

*J. Synchrotron Rad.* (1999), **6**, 521–523

## The effect of germanium on the Co–SiGe thin-film reaction

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Germanium was found to have a strong influence on the path and products of the Co–SiGe reaction, and on the interfacial stability and crystallographic orientation of the silicide film. The segregation of Ge that occurs during the reaction of blanket Co films with SiGe results in thickness effects not present in the reaction of Co with Si. The thickness effect was modelled in terms of the energy cost of Ge segregation, and good agreement with experimental results was obtained. *In situ* EXAFS experiments on sub-monolayer Co films annealed on SiGe substrates indicate a strong preference for the formation of Co–Si bonds at the silicide–SiGe interface. The implications of these results for the stability of the interface and the epitaxial orientation of co-deposited cobalt disilicide (CoSi<sub>2</sub>) films will be discussed.

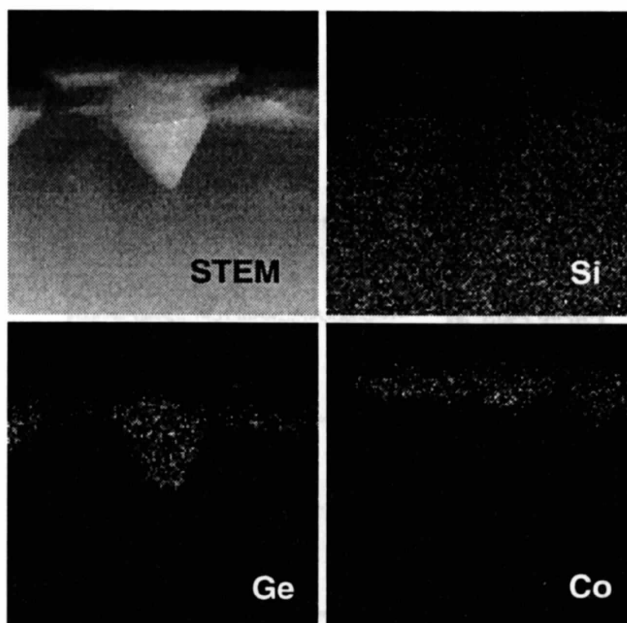
**Keywords:** cobalt silicide, silicon-germanium, thickness effects, interfacial bonding, molecular beam epitaxy

### 1. Introduction

Recently an effort has been made by a number of groups to evaluate the feasibility of cobalt as a contact material for silicon-germanium (SiGe) devices. Studies of the reaction of Co with epitaxial SiGe alloys have shown that blanket Co films on Si<sub>1-x</sub>Ge<sub>x</sub> (x ≤ 0.25) react at annealing temperatures exceeding 700°C to form CoSi, CoSi<sub>2</sub>, and Ge-rich Si<sub>1-z</sub>Ge<sub>z</sub> alloy (z > 0.25). No Co–Ge phases were detected (Wang, Aldrich, Chen, Sayers & Nemanich, 1995). The preferential reaction of Co with Si resulted in Ge segregation and island formation. To gain a better understanding of silicide formation, an investigation of the bulk phase formation and the structure of the silicide–SiGe interface was performed. Full details on sample preparation and data acquisition are provided in the on-line supplement to these proceedings and will not be repeated here.

### 2. Results and Discussion

A TEM cross-sectional micrograph of the silicide–SiGe interface for a 250 Å Co film deposited on 2600 Å of Si<sub>0.79</sub>Ge<sub>0.21</sub> is shown in Fig. 1. The EPMA elemental maps included in the figure indicate the presence of Ge-enriched faceted SiGe grains extending into the Si substrate. The Ge-rich precipitates are undesirable in microelectronic applications, as they enhance the resistivity of the silicide film and may lead to junction spiking.

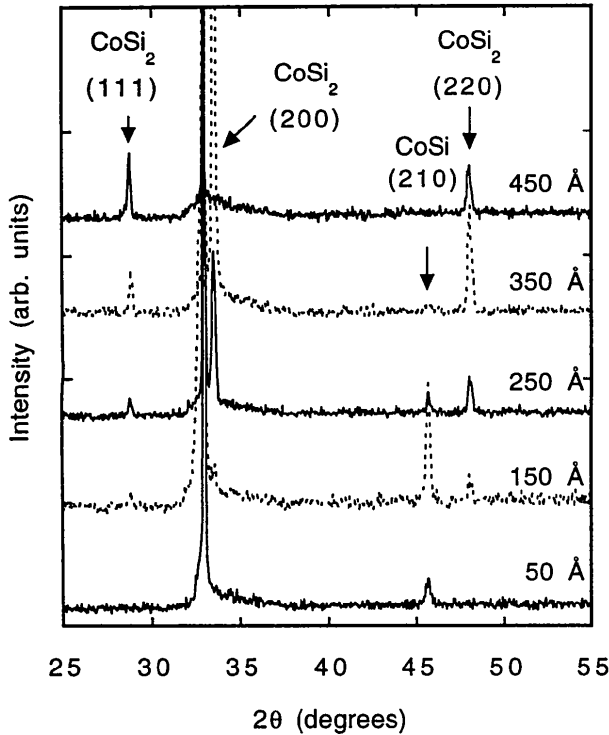


**Figure 1**  
TEM micrograph and elemental maps of a 250 Å Co film annealed on 2600 Å Si<sub>0.79</sub>Ge<sub>0.21</sub> at 800°C for 20 minutes.

XRD scans of a series of Co films annealed for 20 minutes at 800°C on 2600 Å Si<sub>0.79</sub>Ge<sub>0.21</sub> are shown in Fig. 2. The phase content of the films was determined by the presence or absence of the CoSi<sub>2</sub> (111), (200), and (220) peaks, and the CoSi (210) peak. Complete conversion to CoSi<sub>2</sub> 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<sub>2</sub> resulted when the thickness of the Co film was between 150 and 350 Å. This is in sharp contrast to Co films annealed on Si, where the CoSi → CoSi<sub>2</sub> transition occurs at ≈550°C regardless of the thickness of the Co film (Lau, Mayer & Tu, 1978). The only phase observed after the reaction of a 50 Å Co film with Si<sub>0.79</sub>Ge<sub>0.21</sub> was CoSi. The positions of all silicide XRD lines were within 0.05 degrees of those listed in the JCPDS database, indicating that less than 3 percent Ge incorporation had occurred in the CoSi and CoSi<sub>2</sub> phases after annealing at 800°C.

Films 50 Å and thinner were characterised with EXAFS at the Co K-edge. Results are shown in Fig. 3. A qualitative comparison with the reference spectra for bulk CoSi and CoSi<sub>2</sub>, included in Fig. 3 suggests that the predominant phase in these films is CoSi. Quantitative analysis of the EXAFS data did not detect statistically significant Co–Ge bonding.

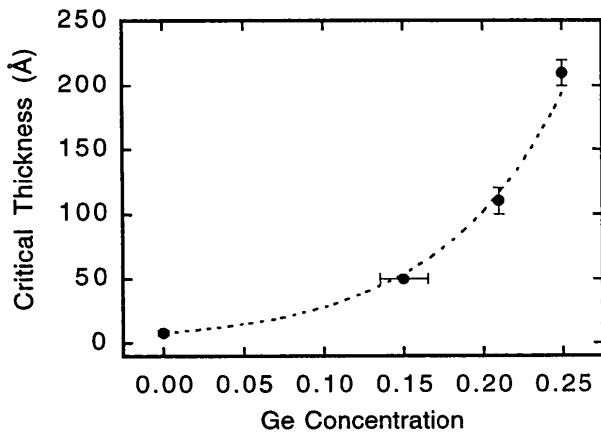
The results in Figs. 2–3 indicate that the onset of CoSi<sub>2</sub> formation depends both on the thickness of the Co film, and on the Ge concentration of the Si<sub>1-x</sub>Ge<sub>x</sub> layer. Further experiments, summarised in Fig. 4, indicated that in the range 0 ≤ x ≤ 0.25 the critical Co thickness for onset of CoSi<sub>2</sub> nucleation increases exponentially, and approximately doubles for every 5.5 percent increase in the Ge concentration. The observed thickness effect may be attributed to the energy cost of Ge segregation. In most solid-state reaction the enthalpy change is at least a few tens of kJ/mole, and entropy effects are a small correction. However, the energy gain from the Co → CoSi<sub>2</sub> transition is only about 7



**Figure 2**

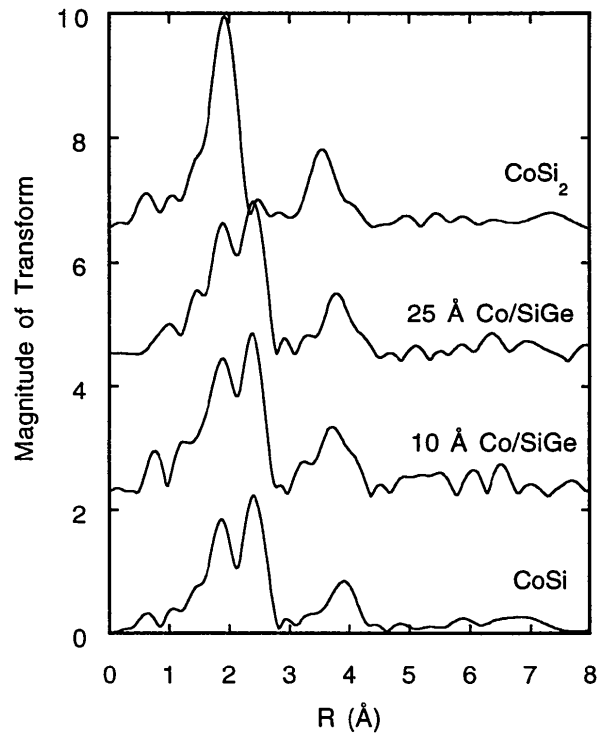
XRD scans of Co films evaporated on 2600-Å-thick  $\text{Si}_{0.79}\text{Ge}_{0.21}$  epitaxial layers and annealed for 20 minutes at 800°C. The thickness of the as-deposited Co film is indicated on each trace. The unlabeled peak at 32.95° is the (200) ghost peak of the Si substrate.

kJ/(mole Co), and the increase in Gibbs energy associated with the redistribution of Ge, -TΔS, can be a significant of the energy gained from the phase transition, thus driving the thickness effect. The thickness effect in the Co-SiGe system has been more fully characterised and complete results have been reported elsewhere (Boyanov, Goeller, Sayers & Nemanich, 1998).



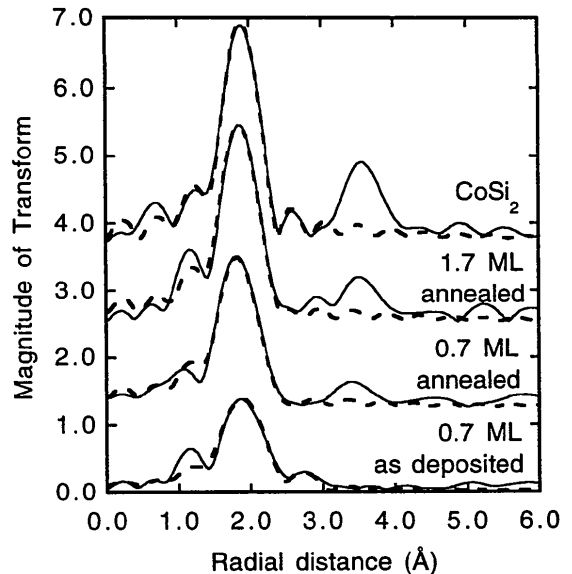
**Figure 4**

Experimentally determined dependence of the critical thickness for onset of  $\text{CoSi}_2$  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 percent increase in  $x$ .



**Figure 3**

Fourier-transformed  $k^2$ -weighted EXAFS spectra of 10 and 25-Å-thick Co films deposited on Si and  $\text{Si}_{0.79}\text{Ge}_{0.21}$ , and annealed for 20 minutes at 800°C. The data was acquired at room temperature at the Co K-edge in fluorescence mode.



**Figure 5**

Fourier-transformed  $k^2$ -weighted EXAFS data (solid line) and fit results (dashed line) for ultra-thin Co films annealed *in situ* on  $\text{Si}_{0.8}\text{Ge}_{0.2}$ . The data was acquired *in situ* in e-yield mode at the Co K-edge. The bottom trace is a reference spectrum for bulk  $\text{CoSi}_2$ . The thickness of the films is indicated in monolayers (ML).

**Table 1**

Structural parameters for the 0.7 monolayer (ML) and 1.7 ML Co/Si<sub>0.79</sub>Ge<sub>0.21</sub> films: edge shift  $E_0$ , coordination number  $N$ , and bond length  $R$ . A single edge shift  $E_0$  was used for all shells in the fits. The Debye-Waller factor for all shells was fixed at  $\sigma^2=0.0020 \text{ \AA}^2$ , as determined from a single-shell Co-Si fit of a similarly prepared 2 ML Co/Si(100) film annealed to 450°C for 10 minutes. The forward transform range is  $\Delta k=3.0-10.1 \text{ \AA}^{-1}$ . The fit range is  $\Delta R=1.0-2.8 \text{ \AA}$  for the annealed films, and  $\Delta R=1.0-3.5 \text{ \AA}$  for the as-deposited sample. The number of independent parameters  $N_{\text{dep}}$  are 11 and 8 for the fits of the as-deposited and annealed films, respectively. The actual number of fitting parameters used are 7 and 5, respectively.

Sample/Shell	$E_0$ (eV)	$N$	$R$ (Å)
0.7 ML, as deposited			
Co-Si	-2.1±2.7	3.5±0.4	2.30±0.03
Co-Ge		1.1±0.5	2.56±0.03
Co-Si		1.1±0.8	3.16±0.07
0.7 ML, annealed			
Co-Si	-0.8±1.8	6.0±0.4	2.30±0.02
Co-Ge		1.1±0.4	2.58±0.03
1.7 ML, annealed			
Co-Si	-2.9±1.9	7.6±0.6	2.30±0.02
Co-Ge		1.0±0.6	2.59±0.03
Bulk CoSi <sub>2</sub>			
Co-Si	-3.0±0.4	8.0±0.3	2.31±0.00

The undesirable thickness effect described above can be avoided by co-deposition of Co and Si in a 1:2 ratio and the use of Si sacrificial layers. However, these techniques do not improve the morphology of the silicide film (Goeller, Boyanov, Sayers & Nemanich, 1997). The cause of this effect was investigated with *in situ* UHV EXAFS experiments on ultra-thin Co layers deposited on Si<sub>0.8</sub>Ge<sub>0.2</sub>. Results for 0.7 and 1.7 monolayer-thick films are shown in Fig. 5, before and after annealing for 10 minutes at 450°C. Multi-shell fits to this data, summarized in Table 1, indicate that the Si:Ge ratio in the first shell of Co is ≈3.5:1 in the unannealed 0.7 ML film. This is roughly equal to the Si:Ge ratio of the Si<sub>0.8</sub>Ge<sub>0.2</sub> substrate. However, the Si:Ge ratio for all annealed films exceeded 6:1, indicating that the preference for Co-Si bonding observed in the bulk silicide (Figs. 2-3) persists at the silicide-SiGe interface (Boyanov, Goeller, Sayers & Nemanich, 1997).

The preference for Co-Si bonding, both in the bulk and at the interface, is thermodynamically driven. The large difference between the enthalpies of formation of CoSi<sub>2</sub> (-99 kJ/mole) and CoGe<sub>2</sub> (-36 kJ/mole) dictates that creation of Co-Si bonds at the expense of Co-Ge bonds is energetically favorable (Aldrich, d'Heurle, Sayers & Nemanich, 1996). The preference for Co-Si bonding has significant consequences for the interfacial stability of CoSi<sub>2</sub> films grown on SiGe, since it implies that any interaction between the metal film and the SiGe substrate must be avoided. In addition, typical methods for growth of epitaxial CoSi<sub>2</sub> on Si(001) require interaction between the silicide and the substrate, either because a template layer (Tung, 1992) or a Co-rich deposition stoichiometry was used (Himenez, Hsiung, Rajan, Schowalter, Hashimoto, Thompson & Iyer, 1990). The preference for Co-Si bonding then suggests that the methods used to grow epitaxial CoSi<sub>2</sub>/Si(100) will fail in the Co-Si-Ge system.

This work was supported by DOE under grant DE-FG05-93ER79236 and DE-FG-05-89ER45384 (D.E.S.), and by NSF under grant DMR-9633547 (R.J.N.). Research was carried out in part at beamline X-11 at the National Synchrotron Light Source (NSLS). The NSLS is supported by DOE, Division of Materials Science and Division of Chemical Science.

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(Received 10 August 1998; accepted 4 January 1999)