Strain in epitaxial $CoSi_2$ films on Si (111) and inference for pseudomorphic growth

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The perpendicular x-ray strain of epitaxial $CoSi_2$ films grown on Si(111) substrates at ~600 °C was measured at temperatures from 24 up to 650 °C. At 600 °C, the perpendicular x-ray strain is −0.86%, which is about the x-ray strain that a stress-free $CoSi_2$ film on Si(111) would have at that temperature. This result shows that the stress in the epitaxial $CoSi_2$ film is fully relaxed at the growth temperature. Strains in the film below the growth temperature are induced by the difference in the thermal expansion coefficient of $CoSi_2$ and Si, $\alpha_f - \alpha_s = 0.65 \times 10^{-5}$/°C. Within experimental error margins, the strain increases linearly with decreasing temperature at a rate of $(1.3 \pm 0.1) \times 10^{-5}$/C. The slope of the strain-temperature dependence, obtained by assuming that the density of misfit dislocations formed at the growth temperature remains unchanged, agrees with the measured slope if the unknown Poisson ratio of $CoSi_2$ is assumed to be $\nu_f = 1/3$. These observations support three rules postulated for epitaxial growth.

Much is now known about the epitaxial growth of $CoSi_2$ films on Si(111) single crystalline substrates because of numerous recent investigations.[1–3] $CoSi_2$ has a CaF_2 structure. At room temperature, the cubic unit cell of $CoSi_2$ has a lattice constant of a_f (24 °C) = 0.537 nm, as opposed to a_s (24 °C) = 0.543 nm for Si. The lattice mismatch

$$f(T) \equiv [a_f(T) - a_s(T)]/a_s(T) \tag{1}$$

is −1.23% at room temperature. $CoSi_2$ films grown on Si(111) are *B* type, i.e., rotated crystallographically by 180° about their [111] axis with respect to the Si substrate.[4] The critical thickness t_{cr} for pseudomorphic growth is ~3 nm.[5]

We report here a measurement of the perpendicular strain on epitaxial $CoSi_2$ films with a thickness t_f of ~ 100 nm (which is much thicker than t_{cr}). The films were formed by codeposition of Co and Si in an ultrahigh vacuum of $\sim 10^{-10}$ Torr base pressure on substrates held either near 600 °C or at room temperture followed by *in situ* annealing. Details of the process are described elsewhere.[6] The surfaces of the substrates were offset from the (111) planes of the Si lattice towards the $[1\bar{1}0]$ direction by offset angles ϕ_s ranging from 0° to 16°.

The strain was measured by x-ray double-crystal diffractometry (rocking curve) with Fe $K_{\alpha 1}$ radiation (0.1936 nm wavelength) diffracted from the (111) planes of high quality Si(111) monochromating crystal. The sample was mounted in air on a heating stage capable of reaching 650 °C.[7] The perpendicular x-ray strain

$$\epsilon^{\perp}(T) \equiv [d_f^{\perp}(T) - d_s^{\perp}(T)]/d_s^{\perp}(T) \tag{2}$$

was extracted from the difference in the positions of symmetrical (111) diffraction peaks of the rocking curve, where $d^{\perp}(T)$ is the interplanar spacing of the (111) diffraction planes at temperature *T*. The parallel x-ray strain $\epsilon^{\parallel}$ defined analogously to $\epsilon^{\perp}$, is related to the lattice mismatch *f* and the perpendicular x-ray strain $\epsilon^{\perp}$,

$$\epsilon^{\perp} = \left(\frac{1+v_f}{1-v_f}\right) f - \left(\frac{2v_f}{1-v_f}\right) \epsilon^{\parallel}, \tag{3}$$

where v_f is the Poisson ratio.

The measured perpendicular x-ray strain at room temperature is $\epsilon^{\perp}(24\,°C) = -1.66 \pm 0.01\%$. That x-ray strain is between that of a fully relaxed film for which $\epsilon^{\perp}_{relaxed}(24\,°C) = f(24\,°C) = -1.23\%$, and that of a pseudomorphic film for which $\epsilon^{\perp}_{coherent}(24\,°C) = -2.46\%$, obtained from Eq. (3) with the parallel x-ray strain $\epsilon^{\parallel} = 0$ and the Poisson ratio $v_f = 1/3$. This value is typical of all thick films ($t_f > t_{cr}$) that we have analyzed, regardless of thickness (from 10 to 250 nm) and offset angle ϕ_s.[8,9] Thus the thick $CoSi_2$ films ($t_f > t_{cr}$) are elastically strained at room temperature with a common perpendicular elastic strain $e^{\perp}$ of $e^{\perp}(24\,°C) \approx \epsilon^{\perp}(24\,°C) - f(24\,°C) = -0.43\%$.

Measurements of the perpendicular x-ray strain at elevated temperatures provide a clue as to why $\epsilon^{\perp}(24\,°C)$ is always nearly −1.66%. Figure 1 shows two sets of experimental data (● and △) for two samples that have slightly different perpendicular x-ray strains at room temperature. As the temperature rises, the x-ray strain decreases because $CoSi_2$ expands faster than Si does upon heating. The slopes are $(1.3 \pm 0.1) \times 10^{-5}$/°C, twice as large as the difference of the bulk thermal expansion coefficients[10] between $CoSi_2$ ($\alpha_f = 0.94 \times 10^{-5}$/°C) and Si ($\alpha_s = 0.29 \times 10^{-5}$/°C), $\alpha_f - \alpha_s = 0.65 \times 10^{-5}$/°C. All strain values remain reversible after ~2 h annealing in air up to 490 °C.

This temperature dependence can be explained if it is assumed that the lateral change in the $CoSi_2$ lattice is constrained to follow that of the Si substrate. The slope of the perpendicular x-ray strain versus temperature is then given by

$$\frac{\delta \epsilon^{\perp}_{constrained}}{\delta T} = \left(\frac{1+\nu_f}{1-\nu_f}\right)(\alpha_f - \alpha_s). \tag{4}$$

We were unable to find the Poisson ratio ν_f of $CoSi_2$ in literature, but if we assume that $\nu_f = 1/3$, the model predicts a slope of 1.3×10^{-5}/°C. This is a good agreement with the measured $(1.3 \pm 0.1) \times 10^{-5}$/°C, considering the simplification of the model and the experimental uncertainty. We

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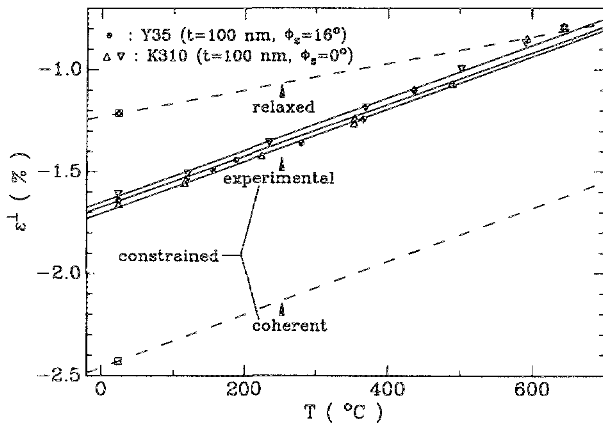

FIG. 1. Perpendicular x-ray strain $\epsilon^\perp$ as a function of sample temperature T for two 100-nm-thick $CoSi_2$ films on (i) a Si substrate whose surface is offset from the [111] direction by 16° towards the [$1\bar{1}0$] direction of the substrate (⊛) and (ii) a Si substrate whose surface is aligned with the (111) planes (△▽). All strain values are reversible below 490 °C. When the latter sample was heated above that temperature to 650 °C and then cooled, a reduced strain was measured (▽), again reversible below 500 °C. The solid lines are linear fits to the data (omitting the two highest temperature points). The strain for a coherent interface is calculated with the Poisson ratio $\nu_f = 1/3$ (lower dashed line). At the temperature at which the samples were grown (~600 °C), the measured strain is that predicted for an elastically relaxed film (upper dashed line).

thus conclude that no new misfit dislocations are created by thermal cycling in air up to 490 °C.

Figure 1 also contains the predicted perpendicular x-ray strains versus temperature for a fully relaxed (stress-free) film labeled "relaxed" and a pseudomorphic film labeled "coherent." At 24 °C, these lines have the known values of -1.23% [from Eq. (3) with $\epsilon^{\parallel} = f$, full square] and -2.46% [from Eq. (3) with $\epsilon^{\parallel} = 0$, open square]. The slope for the fully relaxed film is given by

$$\frac{\delta\epsilon^{\perp}_{\text{relaxed}}}{\delta T} = \frac{\delta f(T)}{\delta T} = (\alpha_f - \alpha_s), \qquad (5)$$

while that for the coherent film is given by Eq. (4). The line for the fully relaxed film intercepts the experimental curves near 600 °C, which is the nominal growth temperature of the films. Within the uncertainties of the experimental data, the epitaxial $CoSi_2$ films grow elastically unstrained at the temperature of their formation. In addition to the observation that no new misfit dislocations are generated upon subsequent cooling of the sample, this explains the common value of strains observed at room temperature for all thick films ($t_f > t_{cr}$). The observed elastic strains originate after the films are formed and are the consequence of the dissimilar thermal contraction of the film and substrate upon cooling.

As a corollary of the above discussion, one can obtain the parallel x-ray strain of the $CoSi_2$ films at room temperature in two ways. For a rigid interface, the parallel x-ray strain at room temperature must be the same as that at the growth temperature. At the growth temperature, the $CoSi_2$ film is fully relaxed, and hence cubic. The parallel x-ray strain $\epsilon^{\parallel}$ at the growth temperature thus equals the perpendicular x-ray strain $\epsilon^{\perp}$ at that temperature. Therefore,

$$\epsilon^{\parallel}(24\,^\circ\text{C}) = \epsilon^{\parallel}(600\,^\circ\text{C}) = \epsilon^{\perp}(600\,^\circ\text{C}) = -0.86\%, \qquad (6)$$

where the numerical value is obtained from Fig. 1. On the other hand, $\epsilon^{\parallel}$ can be obtained from Eq. (3). With $\epsilon^{\perp}(24\,^\circ\text{C}) = -1.66\%$, $f(24\,^\circ\text{C}) = -1.23\%$, and $\nu_f = 1/3$, one finds $\epsilon^{\parallel}(24\,^\circ\text{C}) = -0.80\%$. This consistency supports the notion that the interface does not shear and the parallel strain is independent of temperature with zero elastic strain at the growth temperature. The estimated misfit dislocation density $(b/\epsilon^{\parallel})^2 \sim 10^{11}/\text{cm}^2$ (**b** is the Burgers vector) from the parallel x-ray strain $\epsilon^{\parallel}$ agrees well with the result obtained from the plan-view transmission electron micrograph of the samples produced by the same deposition process, where a misfit dislocation network of an average spacing of ~30 nm is observed,[6,11] giving an areal density of $\sim 10^{11}/\text{cm}^2$.

Furthermore, sample K310 was raised to 600 °C and subsequently to 650 °C in air and rocking curves were measured *in situ*. The perpendicular x-ray strains derived from these measurements indicate that the sample is fully relaxed at these temperatures (Fig. 1). Cooling this sample to room temperature now yields a slightly reduced perpendicular x-ray strain (-1.61% instead of -1.66%). Reheating the sample in air then traces a new line for the perpendicular x-ray strain versus temperature (points marked ▽). That line has the same slope as that measured initially (points marked △). This new curve is reproducible up to 550 °C. This result shows that maintaining the sample in air near or above 600 °C for a sufficient length of time (~3 h) modifies the elastic strain in the film. The x-ray rocking curve of this modified sample (point ▽ in Fig. 1) is shown in Fig. 2 (dotted line). One sees that the interaction of the sample with air at ~650 °C has reduced the perpendicular x-ray strain and has broadened the diffraction peak from the film when compared with the rocking curve of the as-grown sample (solid line). We conclude, therefore, that even though the interface does not shear at temperature below ~600 °C (the growth temperature) in air, the interfacial registry and the film quality are altered by annealing above ~600 °C in air.

As an additional experiment, a piece of the same sample K310 was thermally annealed in vacuum at 700 °C for 40 min. The rocking curve of the sample was then remeasured at room temperature (solid line in Fig. 2). The vacuum treatment produces no detectable change. This indicates that the strain state of an epitaxial $CoSi_2$ film is not altered by an annealing at a temperature higher than $CoSi_2$ formation temperature in vacuum. The change after annealing in air at a temperature above ~600 °C then must be the result of reaction of the epitaxial film with the ambient. All three samples of as-grown, vacuum-annealed, and air-annealed were also analyzed by 2 MeV ^{4}He backscattering and channeling. No significant differences are noted. The minimum yield of 3.2% for the axial [111] channeling indicates very good epitaxy. A clear step in the channeling spectrum corresponding to the $CoSi_2$/Si interface further confirms the presence of misfit dislocation there.

The findings reported here have interesting implications that may have very general validity. We note that for an epitaxial GaAs film grown on a Si(100) substrate, findings like ours have recently been reported.[12] There too, the strain observed at room temperature is explainable in terms of the differential thermal contraction of the film and substrate

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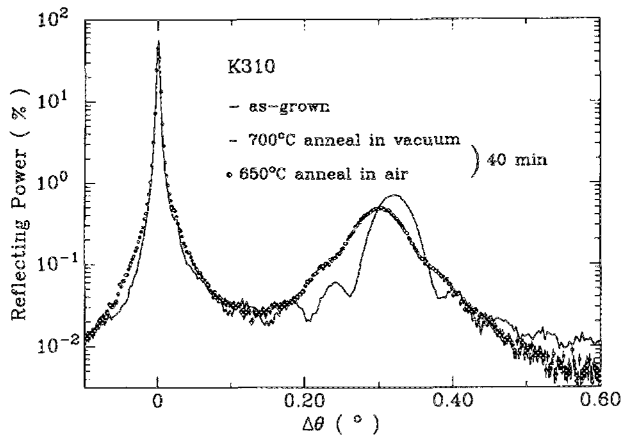

FIG. 2. Three x-ray rocking curves diffracted from symmetrical (111) planes measured at room temperature correspond to sample K310 of as-grown, vacuum-annealed, and air-annealed. The one of the as-grown sample is indistinguishable from that measured after annealing in vacuum at 700 °C for 40 min (solid line). Annealing in air at 650 °C induces an irreversible reduction of the strain in the epitaxial $CoSi_2$ film as indicated by the shift of the peak and broadens the diffraction peak (dotted line).

upon cooling after the epitaxial structure was created at elevated temperature. When two such dissimilar systems behave so similarly, the observation may apply to a large class of epitaxial systems. Generalizing accordingly, we extract the following rules: (1) *Differential thermal expansion does not introduce new misfit dislocations in epitaxial structures such as $CoSi_2$ films on Si(111), even when the film is thicker than the critical thickness. This statement probably applies to all systems where nonionic bonding dominates.* (2) *For pseudomorphic growth in such systems, it is important to minimize the lattice mismatch at the growth temperature.* The importance of a lattice match at the growth temperature for pseudomorphic growth has already been pointed out in the literature.[13,14]

We further note that when an epitaxial $CoSi_2$ film is exposed to a reactive medium (air), irreversible changes take place in the strain state of the film that do not arise in the absence of a reaction. Similar effects have been reported for different systems. A polycrystalline film of Pd_2Si on an epitaxial Pd_2Si film raised to 275 °C in vacuum is stable. The same film undergoes an epitaxial reordering when additional polycrystalline Pd_2Si is formed by a reaction with an overlaid Pd film.[15] The disordering of III-V heterostructures by impurity diffusion is another example where a defect-generating process (here group II lattice vacancies generated by the diffusion of an impurity) destabilizes a structure that is quite (meta)stable in the absence of this process.[16] Yet another example is the epitaxial arrangement of a polycrystalline Ge film on a Si single-crystal substrate induced by thermal annealing in oxygen.[17] The feature common to all these examples is the presence of a defect-generating process (diffusion, reaction, and irradiation). The defects destabilize a metastable state. We are thus led to conclude that (3) *to favor pseudomorphic growth, processes that induce atomic rearrangement should be minimized.*

Procedures advocated in the literature are consistent with that rule. One successful procedure consists of first growing a very thin ($t < t_{cr}$) epitaxial film by solid phase epitaxy followed by codeposition of a thick layer ($t > t_{cr}$) at low temperature and subsequently inducing epitaxial rearrangement of the full layer at elevated temperature.[18] This template procedure minimizes atomic rearrangements. One also understands why codeposition of a compound in the correct atomic ratio is more likely to result in a pseudomorphic structure than its formation by solid phase reaction if the epitaxial film is strained at the formation temperature, or why deposition at low temperature followed by high-temperature annealing is more likely to result in a pseudomorphic structure than deposition at high temperature.[19]

The three rules for pseudomorphic growth enunciated here are in the nature of guidelines, as is evident from the way they are deduced.

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