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## Preferential Co-Si bonding at the Co/SiGe(100) interface

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The initial stages of the reaction of Co with  $Si_{0.79}Ge_{0.21}(100)$  were studied *in situ* with extended x-ray absorption fine structure spectroscopy and reflection high energy electron diffraction. The Si:Ge ratio in the first coordination shell of Co in sub-monolayer Co films was found to increase with film thickness and annealing temperature, indicating preferential formation of Co–Si bonds. The impact of the observed preference for Co–Si bonding on the morphology of epitaxial  $CoSi_2/Si_{1-x}Ge_x$  heterostructures is discussed. © *1997 American Institute of Physics*. [S0003-6951(97)00247-7]

Due to its low resistivity and good thermal stability, cobalt disilicide (CoSi<sub>2</sub>) is considered an attractive contact material for submicron Si devices. Since CoSi2 and Si have similar crystal structures and are closely lattice-matched, it is possible to achieve epitaxial growth of  $CoSi_2$  on both Si(100)and Si(111) substrates.<sup>1,2</sup> However, in order to achieve single-crystal growth on Si(100), the nucleation of CoSi<sub>2</sub> at the Co/Si interface must be carefully controlled through the use of CoSi<sub>2</sub> templates layers.<sup>1-3</sup> The studies indicate that at <2 monolayer (ML) coverage, as-deposited Co/Si(100) exhibits a 2×1 reconstruction and occupies surface sites with twofold symmetry and sevenfold Co-Si coordination, as shown in Fig. 1.<sup>4</sup> In single-crystal CoSi<sub>2</sub>/Si(100) films, the Co atoms at the interface exhibit sixfold coordination with twofold symmetry, and occupy sites that would normally be occupied by Si atoms if the Si(100) lattice is extended across the interface.<sup>5,6</sup> Evidence for additional displacement<sup>7</sup> and compositional<sup>8</sup> modulation at the interface has also been found.

In comparison with the Co/Si(100) system, results for the Co/Si<sub>1-x</sub>Ge<sub>x</sub>(100) system are few and incomplete. The reaction of Co with (100)-oriented epitaxial Si<sub>1-x</sub>Ge<sub>x</sub> films has been shown to lead to formation of pure CoSi<sub>2</sub>, accompanied by complete Ge segregation.<sup>9</sup> Attempts to suppress Ge segregation through co-deposition of co and Si resulted in faceted epitaxial CoSi<sub>2</sub> islands.<sup>10</sup> The structure of the CoSi<sub>2</sub>/Si<sub>1-x</sub>Ge<sub>x</sub>(100) interface has not been determined. The experiments reported in this letter were performed in order to gain an understanding of the initial stage of the reaction of Co with Si<sub>1-x</sub>Ge<sub>x</sub>, and its effect on the nucleation and morphology of CoSi<sub>2</sub> template layers.

The samples used in this work consisted of approximately 0.7 and 1.7 ML of Co deposited at room temperature on 800-Å-thick strained epitaxial  $Si_{0.79}Ge_{0.21}$  films grown at 550 ° on *p*-type Si(100) substrates. Atomically clean surfaces were prepared by spin-etching the Si(100) substrates with a 1:1:10 HF:H<sub>2</sub>O:ethanol solution, followed by *in situ* thermal desorption at 900 °C, and deposition of a 200-Åthick homoepitaxial Si buffer layer at 550 °C. Cobalt coverage was confirmed *ex situ* (with an estimated accuracy of  $\pm 0.2$  ML) by Rutherford backscattering (RBS). Extended x-ray absorption fine structure (EXAFS) data were collected in situ at the Co K edge (7709 eV) in total electron yield mode at beamline X-11A at the National Synchrotron Light source (NSLS). Data was collected both from as-deposited films, and after annealing at 450 °C for 10 minutes. The acquisition time for each sample was 6-8 h at 3  $\times 10^{-10}$  Torr. Surface contamination was monitored periodically with reflection high energy electron diffraction (RHEED). No change in the RHEED patterns was observed during the EXAFS measurements. Approximately 20 EXAFS scans were acquired for each sample at an incidence angle of  $75^{\circ}\pm3^{\circ}$  with respect to the sample surface. Data were acquired in two or three orientations within 3° of each other. Regions from each orientation free from Bragg reflections (glitches) were merged to produce a single data set that was used for further processing. Structural parameters were determined from nonlinear fits with ab initio standards.<sup>11</sup> Confidence limits for the fit parameters were estimated as the deviations of the parameters from their best-fit values which increase the fit residue by 25% when all other parameters are floated.

The freshly prepared Si<sub>0.79</sub>Ge<sub>0.21</sub> films exhibited a sharp 2×8 RHEED pattern. Immediately after Co deposition was initiated a 2×1 RHEED pattern was observed. After annealing for 10 min at 450 °C, a  $(3\sqrt{2} \times \sqrt{2})$  surface diffraction pattern identical to that reported by Stalder *et al.*<sup>12</sup> for the



FIG. 1. Surface adsorption site for Co/Si(100), as proposed by Meyerheim *et al.* (Ref. 4). The open dashed circles correspond to Si atoms at 2.35 Å, and the hatched circles correspond to Si atoms at 2.72 Å. The adsorption site for Co/Si<sub>0.79</sub>Ge<sub>0.21</sub>/Si(100) is shifted from that position by 0.2–0.4 Å, resulting in the relaxation of the Co–Si and Co–Ge bonds to their natural length, and the appearance of a long (3.16 Å) Co–Si(Ge) bond.

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FIG. 2. Normalized and  $k^2$ -weighted EXAFS data for the samples used in this study. The top trace is the data for a 730-Å-thick  $CoSi_2/Si(100)$  film.

CoSi<sub>2</sub> Si-rich surface was observed for both the 0.7 and 1.7 ML samples. The corresponding EXAFS data are shown in Figs. 2 and 3. Data for a 730-Å-thick  $CoSi_2/Si(100)$  film is also included in these figures for comparison. Numerical results for multi-shell fits to the EXAFS data are given in Table I. The results for the as-deposited 0.7 ML film indicate a first shell consisting of approximately 4:1 Si and Ge atoms at distances similar to the natural Co–Si and Co–Ge bond lengths (2.32 and 2.50 Å, respectively). The presence of a higher shell (perhaps mixed with Ge) may be interpreted as a Ge-induced average displacement of the Co atoms from the Si(100) adsorption site in Fig. 1 by 0.4–0.6 Å, resulting in



FIG. 3. Fourier-transformed  $k^2$ -weighted EXAFS data (solid line) and fit results (dashed line) for the samples used in this study. The top trace is the data for a 730-Å-thick  $\text{CoSi}_2/\text{Si}(100)$  film. The transform range is  $\Delta k = 3.0-10.1$  Å<sup>-1</sup>.

TABLE I. Structural parameters for the 0.7 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 Å<sup>2</sup>, as determined from a single-shell Co–Si fit of a similarly prepared 1.7 ML Co/Si(100) films, annealed to 450 °C for 10 min. The forward transform range is  $\Delta k$ =3.0–10.1 Å<sup>-1</sup>. The fit range is  $\Delta R$ =1.0–2.8 Å for the annealed films, and  $\Delta R$ =1.0–3.5 Å for the as-deposited sample. The number of independent parameters are 11 and eight for the fits of the as-deposited and annealed films, respectively. The actual number of fitting parameters used are seven and five, respectively.

Sample/Shell	$E_0$ (eV)	Ν	<i>R</i> (Å)
0.7 ML, as-deposited			
Co-Si	$-2.1 \pm 2.7$	$3.5 \pm 0.4$	$2.30 \pm 0.03$
Co-Ge		$1.1 \pm 0.5$	$2.56 \pm 0.03$
Co–Si		$1.1\pm0.8$	$3.16\pm0.07$
0.7 ML, annealed			
Co-Si	$0.8 \pm 1.8$	$6.0 \pm 0.4$	$2.30 \pm 0.02$
Co–Ge		$1.1~\pm~0.4$	$2.58\pm0.03$
1.7 ML, annealed			
Co-Si	$-2.9 \pm 1.9$	$7.6 \pm 0.6$	$2.30 \pm 0.02$
Co–Ge		$1.0\pm0.6$	$2.59\pm0.05$
730 Å CoSi <sub>2</sub>			
Co–Si	$-3.0\pm0.4$	8.0 ± 0.3	$2.31\pm0.00$

the relaxation of the nearest-neighbor distances and the appearance of a Co-(Si,Ge) shell at ≈3.16 Å. It should be noted that the first-shell Si:Ge ratio of the as-deposited films is similar to the stoichiometry of the  $Si_{0.79}Ge_{0.21}$  substrate. Annealing of the 0.7 ML film at 450 °C for 10 min resulted in the formation of a structure similar to that of CoSi<sub>2</sub> (Fig. 3), with sixfold Co-Si coordination in the first shell. The transition to a CoSi<sub>2</sub>-like structure is accompanied by an increase of the Si:Ge ratio in the first shell to approximately 6:1. The sixfold Si coordination of the Co atoms at the Co/ SiGe interface is identical to that of Co atoms at the CoSi<sub>2</sub>/Si(100) interface.<sup>5,6</sup> The average Co–Si coordination in the 1.7 ML annealed films is  $7.6\pm0.6$ , which is similar to the eightfold coordination of Co in bulk CoSi<sub>2</sub>. The Si:Ge ratio in the first shell of the annealed 1.7 ML film is approximately 8:1.

The increase in the Si:Ge ratio in the first coordination shell of the annealed films indicates a preference for the formation of Co-Si bonds. Such preference may be explained in terms of a thermodynamic model previously developed by Aldrich *et al.*<sup>13</sup> The large difference between the enthalpies of formation of CoSi2 (-99 kJ/mole) and CoGe2 (-36 kJ/ mole) dictates that creation of Co-Si bonds at the expense of Co-Ge bonds is energetically favorable, resulting in CoSi<sub>2</sub> formation and Ge segregation. The preference for Co-Si bonding has significant consequences for the control of misoriented grains in  $CoSi_2$  films grown on (100)-oriented  $Si_{1-x}Ge_x$  substrates, since it implies that interaction between the metal layer and the SiGe substrate should be avoided. If Ge is uniformly distributed on the Sige surface, as indicated by the EXAFS results for the as-deposited 0.7 ML film, the preference for Co-Si bonding will result in Ge enrichment of portions of the Co/SiGe interface, and islanding of the CoSi2 template. Assuming sixfold coordination in the first ML, eightfold coordination in the second ML, and Si-rich surface termination, the average Co-Si coordination of a 1.7 ML  $CoSi_2$  film should be no greater than 7.0. The experimentally observed Co–Si coordination for the 1.7 ML film is 7.6±0.6, suggesting that islanding is indeed occurring.

In conclusion, we have studied the initial stages of the reaction of Co with  $Si_{0.79}Ge_{0.21}$ . At room temperature Co is adsorbed at displaced surface sites, resulting in approximately stoichiometric Si:Ge ratio in the first coordination shell, and the appearance of long (3.16 Å) Co–Si(Ge) bonds. The Si:Ge ratio in the first coordination shell of Co in the annealed films has been found to increase rapidly with film thickness, to 6:1 in 0.7 ML films and 8:1 in 1.7 ML films, indicating preferential formation of Co–Si bonds.

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