra taken in spot mode from the regions labeled j–q are shown at the bottom of Fig. 9, and the quantification results for these spectra are listed in Table I. The spectrum from the center of the upper grain labeled k contains a small Ge peak, and the quantification results for this region indicate a composition of  $Si_{0.98}Ge_{0.02}$ . As with the Co containing grain in the Co(25 nm)/SiGe(240 nm):(700 °C/10 min) sample, a



FIG. 7. Strong beam (CDF) images ([110] z.a.,  $g_{\overline{220}}$ ) of the Co(25 nm)/SiGe(240 nm):(800 °C/10 min) sample: (a) dark-field image and (b) bright-field image.



FIG. 8. XRD scans for samples prepared on strained SiGe substrates: (a) 20 nm Co/64 nm Si<sub>0.80</sub>Ge<sub>0.20</sub>/Si(001) annealed at 700 °C/20 min, (b) 5 nm Co/64 nm Si<sub>0.80</sub>Ge<sub>0.20</sub>/Si(001) annealed at 750 °C/10 min.

small overlap of the grain from spectrum k with the surrounding  $Si_{1-x}Ge_x$  film is likely the cause of the Ge peak in the spectrum. The XRD results [Fig. 8(b)] indicate pure CoSi. The spectrum labeled o taken from the

center of the larger grain contained a more significant amount of Ge; however, the overlap of this grain with the Si<sub>1-x</sub>Ge<sub>x</sub> film is clearly evident from the STEM images in Fig. 9. The spectra from the spots labeled j, l, and p were obtained from locations within the Si<sub>1-x</sub>Ge<sub>x</sub> film near the Si<sub>1-x</sub>Ge<sub>x</sub>-Si interface. The quantitative results for these spectra were nearly the same—approximately 77% Si and 23% Ge. The region labeled m, obtained from a point near the center of the Si<sub>1-x</sub>Ge<sub>x</sub> film also quantified to 77% Si and 23% Ge. Points n and q, from locations near the surface of the film, were determined to be Ge-enriched regions with compositions 55% Si, 45% Ge and 70% Si, 30% Ge, respectively.

## **IV. DISCUSSION**

The XRD results for the relaxed alloy samples (Fig. 1) indicate a transition from CoSi to a mixture of  $CoSi_2$  and CoSi with increasing annealing temperature and time. On pure Si substrates, using a Co thickness of 25 nm, pure  $CoSi_2$  would be expected on all samples at all the annealing temperatures and times used in this study. A thickness effect for Co deposited onto  $Si_{1-x}Ge_x$  alloys has been previously observed.<sup>39</sup> According to this study, complete conversion to  $CoSi_2$ , as indicated by the absence of the CoSi (210) XRD peak, does not occur until Co thicknesses of 45 nm or greater are deposited on relaxed  $Si_{0.8}Ge_{0.2}$  alloys. Thus, the observations here of mixed CoSi and  $CoSi_2$  phases using 25-nm-thick Co layers are consistent with the earlier findings.

The Si<sub>1-x</sub>Ge<sub>x</sub> alloy peak in each of the scans in Fig. 1 corresponds to essentially the same composition, Si<sub>0.78</sub>Ge<sub>0.22</sub>, except for the (700 °C/20 min) sample, where the alloy peak corresponds to a composition of Si<sub>0.73</sub>Ge<sub>0.27</sub>. This difference is attributed to drift in the Si



FIG. 9. (a) Bright-field TEM image ([110] z.a.); (b) EDS map, and (c) EDS spectra from the  $Co(5 \text{ nm})/SiGe(64 \text{ nm}):(750 \text{ }^{\circ}C/10 \text{ min})$  sample.

or Ge thickness monitors during deposition of the alloy layer of this sample. The composition of  $Si_{0.78}Ge_{0.22}$ , determined from the XRD peak, correlates well with the EDS quantification of the three alloy regions d, e, and f of the (700 °C/10 min) sample (see Fig. 2 and Table I). These regions are near the alloy–substrate interface, where the unreacted alloy giving rise to the  $Si_{1-x}Ge_x$ alloy XRD peak is present.

The Ge segregation peaks for the Co(25 nm)/ SiGe(240 nm):(700 °C/10 min) and (700 °C/20 min) samples, which formed predominantly CoSi, correspond to nearly the same composition, ~Si<sub>0.50</sub>Ge<sub>0.50</sub>, whereas the segregation peaks for the Co(25 nm)/ SiGe(240 nm):(800 °C/10 min) and (800 °C/20 min) samples, which formed predominantly CoSi<sub>2</sub>, correspond to the same composition of  $Si_{0.60}Ge_{0.40}$ . The reason for the decrease in Ge concentration of the segregation peaks in the 800 °C annealed samples may be that the triangular, Ge-enriched precipitates (growing into the substrates of these samples) remove a portion of the Ge from the alloy regions, which give rise to the segregation peaks. As is evident from the STEM cross-sectional image of the (800 °C/20 min) sample in Fig. 3, the upper surfaces of the triangular precipitates are situated near the center of the SiGe layer. The x-ray map in this figure shows that above each precipitate is an adjoining Co-containing region. The quantitative EDS measurements of this sample show that a region near the surface of the film adjacent to a silicide grain (region h) is slightly Ge depleted. Regions near the surface of the film (a, c) in the (700 °C/10 min) sample (Fig. 2, Table I), however, are consistently Ge enriched. Diffusion of Ge from the near-surface region of the film in the 800 °C annealed samples is thus the likely source of the Ge in the Ge-enriched precipitates. The explanation for the fact that a third SiGe peak, due to the Ge-enriched precipitates themselves, does not appear in the XRD scan for the 800 °C annealed samples is that the volume of the Ge-enriched precipitates is substantially less than that of the Ge-depleted surface regions and therefore does not give rise to an XRD peak. A similar effect is observed for the Co (5 nm)/SiGe (64 nm): (750 °C/10 min) sample. No SiGe segregation peak is present in the XRD scan of this sample [Fig. 8(b)], even though the EDS spectra for this sample clearly show that Ge segregation has occurred. The thin Co layer reacts to form only 9.1 nm of CoSi; thus, the amount of Ge segregation is low and is not expected to give rise to a segregation peak in the XRD scan.

For the Co(5 nm)/SiGe(64 nm):(750 °C/10 min) sample, the single alloy peak originates from the unreacted alloy layer and, under the assumption that the alloy layer remains fully strained after the annealing, the composition of the alloy calculated using Eq. (5) is  $83 \pm 2.5$  at.% and  $17 \pm 2.5$  at.% Ge. The EDS quantification of this sample (Fig. 9, Table I) from regions near the alloy–

substrate interface (j, l, p) and near the middle of the alloy layer (m) all agree to the same composition of  $\sim$ Si<sub>0.77</sub>Ge<sub>0.23</sub>. With typical error bars of 1.2 at.%, this value is in fairly close agreement with the composition calculated by XRD. Relaxation of metastable SiGe alloys is affected by the processing temperature, and if the annealing of this sample caused a slight relaxation of the alloy layer, Eq. (5) would calculate a Ge fraction lower than the actual.

As with Co directly deposited onto relaxed Si<sub>1-x</sub>Ge<sub>x</sub> alloy layers, Co on strained Si<sub>1-x</sub>Ge<sub>x</sub> exhibits a thickness effect and does not completely convert to CoSi<sub>2</sub> until Co thicknesses of  $\approx$ 35 nm or greater are deposited.<sup>14</sup> The XRD scan of the Co(20 nm)/SiGe(64 nm):(700 °C/20 min) sample [Fig. 8(a)] indicates that while the disilicide phase predominates, there is still some quantity of the monosilicide present. The single alloy peak corresponding to Si<sub>0.59</sub>Ge<sub>0.41</sub> indicates that the Co has reacted with all the original Si<sub>0.80</sub>Ge<sub>0.20</sub> alloy deposited during the annealing. Thus, this peak represents a Ge segregation peak in this XRD scan.

The probed regions (n, q) near the surface of the (750 °C/10 min) sample indicate a high Ge concentration relative to regions near the alloy layer-substrate interface. This finding is similar to that observed for the (700 °C/10 min) sample prepared on the relaxed SiGe layer. Thus, Ge segregation is apparently manifested by Ge enrichment of the  $Si_{1-x}Ge_x$  alloy between the silicide grains at the surface of the film in the case of samples (i) that do not form CoSi2 (700 °C annealed samples on relaxed SiGe) or (ii) are prepared on strained  $Si_{1-r}Ge_r$ layers (700 °C/20 min and 750 °C/10 min samples on strained SiGe). Ge segregation on samples that form  $CoSi_2$  and are prepared on relaxed  $Si_{1-x}Ge_x$  alloys induces the formation of Ge-enriched precipitates, which grow into the Si substrate with an accompanying reduction of the Ge content in the near surface region of the alloy film. The remainder of the discussion section attempts to explain the mechanism of formation of these precipitates.

The Ge-enriched precipitates that grow into the silicon substrate in the relaxed (800 °C/10 min) and (800 °C/20 min) samples have not been previously reported. Cobalt implanted into Si(100) substrates and annealed at 950 °C has been observed to form faceted  $\text{CoSi}_2$  precipitates that grow along {111} planes into the Si substrate,<sup>41,42</sup> in a V shape. These  $\text{CoSi}_2$  precipitates appear similar to the precipitates in our samples in cross section. However, in our case, the EDS spectra clearly indicate the absence of Co in the triangular structures. If the precipitates in Fig. 3 were initially a  $\text{Co}(\text{Si}_{1-x}\text{Ge}_x)$  ternary at low annealing temperatures, which then expelled the Ge as the temperature was raised, then the Co would have had to diffuse back to the sample surface to form the CoSi and  $\text{CoSi}_2$  that is present there. This scenario is highly unlikely because the triangular precipitates would then also be expected to appear in the Co(25 nm)/SiGe(240 nm):(700 °C/10 min) sample, which contains only CoSi as the silicide phase, as indicated by XRD. The STEM images of this sample (Fig. 2), however, do not show evidence of the precipitates.

We suggest that the triangular, Ge-enriched precipitates observed in the relaxed (800 °C/10 min) and (800 °C/20 min) samples require the formation of CoSi<sub>2</sub> and the presence of misfit dislocations at the  $Si_{1-x}Ge_x$ -Si substrate interface in order to form. It is observed that the samples prepared on relaxed  $Si_{1-x}Ge_x$  layers, which were annealed to 700 °C for 10 and 20 min, do not form CoSi2 or the triangular precipitates. Only on the relaxed  $Si_{1-x}Ge_x$  layers annealed to 800 °C for 10 and 20 min is CoSi<sub>2</sub> formed with the concurrent formation of the precipitates. In contrast, the XRD results for the Co(20 nm)/ SiGe(64 nm):(700 °C/20 min) sample indicated the presence of both CoSi and CoSi<sub>2</sub>, but no precipitates were formed. The thickness of the strained layer was 64 nm, well below  $T_{\rm c}$ , and thus this sample would not be expected to contain a significant number of misfit dislocations.

In forming  $\text{CoSi}_2$  from the reaction of pure Co with Si, the reaction proceeds from the metal-rich to the Si-rich phases with increasing temperature:  $\text{Co}_2\text{Si} \rightarrow \text{CoSi} \rightarrow$  $\text{CoSi}_2$ . It is generally agreed that the dominant moving species during  $\text{Co}_2\text{Si}$  formation is Co and the dominant moving species during CoSi formation is  $\text{Si}.^{43-45}$  There is conflicting evidence about which is the dominant moving species during  $\text{CoSi}_2$  formation, but recent work by Comrie<sup>46</sup> suggests that it is Si and this assumption is used here.

As mentioned previously, a  $Co(Si_{1-\nu}Ge_{\nu})$  phase is believed to form initially at low annealing temperatures, which then expels the Ge as the temperature is increased. During this reaction, which covers the temperature range 300–700 °C, there is still enough Si in the proximity of the Co atoms to complete the  $Co(Si_{1-\nu}Ge_{\nu}) \rightarrow CoSi$  transition without requiring long-range diffusion of Si. As the Ge is expelled from the ternary phase, the Ge concentration between the CoSi grains becomes high, which increases the stress in the film as well as depletes the surrounding region of Si. The increased film stress may propagate threading segments from the misfit dislocations present at the substrate- $Si_{1-x}Ge_x$  interface further into the substrate in the form of half loops.<sup>38</sup> It is known that for relaxed  $Si_{1-x}Ge_x$  alloys on Si(001), where 0.02 < $x \le 0.2$ , plastic deformation of the near-interface substrate region occurs.<sup>47</sup> Thus, dislocation half loops propagating a short distance into the substrate are already present even before Co deposition because of the relaxation of the  $Si_{1-x}Ge_x$  film. Upon annealing to 800 °C, the formation of CoSi2 requires the long-range transport of Si due to the Si depletion in the region between each CoSi grain. Although there is enough Si in the remaining  $Si_{1-x}Ge_x$  film to complete the CoSi  $\rightarrow$  CoSi<sub>2</sub> reaction without the need for Si from the substrate, we suggest that Si diffusion is occurring along the threading dislocation segments, which propagate into the substrate, and that this diffusion is accompanied by vacancy injection into the substrate.

There is much evidence of point defect generation during silicide formation on silicon. Wen et al.<sup>48</sup> showed that Ti silicidation eliminated interstitial dislocation loops created by ion implantation damage in Si(100). They attributed the annihilation of the defects to injection of vacancies into the substrate during the silicide reaction. Herner et al.49 performed a similar study with Ti deposited onto Si wafers to form TiSi2, which eliminated end-of-range dislocation loops. They attributed the effect to a supersaturation of vacancies due to the presence of the TiSi2 film. Honeycutt<sup>50</sup> performed studies on the effects of Ti and Co silicidation on point-defect concentrations in silicon by dopant diffusion and defect marker layers. It was concluded that the excess interstitial concentrations induced during implantation are significantly reduced by the formation or presence of CoSi<sub>2</sub> and TiSi<sub>2</sub>.  $Hu^{51}$  observed that  $TaSi_{1.8}$  films sputtered onto Si(100) substrates and annealed to 950 °C caused enhanced diffusion of boron and antimony in buried layers and took this as evidence of vacancy supersaturation.

In light of the evidence of point-defect generation during silicidation cited above, it is argued that it is likely that the cobalt reaction with the Si<sub>1-x</sub>Ge<sub>x</sub> films, which produces CoSi<sub>2</sub> in the relaxed (800 °C/10 min) and (800 °C/20 min) samples in the present work, injects vacancies into the Si substrate as it removes Si atoms. It is suggested that Ge from the Ge-rich regions around the silicide grains embedded in the Si<sub>1-x</sub>Ge<sub>x</sub> film then diffuses to the vacancies accumulated in the substrate.

The formation mechanism of the tetrahedral precipitates is unclear at this point. High-resolution TEM lattice imaging of the relaxed (800 °C/20 min) sample has indicated that the edges of the triangular precipitates lie along {111} planes, which are the glide planes for dislocation propagation in diamond cubic lattices. The plastic deformation observed in the work by Vdovin, cited earlier, was manifested by dislocation half loops gliding from the misfit dislocation network along {111} planes into the substrate in the near-interface region.<sup>47,52</sup> In the present study a control sample was prepared, in which 240 nm of Si<sub>0.80</sub>Ge<sub>0.20</sub> was deposited at 550 °C onto a Si(001) substrate and annealed at 800 °C for 20 min. Cross-sectional TEM images revealed the presence of dislocation half loops emanating into the silicon substrate from the  $Si_{1-x}Ge_x$ -Si interface. In some cases the threading arm of a misfit dislocation could be observed propagating from one end of a half loop, through the epilayer, to the surface of the film. The dislocation bounding a diamond defect,

as first noted by Eaglesham *et al.*,<sup>53,54</sup> was also observed within the epilayer. The diamond defect, an  $a/6 \langle 114 \rangle$  stacking fault, was shown to be a nucleation source for  $a/2 \langle 110 \rangle$  dislocations within the epilayer. No precipitates were observed anywhere within the epilayer or the substrate in the control sample.

A possible growth mechanism for the precipitates is the bowing out of dislocation half loops from the interface into the substrate along {111} planes due to the absorption of vacancies. It is known that supersaturation of vacancies causes dislocation climb. The triangular faces of the precipitates visible in the [011] zone axis TEM cross section (Fig. 3) lead to the supposition that the structures began as stacking fault tetrahedra (SFT). These defects are tetrahedron-shaped regions of material bound by intrinsic stacking faults and stair-rod dislocations. One mechanism of formation is the extension of a Frank partial-dislocation loop formed by vacancy condensation. Once SFT are formed, they can grow by vacancy absorption at jog lines. Vacancy supersaturation causes the climb of extended dislocations with nearly perfect sink efficiency.55 The tetrahedron-shaped precipitate in the TEM plan view image of Fig. 5, which was prepared from the relaxed (800 °C/20 min) sample with the silicide/Si<sub>1-x</sub>Ge<sub>x</sub> layer removed, shows that the Ge-enriched precipitates are indeed in the shape of tetrahedra.

The driving force for the preferential diffusion of Ge to the precipitate structures is suggested to be the relatively high Ge concentration in the epilayer between the  $CoSi_2$ grains. Ge diffusion in  $Si_{1-x}Ge_x$  alloys is dependent on the local Ge concentration.<sup>56,57</sup> McVay and DuCharme's study of diffusion of Ge in  $Si_{1-x}Ge_x$  alloys showed that the activation energy for diffusion of Ge remains close to 3 eV for pure Ge up to films with nearly 70 at.% Si.<sup>57</sup> At high Si concentrations, the activation energy rises sharply until, for almost pure Si, it is ~5 eV, which is the value measured for Si self-diffusion.

Thus, in the present study, it is reasonable to conclude that as the local Ge concentration in the  $Si_{1-x}Ge_x$  film surrounding the silicide grains increases because of the silicidation reaction, the activation energy for diffusion of Ge will decrease. If vacancy injection into the substrate occurs before any appreciable Ge diffusion, SFT may nucleate and grow and then act as a sink for Ge diffusion. The diffusion of Ge into the substrate would then occur because of the high localized Ge concentration around the silicide grains in the epilayer, which lowers the activation energy for Ge diffusion. The Ge diffusion would follow the same dislocation lines into the substrate as the vacancies. It is likely some quantity of Si from the epilayer is also diffusing into the substrate, but it cannot be determined what fraction of the diffusing species is Si. The quantitative EDS measurement taken from the center of the large precipitate in the relaxed (800 °C/20 min) sample (see Fig. 3 and Table I) indicates a Si<sub>0.68</sub>Ge<sub>0.32</sub> composition; however, we suspect the Ge concentration may be even higher because the precipitates lie beneath the substrate surface and there may be Si from the substrate overlapping the precipitate when imaged in cross section.

The presence of the plastic deformation within the substrate, due to the  $Si_{1-x}Ge_x$  film relaxation, appears to be a key factor for the formation of the precipitates. For the Co(20 nm)/SiGe(64 nm):(700 °C/20 min) sample, the amount of Co deposited is more than enough to consume all the Si present in the  $Si_{1-x}Ge_x$  layer, yet crosssectional TEM analysis indicated only CoSi and CoSi<sub>2</sub> grains amid regions of Ge-enriched  $Si_{1-x}Ge_x$  at the film surface. Some of the CoSi and CoSi<sub>2</sub> grains, rounded in shape, were partly embedded below the Si substrate surface, but no Ge-enriched precipitates were seen below the substrate surface. It might be argued that it is simply the higher annealing temperature of 800 °C that initiates formation of the triangular precipitates due to increased Ge diffusion. However, in this case, the control sample prepared without Co, which was annealed to 800 °C, would also be expected to exhibit some Ge diffusion into the substrate. As mentioned previously, cross-sectional TEM imaging of the control sample did not reveal the presence of any precipitates within the epilayer or substrate.

### V. CONCLUSIONS

Ge segregation resulting from the reaction of Co with strained and relaxed Si<sub>0.80</sub>Ge<sub>0.20</sub> alloys was studied. The nature of the segregation was observed to be dependent on whether CoSi<sub>2</sub> was formed during the annealing of the films. In the case of strained  $Si_{1-x}Ge_x$  films, CoSi and CoSi<sub>2</sub> formation resulted in regions of Ge-enriched  $Si_{1-x}Ge_x$  located between the silicide grains at the surface of the film. In the case of relaxed  $Si_{1-x}Ge_x$  films, CoSi formation resulted in Ge-enriched regions of  $Si_{1-r}Ge_r$ lying at the surface of the film similar to the strained case. In relaxed films where CoSi<sub>2</sub> was formed, however, Ge segregation included the formation of large, tetrahedron-shaped Ge-enriched precipitates, which grew into the Si substrate along {111} planes. Although the exact mechanism for formation of these precipitates is not yet known, an explanation based on vacancy injection into the substrate during the silicidation reaction coupled with a decreased activation energy for Ge diffusion was presented.

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