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B. I. Boyanov, P. T. Goeller, D. E. Sayers, et al.

Film thickness effects in the Co–$Si_{1-x}Ge_x$ solid phase reaction

B. I. Boyanov, P. T. Goeller, D. E. Sayers, and R. J. Nemanich[a)]
Department of Physics and Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695

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The thickness dependence of the reaction of cobalt with epitaxial silicon–germanium alloys ($Si_{1-x}Ge_x$) has been studied. The reaction products of Co with (100)-oriented $Si_{0.79}Ge_{0.21}$ after annealing at 800 °C depended on the thickness of the Co film. Complete conversion to $CoSi_2$ occurred only when the thickness of the Co layer exceeded 350 Å. Interface reactions with Co layers thinner than 50 Å resulted in CoSi formation, while a mixture of CoSi and $CoSi_2$ was formed at intermediate thicknesses. X-ray diffraction and extended x-ray absorption fine structure measurements indicated no measurable incorporation of Ge had occurred in either the CoSi or $CoSi_2$. The threshold thickness for nucleation of $CoSi_2$ on (100)-oriented $Si_{1-x}Ge_x$ was determined in the range $0 \leqslant x \leqslant 0.25$. The threshold thickness increased superlinearly with the Ge concentration x, and did not depend on the doping of the Si(100) substrate or the strain state of the $Si_{1-x}Ge_x$ film. The observed thickness effect was attributed to preferential Co–Si bonding in the reaction zone and the energy cost of Ge segregation, which accompanies the formation of CoSi and $CoSi_2$ during the reaction of Co with $Si_{1-x}Ge_x$. © *1998 American Institute of Physics.* [S0021-8979(98)05620-5]

I. INTRODUCTION

Due to its low resistivity, low Schottky barrier, and good thermal stability, cobalt disilicide ($CoSi_2$) is considered an attractive contact material for deep submicron Si devices. In the absence of oxygen contamination, the reaction of blanket cobalt films with Si(100) substrates proceeds in three stages: Co_2Si formation above 250 °C, CoSi formation above 350 °C, and $CoSi_2$ formation above 550 °C.[1] The silicide phase in stable equilibrium with Si is $CoSi_2$, but the CoSi→$CoSi_2$ transition may be reversed by adding appropriate amounts of Co to the system and re-annealing.[2] The resistivity of $CoSi_2$ (15–20 $\mu\Omega$ cm) is approximately ten times lower than that of CoSi (147 $\mu\Omega$ cm), making $CoSi_2$ the desirable phase for microelectronics applications.[3] There have been no prior reports indicating that the temperature of the CoSi→$CoSi_2$ transition depends on the thickness of the Co film. This is in contrast to Ti, where the temperature of the C49→C54 transition has been found to depend strongly both on film thickness[4,5] and feature size.[6,7] The lack of such thickness effects may make Co better suited than Ti for contacts in deep submicron device applications.

Recently an effort has been made by a number of groups to evaluate the feasibility of cobalt as a contact material for silicon–germanium ($Si_{1-x}Ge_x$) devices.[8–13] The driving force behind this research has been the potential of fabricating high-frequency devices using existing silicon technology. One of the major difficulties in using cobalt as a contact material to $Si_{1-x}Ge_x$ appears to be the preferential reaction of Co with Si, which leads to Ge segregation and film islanding, resulting in high-resistivity contacts. In addition, there have been conflicting reports on the path and products of the Co/$Si_{1-x}Ge_x$ reaction. For example, Wang *et al.* have reported that the final products of the Co/$Si_{1-x}Ge_x$ reaction are $CoSi_2$ and a Ge-rich $Si_{1-y}Ge_y$ alloy ($y > x$),[12] while Glück *et al.* did not observe $CoSi_2$ formation.[13] It will be shown that the apparent controversy may be due to the fact that the reaction of Co with $Si_{1-x}Ge_x$ is subject to a thickness effect similar to that observed in the reaction of Ti with both Si (Ref. 4) and $Si_{1-x}Ge_x$.[14]

II. EXPERIMENT

The majority of the samples used in this work consisted of Co films deposited at room temperature on 2600-Å-thick epitaxial $Si_{1-x}Ge_x$ films. The $Si_{1-x}Ge_x$ films were grown by molecular beam epitaxy (MBE) at 550 °C on boron-doped Si(100) substrates with a resistivity of 0.8–1.2 Ω cm (Virginia Semiconductor). The $Si_{1-x}Ge_x$ layers were not intentionally doped. The thickness of the as-deposited Co films ranged from 10 to 450 Å, and the Ge index x of the $Si_{1-x}Ge_x$ film was varied in the range $0 \leqslant x \leqslant 0.25$. In order to determine the effect of the substrate dopant and the strain state of the $Si_{1-x}Ge_x$ film on the formation of $CoSi_2$, several samples were also prepared on phosphorous-doped Si(100) wafers of similar resistivity, and on 800-Å-thick $Si_{1-x}Ge_x$ films with $x \leqslant 0.21$. Atomically clean surfaces were prepared by spin etching the Si(100) substrates with a 1:1:10 HF:H_2O:ethanol solution, followed by *in situ* thermal desorption at 900 °C and deposition of a 200-Å-thick homoepitaxial Si buffer layer at 550 °C.[15] The deposition was controlled with quartz crystal thickness monitors. The deposition rates for all materials were below 0.5 Å/s. The Co films were annealed *in situ* for 20 min at 800 °C. The base pressure of the ultrahigh vacuum (UHV) chambers used for deposition and annealing was below 5×10^{-10} Torr. In order to reduce oxidation during the subsequent characterization, all Co films 25 Å and

a)Electronic mail: Robert_Nemanich@ncsu.edu

thinner were additionally capped after annealing with a 25-Å-thick Si film deposited at room temperature. Since multiple phases were formed after annealing, samples will be referred to by the thickness of the as-deposited Co film in order to avoid ambiguity, e.g., 50 Å $Co/Si_{0.79}Ge_{0.21}$ will refer to a 50 Å Co film deposited on a $Si_{0.79}Ge_{0.21}$ substrate.

Film growth and annealing were monitored *in situ* with reflection high-energy electron diffraction (RHEED). The annealed films were characterized *ex situ* with x-ray diffraction (XRD), atomic force microscopy (AFM), and extended x-ray absorption fine structure (EXAFS). XRD data were collected in the $\theta-2\theta$ mode between 25° and 70° 2θ with Cu K_α radiation on a Rigaku Geigerflex instrument equipped with a graphite(0001) monochromator. The Cu anode was operated at 27.5 kV and 20 mA. AFM data were acquired in noncontact mode with a Park Scientific Autoprobe M5 instrument. The typical size of the AFM tips used is reported by the manufacturer to be approximately 100 Å. EXAFS data were collected at the Co *K* edge (7709 eV) in fluorescence mode with a Canberra 13 element Ge counting detector at beamline X-11A at the National Synchrotron Light Source (NSLS). The incident photon beam was monochromatized with a double-crystal Si(100) monochromator detuned 60% to suppress higher harmonics. Energy resolution was estimated to be about 3 eV by the Cu foil near-edge feature. Energy calibration was set to 7707 eV at the Co foil *K*-edge inflection point. All EXAFS data processing and analysis were performed with MacXAFS 4.0.[16,17]

III. RESULTS

The thickness dependence of the thin-film reaction of Co with $Si_{1-x}Ge_x$ was explored with a series of Co films ranging in thickness from 10 to 450 Å. The Co films were deposited on 2600-Å-thick $Si_{0.79}Ge_{0.21}$, and were annealed for 20 min at 800 °C. Cobalt films 50 Å and thicker were examined with XRD, while films 25 Å and thinner were characterized with EXAFS. The main reason for using EXAFS on the thinner films was that the limited sensitivity of our XRD instrument did not permit the characterization of Co films thinner than 50 Å.

The XRD results are summarized in Fig. 1. The phase content of the films was determined by the presence or absence of the $CoSi_2$(111) and (220) peaks at 28.80° and 47.90°, respectively, and the CoSi(210) peak at 45.65°. The reaction products were found to be dependent on the thickness of the Co film. Complete conversion to $CoSi_2$ occurred only for the 450-Å-thick Co film, as indicated by the absence of the CoSi(210) peak. A mixture of CoSi and $CoSi_2$ resulted when the thickness of the Co film was between 150 and 350 Å. The only phase observed after the reaction of a 50-Å-thick Co film with $Si_{0.79}Ge_{0.21}$ was CoSi. The positions of all CoSi and $CoSi_2$ XRD lines were within 0.05° of those listed in the JCPDS database,[18] indicating that less than 3% Ge incorporation had occurred in the CoSi structure after annealing at 800 °C (in agreement with our prior results).[19]

Two types of RHEED patterns were observed for the annealed Co films: weak disordered spots on a strong diffuse background for the 50, 150, and 450 Å films and distinct

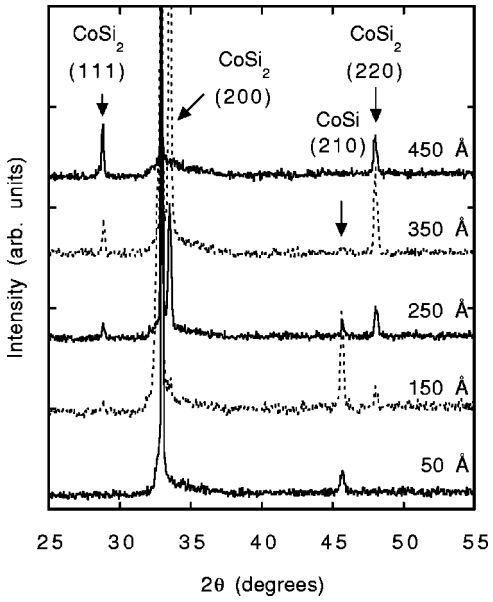

FIG. 1. XRD scans of Co films evaporated on 2600-Å-thick $Si_{0.79}Ge_{0.21}$ epitaxial layers and annealed for 20 min at 800 °C. The thickness of the as-deposited Co film is indicated on each trace. The unlabeled peak at 32.95° is the (200) ghost peak of the Si substrate.

vertical streaks for the 250 and 350 Å films. The appearance of a streaky RHEED pattern correlated with the presence of $CoSi_2$(200) and (400) peaks in the XRD scans of the 250 and 350 Å films (Fig. 1). The $CoSi_2$(200) and (400) peaks were at 33.55° and 70.70°, respectively, corresponding to an out-of-plane lattice constant of 5.332 ± 0.006 Å. The lattice constant of bulk $CoSi_2$ is 5.3640 Å,[18] indicating that the $CoSi_2$ phase is under tensile strain in the plane of the interface. In all cases the intensity of the (200) and (400) peaks exceeded that of the (220) peak at least by a factor of 2. Since the JCPDS relative intensities of the (200), (400), and (220) peaks in polycrystalline $CoSi_2$ are 2%, 14%, and 100%, respectively,[18] we attribute the presence of intense (200) and (400) peaks in the XRD scans of the 250- and 350-Å-thick films as indicating the formation of epitaxial (100)-oriented $CoSi_2$. The tensile strain of the $CoSi_2$ phase detected in the XRD measurement also supports this conclusion. Similar epitaxial effects have been reported previously by Donaton *et al.* for Co/SiGeC and Co/SiGe.[20]

The results of EXAFS measurements for identically annealed 10- and 25-Å-thick Co films on $Si_{0.79}Ge_{0.21}$ are shown in Fig. 2. Comparison with the reference EXAFS spectra for CoSi and $CoSi_2$ included in this figure indicates that the predominant phase formed in both films is CoSi. Quantitative analysis of the EXAFS data showed no statistically significant Co–Ge bonding in the annealed films. Since the sensitivity limit of EXAFS for mixed phases is typically less than 10%, the lack of detectable Co–Ge bonding indicates that Ge incorporation in the CoSi structure is less than 10%.

The XRD and EXAFS results indicate that the thin-film reaction of Co with $Si_{0.79}Ge_{0.21}$ exhibits a dependence on the thickness of the Co layer, which is not observed for the reaction of Co with Si(100). The effect of Ge on this thickness effect was explored by examining the reaction of Co with $Si_{1-x}Ge_x$ films of varying Ge concentration. Figure 3 shows

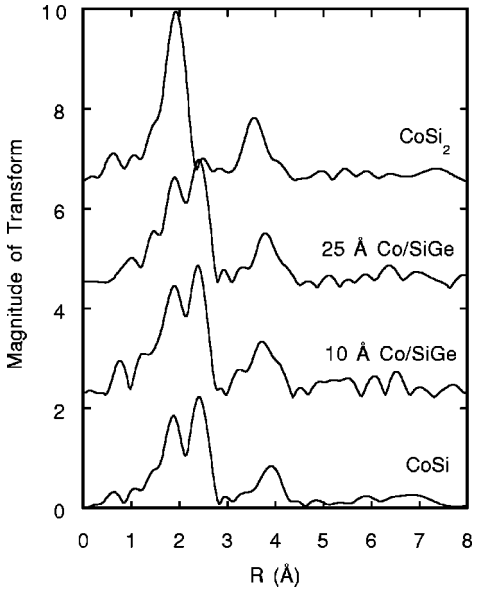

FIG. 2. Fourier-transformed k^2-weighted EXAFS spectra of 10- and 25-Å-thick Co films deposited on $Si_{0.79}Ge_{0.21}$, and annealed for 20 min at 800 °C. Reference spectra for CoSi and $CoSi_2$ are also shown for comparison. The Fourier transform range is 3.5–13.8 $Å^{-1}$.

a series of XRD measurements for 50-Å-thick Co films annealed for 20 min at 800 °C on various $Si_{1-x}Ge_x$ substrates. The reaction product of Co with a $Si_{1-x}Ge_x$ film containing 9% Ge was predominantly polycrystalline $CoSi_2$, as indicated by the presence of $CoSi_2$(111) and (220) lines. The reaction of Co with the $Si_{1-x}Ge_x$ films containing 15% Ge resulted in the formation of a mixture of CoSi and $CoSi_2$, as indicated by the presence of both the $CoSi_2$(111) and (220) lines, and the CoSi(210) line. As the Ge concentration x was increased, the CoSi phase was stabilized to the point where

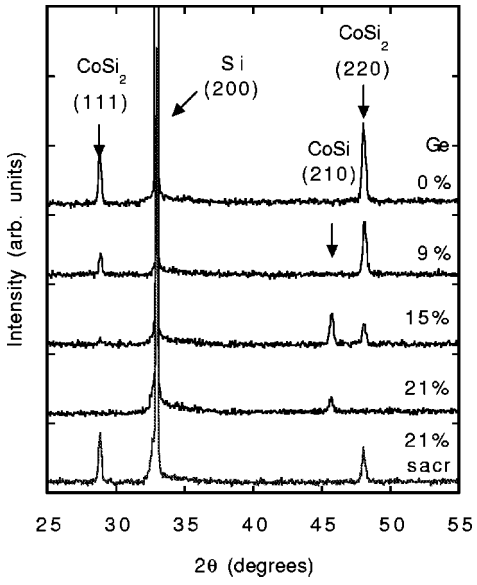

FIG. 3. XRD scans of 50-Å-thick Co films deposited on $Si_{1-x}Ge_x$ layers with various Ge concentrations. The films have been annealed for 20 min at 800 °C. The Ge concentrations are indicated on each trace. The bottom trace is for a Co film deposited on a 183-Å-thick sacrificial Si layer.

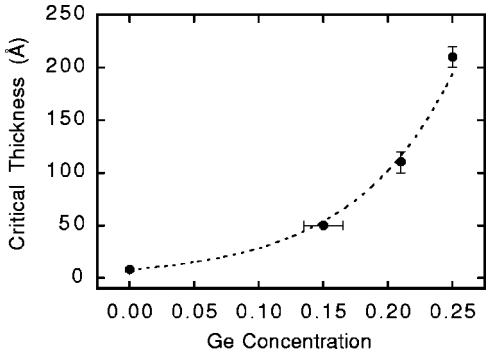

FIG. 4. Experimentally determined dependence of the critical thickness for the onset of $CoSi_2$ formation on the initial Ge concentration x. The line is drawn as a guide to the eye. The critical thickness doubles for approximately every 5.5% increase in x.

CoSi was the only phase detected in the $Si_{0.79}Ge_{0.21}$ film, indicating that the threshold thickness for the onset of $CoSi_2$ formation increases with Ge concentration.

In order to further determine how the formation of $CoSi_2$ is affected by the presence of Ge at the silicide–$Si_{1-x}Ge_x$ interface, the reaction of Co with a sacrificial Si layer deposited on the $Si_{1-x}Ge_x$ film was examined. The bottom trace in Fig. 3 is for a 50-Å-thick Co film annealed on a 183-Å-thick Si sacrificial layer deposited on a 2600-Å-thick $Si_{0.79}Ge_{0.21}$ substrate. The thickness of the sacrificial layer was such that the layer was entirely consumed by the Co film. Since the $Si_{0.79}Ge_{0.21}$ film was relaxed, the sacrificial Si layer was most likely strained. The only detectable XRD lines for that sample were the $CoSi_2$(111) and (220) lines, indicating the predominant formation of polycrystalline $CoSi_2$ when Ge was not present in the reaction zone.

The results in Figs. 1–3 clearly show that the onset of $CoSi_2$ formation depends both on the thickness of the Co film, and on the Ge concentration of the $Si_{1-x}Ge_x$ layer. We define the critical thickness for $CoSi_2$ formation as the thickness of the as-deposited Co layer at which a *detectable* quantity of $CoSi_2$ was formed after annealing for 20 min at 800 °C. Our measurements of the critical thickness in the range $0 \leqslant x \leqslant 0.25$ are summarized in Fig. 4. The $CoSi_2$(111) and (220) XRD lines were monitored to determine the onset of $CoSi_2$ formation. The critical thickness depends strongly on the initial Ge concentration of the $Si_{1-x}Ge_x$ layer, and increases superlinearly as the Ge concentration increases.

The effects of the doping of the Si(100) substrate and the strain in the $Si_{1-x}Ge_x$ layer on the reaction of Co with $Si_{1-x}Ge_x$ were explored by examining control samples on phosphorous-doped Si(100) substrates and on strained $Si_{1-x}Ge_x$ films. According to the work of Bean *et al.*, the critical thickness for strain relaxation of epitaxial $Si_{0.8}Ge_{0.2}$ films grown at 550 °C is approximately 2000 Å.[21] Several control samples were prepared: 50 Å Co/800 Å $Si_{0.79}Ge_{0.21}$ (strained) grown on boron-doped Si substrates; 50 Å Co/2600 Å $Si_{0.79}Ge_{0.21}$ (relaxed) grown on phosphorous-doped Si; and 50 Å Co/800 Å $Si_{0.79}Ge_{0.21}$ (strained) grown on phosphorous-doped Si. All films were annealed for 20 min at 800 °C. The only phase observed in the control samples was CoSi, suggesting that dopants and strain do not

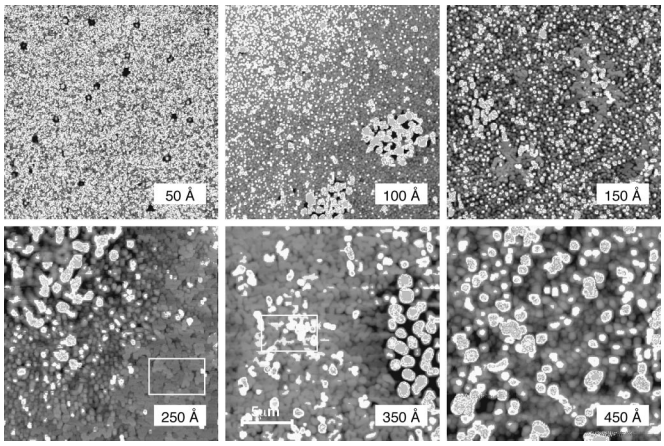

FIG. 5. AFM images of Co films evaporated on 2600-Å-thick $Si_{0.79}Ge_{0.21}$ epitaxial layers and annealed for 20 min at 800 °C. The thickness of the as-deposited Co film is indicated on each image. The boxed regions correspond to flat regions that have been tentatively identified as (100)-oriented $CoSi_2$.

have a significant effect on the critical thickness for $CoSi_2$ nucleation.

The presence of at least two phases in most of the reacted films (polycrystalline CoSi and $CoSi_2$) is expected to result in morphologically distinct regions and rough surfaces. The surface morphology of the reacted films was examined with AFM. Results for the 50 to 450-Å-thick Co films on $Si_{0.79}Ge_{0.21}$ are shown in Fig. 5. As before, the films were annealed for 20 min at 800 °C. The 50 Å $Co/Si_{0.79}Ge_{0.21}$ film consists entirely of fine-grained regions. Regions consisting only of larger grains are observed for the 450 Å $Co/Si_{0.79}Ge_{0.21}$ film. Since the predominant phases present in the 50 and 450 Å $Co/Si_{0.79}Ge_{0.21}$ films are polycrystalline CoSi and $CoSi_2$, respectively, we tentatively associate these two morphologies with polycrystalline CoSi and $CoSi_2$, respectively. Both types of regions are present in the 100–350 Å films, which contain a mixture of polycrystalline CoSi and $CoSi_2$. In addition, a third type of morphology was observed in the 250 and 350 Å films (Fig. 5, boxed regions). This morphology is similar to that observed by Tung *et al.* in transmission electron microscope (TEM) micrographs of epitaxial $CoSi_2$ on Si(100).[22,23] These regions were present only in samples containing epitaxial (100)-oriented $CoSi_2$ (as determined from the XRD measurements). Therefore, we tentatively identify them as epitaxial (100)-oriented $CoSi_2$. It should be noted that isolated regions of similar morphology were also detected in the 150-Å-thick films [note the weak $CoSi_2(200)$ peak in the corresponding trace in Fig. 1 and the boxed region in Fig. 5]. However, the area density of these regions is considerably lower than that found in the 250 and 350 Å samples, where they comprised at least 40% of the surface.

IV. DISCUSSION

In this study it was found that the final phase formed in the reaction of Co with $Si_{1-x}Ge_x$ alloys is dependent on the thickness of the Co film and the relative concentration of Ge in the alloy. Similar thickness effects have been observed previously in the Ti/Si and Ti/SiGe systems, where they have been attributed to the difference in interfacial and surface free energies of the C49 and C54 phases.[5,14,24]

In order to determine the driving force for the thickness effect in the $Co/Si_{1-x}Ge_x$ system, the energetics of the reaction in question must be examined. The nucleation of one phase in another can be described in terms of classical nucleation theory. The phase transformation is driven by the change in free energy ΔG that accompanies the nucleation of a new phase

$$\Delta G(r) = Br^2(\delta\sigma) + Ar^3(\delta G), \tag{1}$$

where r is the size of the product nucleus, Br^2 is the area of the interface between the parent and product phases, $\delta\sigma$ is the change in energy per unit area of the interface, Ar^3 is the volume of the nucleus, δG is the free energy difference per unit volume between the two phases, and and A and B are constants that depend on the shape of the nucleus.[14] When $\delta\sigma$ is positive and δG is negative ΔG will initially increase with nucleus size, pass through a maximum at some critical radius r_c, and then decrease and eventually become negative. The critical radius r_c represents the size of the nucleus above which the nucleus will grow spontaneously. For a spherical nucleus

$$r_c = -2\,\delta\sigma/\delta G. \tag{2}$$

In order to estimate the value of r_c, knowledge of both $\delta\sigma$ and δG are necessary:

$$\delta G = \delta H - T\,\delta S, \tag{3}$$

where δH is the enthalpy difference per unit volume between the two phases, T is the reaction temperature, and δS is the change in entropy per unit volume during the reaction. Usually in solid-state reactions δG is dominated by the enthalpy, and the entropy term is a small correction. However, the difference in the enthalpies of formation of CoSi and $CoSi_2$ is only $\Delta H \approx -3$ kJ/mole of Co atoms,[25] and the entropy term can be a substantial correction, as described below.

As is evident from the results presented here, the energetics of the reaction in the $Co/Si_{1-x}Ge_x$ system are additionally affected by the presence of Ge in the reaction zone. Previous work by our group has shown that in the presence of excess $Si_{1-x}Ge_x$ the reaction proceeds in three stages: (i) $Co(Si_{1-x}Ge_x)$ formation; (ii) Ge expulsion and CoSi formation; and (iii) as the reaction proceeds to $CoSi_2$ there is further Ge segregation.[12] The Ge segregation in steps (ii) and (iii) is driven by the large differences in the enthalpies of formation of CoSi and CoGe, and $CoSi_2$ and $CoGe_2$, respectively, and is a necessary condition to establish bulk equilibrium between all co-existing phases at each stage of the reaction.[26]

In the last stage of the reaction of Co with $Si_{1-x}Ge_x$, the formation of $CoSi_2$ from the reaction of CoSi with the $Si_{1-x}Ge_x$ substrate may therefore be expressed symbolically as

$$CoSi + m\,Si_{1-x}Ge_x \rightarrow CoSi_2 + (m-1)\,Si_{1-y}Ge_y, \tag{4}$$

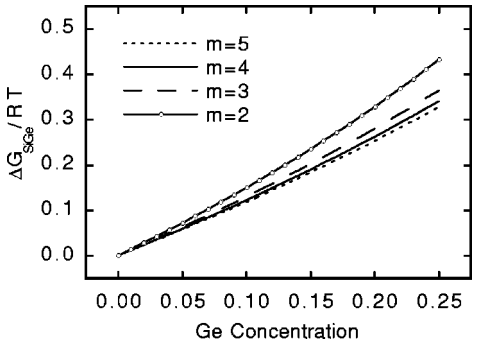

FIG. 6. The entropy term ΔG_{SiGe} [second term in Eq. (8)] as a function of initial Ge concentration and the number of moles m participating in the reaction.

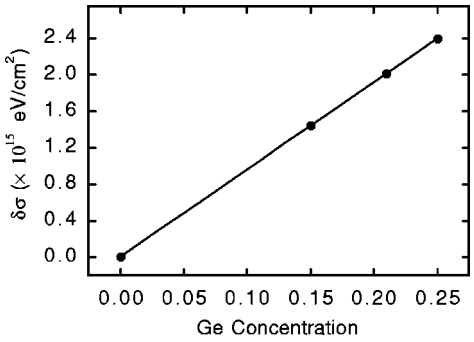

FIG. 7. Estimated surface/interface energy $\delta\sigma$ for the $CoSi \rightarrow CoSi_2$ transition on $Si_{1-x}Ge_x$. The bullets are the values estimated from the experimental data. The solid line is a linear fit to the estimated values.

where m is the number of moles of $Si_{1-x}Ge_x$ participating in the reaction, and $y=m/(m-1)x$ from mass conservation. In order to determine the critical thickness at which $CoSi_2$ nucleation occurs, the energetics of Eq. (4) must be examined:

$$\Delta G=\Delta G_{\mathrm{Co/Si}}+RT\{(m-1)[y\ \ln y+(1-y)\ln(1-y)] -m[x\ \ln x+(1-x)\ln(1-x)]\}. \quad (5)$$

Here ΔG is the net change in Gibbs energy during the reaction, R is the universal gas constant, and $\Delta G_{\mathrm{Co/Si}}$ is the energy gain of the $CoSi \rightarrow CoSi_2$ transition, which is equal to the net change ΔG for the $CoSi \rightarrow CoSi_2$ transition on Si(100). The second term in Eq. (5), ΔG_{SiGe}, is due to the entropy change that accompanies the Ge expulsion and formation of Ge-rich $Si_{1-y}Ge_y$ [Eq. (4)]. The energetics in Eq. (5) are expressed per unit mole of Co atoms for clarity, instead of per unit volume as required by Eq. (2).

The second term in Eq. (5) is plotted as a function of x for a several values of m in Fig. 6. It should be noted that at 550 °C ($RT=6.8$ kJ/mol) the energy cost of Ge segregation may be a substantial fraction of the energy gained from the $CoSi \rightarrow CoSi_2$ transition itself ($\Delta G_{\mathrm{Co/Si}} \approx -7$ kJ/mol of Co atoms). The net effect will be a decrease in the absolute value of δG and a corresponding increase in r_c, per Eq. (2), thus driving the thickness effect described in Sec. III.

A quantitative calculation of r_c within the framework of this model requires that the parameters $\delta\sigma$, $\Delta G_{\mathrm{Co/Si}}$, and m be specified, per Eqs. (2)–(5). With the exception of $\Delta G_{\mathrm{Co/Si}}$, these are not known. Nevertheless, the following observations about the possible ranges for these parameters can be made.

The dependence of the entropy term ΔG_{SiGe} on the number of moles m participating in the reaction is weak for $m \geqslant 3$ (Fig. 6), which is an expected result. As the thickness of the $Si_{1-x}Ge_x$ layer increases beyond the thickness consumed by the reaction, most of the layer will simply be a passive spectator, and will not be affected by the reaction. Since each angstrom of Co consumes 3.65 Å of pure Si to form $CoSi_2$, it is reasonable to expect that the thickness of the $Si_{1-x}Ge_x$ layer which participates in the reaction is $\approx 3.65t/(1-x)$, where t is the thickness of the as-deposited Co layer. This corresponds to $m \approx 1/(1-x)$, i.e., $1 \leqslant m \leqslant 1.5$ for $0 \leqslant x \leqslant 0.3$. Even if the amount of $Si_{1-x}Ge_x$ participating in the reaction deviates from that number significantly, it is seen from Fig. 6 that this will result in a correction in ΔG_{SiGe} of approximately 20%.

The surface/interface term $\delta\sigma$ contains contributions from several sources: the energy of the free $CoSi_2$ surface, the energy of the $CoSi_2$/CoSi and $CoSi_2$/SiGe interfaces, and the surface/interface energy of the Ge-rich precipitates. Because of the apparent complexity of the problem and lack of relevant experimental data, we have chosen to treat $\delta\sigma$ as an adjustable parameter that depends on the Ge concentration x. Given the preference for formation of Co–Si bonds at the $CoSi_2$/SiGe interface,[27] some dependence of $\delta\sigma$ on x is to be expected. Furthermore, if it assumed that $\delta\sigma$ is proportional to the Ge concentration at the interface, it is reasonable to expect that $\delta\sigma$ is an approximately linear function of x. Since there is no known threshold for $CoSi_2$ growth on Si, it may be additionally assumed that $\delta\sigma(0) \approx 0$. Therefore only one adjustable parameter, the slope of $\delta\sigma(x)$, is required.

The following procedure may be used to estimate the slope of $\delta\sigma(x)$ from our experimental results. First, the value of ΔG is calculated from Eq. (5) for the Ge concentrations at which experimental results for r_c are available (Fig. 4). The calculated ΔG and experimental r_c are then used to estimate $\delta\sigma$ from Eq. (2), and a straight line is fit to these values to determine the slope of $\delta\sigma(x)$, which may then be used to calculate r_c at any value of x. The results from such calculations with $m=1/(1-x)$ are shown in Figs. 7 and 8, where a surprisingly good fit with the experimental results was achieved.

It should be noted that calculations described in the previous paragraph depend on the choice of m. The results in Figs. 7 and 8 were obtained with the assumption that the thickness of the $Si_{1-x}Ge_x$ layer involved in the reaction is determined solely by the amount of Si consumed in the $CoSi \rightarrow CoSi_2$ phase transition. While this is a plausible assumption, it completely ignores effects such as the possible redistribution of the segregated Ge. Since the reaction temperature (800 °C) is close to the melting point of Ge (938 °C), Ge diffusion following the segregation is to be expected. Therefore it may not be possible to determine the value of m in Eq. (5) experimentally, e.g., by measuring the volume and composition of the Ge-rich precipitates formed in the reaction, since they may not be representative of the

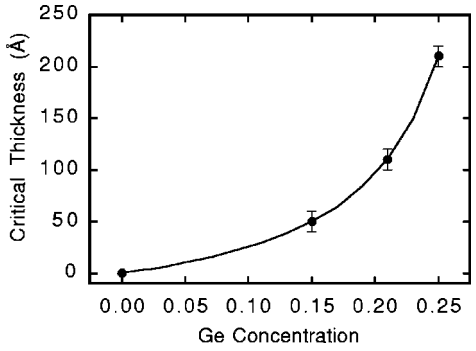

FIG. 8. Comparison of experimental measurements (bullets) and theoretical calculation (solid line) of the critical thickness for $CoSi_2$ nucleation on $Si_{1-x}Ge_x$. The theoretical calculation assumes that the surface/interface energy $\delta\sigma$ depends linearly on the Ge concentration x, per Fig. 7.

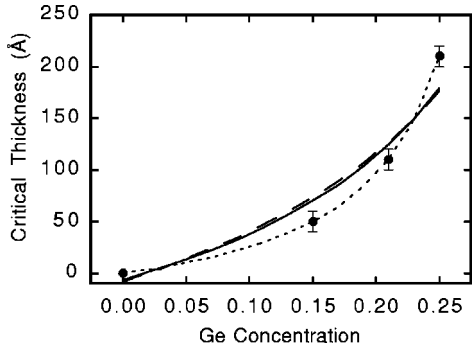

FIG. 9. Comparison of experimental measurements (bullets) and theoretical calculations of the critical thickness for $CoSi_2$ nucleation on $Si_{1-x}Ge_x$. The calculations assume that the number of moles of $Si_{1-x}Ge_x$ involved in the reaction is $m=1/(1-x)+\delta$, where $\delta=0$ (dotted line), $\delta=0.5$ (solid line), $\delta=1.0$ (dashed line).

amount of $Si_{1-x}Ge_x$ involved in the $CoSi \rightarrow CoSi_2$ transition itself (post-transition redistribution of Ge will have no effect on the nucleation of $CoSi_2$). Furthermore, since Ge is also segregated at previous stages of the reaction of Co with SiGe, it is not possible to associate unambiguously Ge-rich precipitates that might be observed with the $CoSi \rightarrow CoSi_2$ transition, even if it is assumed that no Ge redistribution is occurring. Calculations of r_c with $m=1/(1-x)+\delta$, where $\delta=0.0$, 0.5, and 1.0, are shown in Fig. 9. It is seen that all calculations are in qualitative agreement with the experimental results, suggesting that the nucleation model adequately accounts for the major features of the observed thickness effect.

The model presented here is based entirely on classical thermodynamics, and can therefore be applied only to systems in thermal equilibrium. Previous experiments on the Co/SiGe system have shown that the Co film is entirely consumed after annealing in UHV for as little as 5 min, and that the reaction is essentially complete at 700 °C.[12,19] Therefore we do not expect that longer annealing times and/or higher annealing temperatures will affect the reaction products, although they may affect the film morphology. However, short rapid thermal anneals (RTAs) in a gas ambient may affect the reaction products to some extent, due either to the formation of intermediate phases and/or modification of the free surface by the ambient, or to the nonequilibrium nature of the RTA process. For example, Donaton *et al.* have reported that 170-Å-thick Co films deposited on $Si_{0.8}Ge_{0.2}$ convert completely to $CoSi_2$ after a 30 s RTA anneal at 900 °C in a N_2 ambient.[20] However, it should be noted that the thickness of the SiGe film in these experiments was only 350 Å, and therefore at least 70 Å of the Co film reacted directly with the Si(100) substrate. In effect this lowers the Ge concentration of the SiGe film, and therefore reduces the thickness of the film at which complete conversion to $CoSi_2$ is expected (Fig. 4).

V. CONCLUSIONS

Film thickness effects were observed in the $CoSi \rightarrow CoSi_2$ transition for the reaction of Co with epitaxial $Si_{1-x}Ge_x$ layers. The threshold for onset of $CoSi_2$ nucleation was determined in the range $0 \leqslant x \leqslant 0.25$. The nucleation threshold doubled for approximately every 5.5% increase in x. The thickness effect appeared to be independent of the doping of the Si(100) substrate or the strain state of the $Si_{1-x}Ge_x$ film. The reacted layers exhibited distinct morphological features corresponding to polycrystalline CoSi and $CoSi_2$, and (100)-oriented $CoSi_2$. Experiments with sacrificial Si layers deposited between the Co and $Si_{1-x}Ge_x$ films indicated that the thickness effect is driven by the presence of Ge in the reaction zone. The effect can be accounted for qualitatively in terms of the energy cost of Ge segregation which accompanies the formation of CoSi and $CoSi_2$ during the reaction of Co with $Si_{1-x}Ge_x$.

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