

# Study of CoSi<sub>2</sub>/Si strained layers grown by molecular beam epitaxy

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In this paper, we report a study of the strain and its relaxation of epitaxial CoSi<sub>2</sub> grown on Si by molecular beam epitaxy (MBE). The strain is measured by a x-ray rocking curve technique and misfit dislocations are determined by transmission electron microscopy (TEM) as the strain relaxes. Results show that the critical thickness of pseudomorphic growth is about 30 nm for growth temperature of 550 °C although there is still a residual strain remained for the thicker films. No apparent complete relaxation of the strain is obtained. Thermal annealing of CoSi<sub>2</sub> films is performed and the results of the strain relaxation are discussed.

## I. INTRODUCTION

Epitaxial silicides on Si such as CoSi<sub>2</sub> have attracted much attention due to their high quality metallic properties. Single crystal growth of CoSi<sub>2</sub> epilayers onto Si has been achieved by deposition and/or reaction under ultrahigh vacuum (UHV) conditions.<sup>1,2</sup> However, as the thickness of the silicide epilayer increases, the strain energy stored in the film due to the lattice mismatch,  $\Delta a = -1.2\%$ , between CoSi<sub>2</sub> and Si, causes generation of misfit dislocations to relieve the interfacial stress.<sup>3</sup> These dislocations seriously degrade the quality of this heterostructure. Therefore, pseudomorphic growth of strained CoSi<sub>2</sub> epilayers when the lattice mismatch is entirely accommodated by elastic strains is important for application of this heterostructure. It is well recognized that the thickness of the epilayer has to be kept below a characteristic critical thickness in order to accomplish pseudomorphic growth.<sup>4</sup> Thus it is desirable to establish the pseudomorphic growth conditions and determination of the critical thickness. Moreover, the stability of the epitaxial strained layers during postgrowth thermal processing is of interest in device application, where temperature cycling is often used.

In this paper, the results of the critical thickness determination and strain relaxation on thermal treatment for CoSi<sub>2</sub> epitaxial layers are presented. Rutherford backscattering (RBS) using 2-MeV helium ions is employed to determine the Co distribution and CoSi<sub>2</sub> stoichiometry. The epitaxial strains were measured using x-ray rocking curves for as-grown and annealed samples having various thicknesses ranging from 20 to 100 nm. Planar view transmission electron microscopy (TEM) is used to determine the dislocation and pinhole densities. It is found that commensurate layers can be grown if the thickness is < 30 nm and the commensurate-to-incommensurate transition occurs for thickness between 30–50 nm. Some residual strains are still present even for thick films of 100 nm, possibly due to the presence of pinholes. The possible correlation of the pinhole formation to the strain relaxation is discussed.

## II. EXPERIMENT

In this study, (111) Si was used as a substrate for epitaxial silicide growth. Prior to the introduction of the sample to the vacuum system, the surface was prepared with a variation of the standard RCA procedure to chemically preclean the Si substrate. The procedure involved a series of repeated oxidation and etching of the substrate surface followed by the growth of a protective oxide layer. The repeated etching process insured that the carbon content at the final oxide-Si interface was minimized. A flash temperature to 900 °C removed the oxide and yielded an atomically clean surface for epitaxial growth. No C and O signals were detected by Auger electron spectroscopy (AES). All depositions were carried out in a metal-sealed UHV chamber with a base pressure of  $1 \times 10^{-10}$  Torr and a growth pressure of  $2 \times 10^{-9}$  Torr. Silicide layers were grown by codepositing Co and Si (MBE) with the substrate held at temperature around 550 °C. The Si and Co deposition rates were measured and stabilized by a feedback control using two Inficon thickness monitors. The deposition rates were 0.18 nm/s and 0.05 nm/s for Si and Co, respectively, for maintaining a Si/Co flux ratio of about two and the stabilities of Si and Co deposition rates were ~3% and ~6%, respectively. The thickness of the CoSi<sub>2</sub> epilayers used in this study ranged from 20 to 100 nm. Thermal treatment for the grown films was performed at 750, 850, and 1000 °C under two conditions, either a vacuum of  $2 \times 10^{-7}$  Torr or N<sub>2</sub> ambient.

Lattice deformation and relaxation for as-grown and annealed samples were studied by x-ray rocking curves, RBS channeling, and TEM. In the x-ray rocking curve technique, a collimated FeK $\alpha$ 1 x-ray beam was rendered nearly monochromatically by a (100) GaAs first crystal. Samples were analyzed using the (111) symmetric reflection to measure the perpendicular strains while the (331) asymmetric reflection was used for the parallel strain measurements. The silicide lattice spacings both parallel and normal to the interface were thus determined from the measured strains. RBS was routinely used to check the film thicknesses and composi-

tions. Additionally, the Co concentration profile and CoSi<sub>2</sub> stoichiometry after thermal treatment at various temperatures were also measured from the Co peak of RBS spectra. The channeling technique was used mainly to confirm the crystallinity of the samples, and the dechanneling of the aligned Co peak was used to study the interfacial quality. TEM was used to determine misfit dislocation networks and for estimating the pinhole density. All the planar view micrographs were taken with the [220] bright field image.

### III. EXPERIMENTAL RESULTS

It is convenient to define the "x-ray perpendicular strain,"  $\epsilon^\perp = (a_{\text{epi}}^\perp - a_{\text{sub}}^\perp)/a_{\text{sub}}^\perp$ , and "x-ray parallel strain,"  $\epsilon^\parallel = (a_{\text{epi}}^\parallel - a_{\text{sub}}^\parallel)/a_{\text{sub}}^\parallel$ , of an epitaxial film with respect to the substrate, since these are determined directly from the rocking curve.<sup>5</sup> For cubic crystals such as Co and Si, layers grown along  $\langle 111 \rangle$  direction, the x-ray strains,  $\epsilon^\perp$  and  $\epsilon^\parallel$ , are the fractional differences in the interatomic spacings between the film and the substrate. It is a simple matter to convert the x-ray strain defined relative to the substrate to the strain from elasticity theory defined relative to the free lattice of the epilayers.

Figure 1 shows the x-ray rocking curves measured on a 40-nm thick CoSi<sub>2</sub>/Si sample. The Bragg angle separation of the CoSi<sub>2</sub> and substrate Si peaks ( $P_{\text{CoSi}_2}$  and  $P_{\text{Si}}$ ),  $\Delta\theta_B$ , is a direct measure of the strain of the CoSi<sub>2</sub> film with respect to the substrate, and is given by

$$-\Delta\theta_B = K_1 \langle \epsilon^\perp \rangle + K_2 \langle \epsilon^\parallel \rangle,$$

$$K_1 = \cos^2 \Psi \tan \theta_B + \sin \Psi \cos \Psi, \quad (1)$$

and

$$K_2 = \sin^2 \Psi \tan \theta_B + \sin \Psi \cos \Psi,$$

where  $\Psi$  is the angle between the reflecting plane and the sample surface, and the Bragg angle  $\theta_B$  is measured between the analyzing beam and the reflecting plane.<sup>6</sup> For symmetric reflections, only the perpendicular strain  $\epsilon^\perp$  is measured. Figure 1 (a) shows the rocking curve for the symmetric (111) reflection. The angular separation  $\Delta\theta_B = 0.385^\circ$  yields an average perpendicular strain of  $\epsilon^\perp = -2.08\%$ . This indicates that the CoSi<sub>2</sub> film is under tensile stress par-

allel to the (111) surface plane. Using this  $\epsilon^\perp$  value along with the rocking curve for the asymmetric (331) reflection of Fig. 1 (b), the parallel strain  $\epsilon^\parallel = -0.12\%$  is obtained. Assuming that the parallel strain is uniform and isotropic over the film thickness, this  $\epsilon^\parallel$  value indicates that there are 12 extra CoSi<sub>2</sub> unit cells over a distance of  $10^4$  Si unit cells, and the strain is partially accommodated by misfit dislocations. The perpendicular strain data measured are plotted in Fig. 2 [curve (a)] for film thickness from 25 to 100 nm. As seen in the curve, the 25-nm film is most strained and the CoSi<sub>2</sub> lattice spacing is smaller than that of the Si substrate by 2.15% in the normal direction. This value is in good agreement with a theoretical value of  $-2.16 \pm 0.03\%$  estimated from the elasticity theory,<sup>7</sup>

$$\epsilon^\perp = \left( \frac{1+\nu}{1-\nu} \right) \left( \frac{a_{\text{CoSi}_2} - a_{\text{Si}}}{a_{\text{Si}}} \right). \quad (2)$$

Here we assume in-plane coherence. The Poisson's ratio  $\nu$  of  $0.285 \pm 0.006$  is achieved from the  $\epsilon^\perp$  and  $\epsilon^\parallel$  values obtained from those partially strained films such as the one shown in Fig. 1. As the thickness increases from 30 to 55 nm, the x-ray perpendicular strain decreases rapidly toward an intermediate value of 1.77%, implying a progressive lattice relaxation of the epilayer. However, for the films of 55–100-nm thick, the strain is all about 1.77% and there is little thickness dependence. The x-ray strain does not, however, seem to relax to 1.2%, the mismatch between free lattice CoSi<sub>2</sub> and Si, as might be expected for a totally relaxed CoSi<sub>2</sub> alloy.

Next, the dependence of the thermal stability of strained layer CoSi<sub>2</sub> films on film thickness is studied. Samples are annealed at 750, 850, and in some cases up to 1000 °C for 45 min. Curves (b) and (c) of Fig. 2 show the perpendicular strain obtained for annealing temperatures at 750 and 850 °C, respectively. For films thinner than 30 nm, the thermal annealing shows a much slower relaxation of the strain. However, there is a large difference of the strains for the as-grown (at 550 °C) films and samples annealed at 750 °C in the range of film thickness between 30–50 nm. For films that are thicker than 50 nm, only a minor difference of the strain is seen for the as-grown films and the samples annealed up to 850 °C. For samples annealed at 1000 °C, an entirely differ-

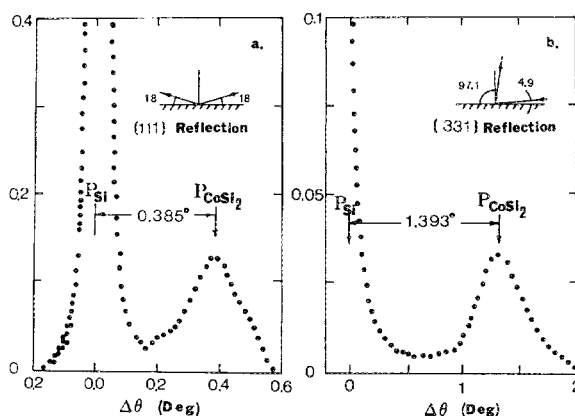


FIG. 1. X-ray rocking curves measured on a 40-nm thick CoSi<sub>2</sub>/Si sample. (a) (111) symmetric reflection, and (b) (331) asymmetric reflection.

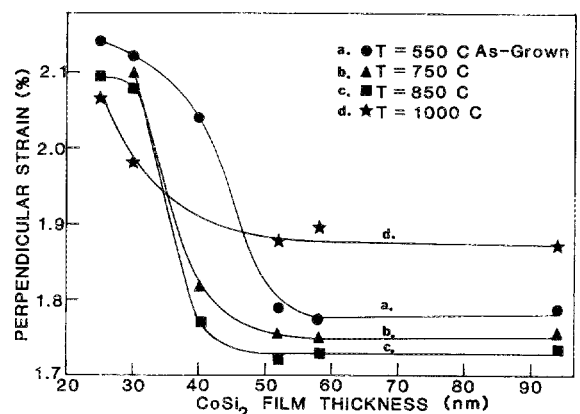


FIG. 2. Perpendicular strain measured on CoSi<sub>2</sub> as a function of thickness. Curve (a) as grown,  $T_{\text{growth}} = 550^\circ\text{C}$ . (b)  $750^\circ\text{C}$ , 45 min. (c)  $850^\circ\text{C}$ , 45 min. (d)  $1000^\circ\text{C}$ , 45 min.

ent behavior is observed as shown in curve (d). After 1000 °C annealing for the film thickness beyond 50 nm, it is extremely interesting to note that the strain actually increases. To see the thermal stability clearly, the perpendicular strain is replotted as a function of temperature as shown in Fig. 3. As can be seen, thinner films (< 30 nm) relax slowly as the annealing temperature is increased. For the 40-nm film, the strain relaxes rapidly after thermal treatment as shown in curve (c); for the film with thickness from 50 nm up to 100 nm, the general behavior for the strain to relax slightly and then increase after 1000 °C annealing is common in this thickness range [curve (d)]. The increase of the strain is consistent with planar view TEM micrographs taken on a 94-nm film displayed in Fig. 4, showing a decrease in the dislocation density from  $8 \times 10^8 \text{ cm}^{-2}$  in the as-grown film to  $1 \times 10^7 \text{ cm}^{-2}$  after 1000 °C annealing. However, most of this decrease is due to removal of threading dislocations as opposed to interfacial dislocations. Meanwhile, increase in the pinhole density from  $1.5 \times 10^6 \text{ cm}^{-2}$  to  $1 \times 10^7 \text{ cm}^{-2}$  after annealing is also observed.

While annealing causes change on the strain in the film, the RBS spectra as shown in Fig. 5 for the as-grown and 1000 °C annealed samples show that the Co concentration profile at the interface with the substrate is the same within the accuracy of our measurement, which is 2% or about 2 nm. This suggests that the interface abruptness changes by < 2 nm despite the heat treatment. We also observe no significant change in stoichiometry, indicating high temperature stability of these films.

#### IV. DISCUSSION

The strain behavior of the CoSi<sub>2</sub> epilayers may be divided into three regions of film thickness. In region I, for film thickness less than 30 nm, the growth is found to be commensurate. TEM micrographs show very few misfit dislocations. In region II, for film thickness between 30–50 nm, the strain progressively relaxes and the in-plane lattice constant decreases from the Si bulk value while misfit dislocations are generated. In region III, for film with thickness from 50 nm up to 100 nm, the strain of the CoSi<sub>2</sub> films is partially relaxed to about 1.77% relative to the substrate lattice spacing and there is little difference for all thicknesses in these range. It appears that energy relaxation expected during annealing is

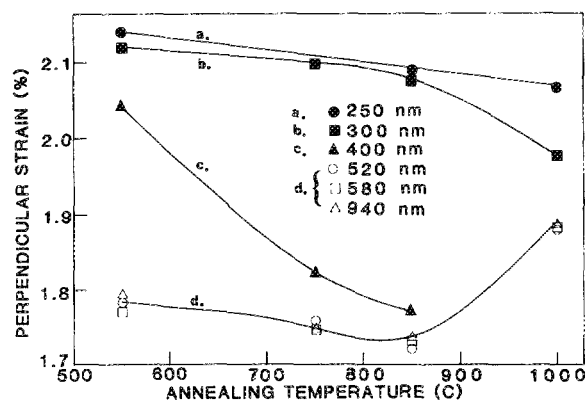


FIG. 3. Perpendicular strain measured on CoSi<sub>2</sub> as a function of temperature. Curve (a) 25 nm; (b) 30 nm; (c) 40 nm; (d) 52, 58, and 94 nm.

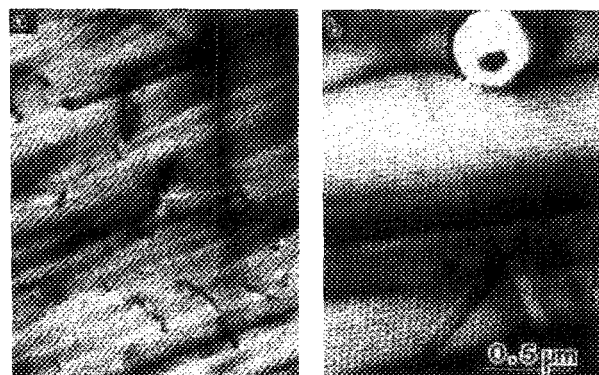


FIG. 4. Planar view TEM bright-field images for a 94-nm thick CoSi<sub>2</sub> film on (111) Si. (a) As grown, and (b) 1000 °C, 45 min thermal annealing.

accommodated by pinhole formation. In the normal case, strain relaxation causes increase in the misfit dislocation density. However, in our case, we have not observed increase in the misfit dislocation density as the film becomes thicker, while the pinhole density increases by an order of magnitude after annealing. The size of pinholes ranges from 70 to several hundred nm. The lattice constant of the CoSi<sub>2</sub> film does not completely relax to the bulk CoSi<sub>2</sub> value as might be expected for a unstrained CoSi<sub>2</sub> film. Detailed study of pinhole formation mechanism is needed for further understanding of the pseudomorphic growth of this system. It is worth noting that the  $\chi_m$  measured on this relaxed CoSi<sub>2</sub> film is about 3.6%, which is only slightly higher than that of a perfect (111) oriented Si, indicating the film has high crystalline quality regardless the strain relaxation.

#### V. SUMMARY

Strain data of epitaxial CoSi<sub>2</sub> for various film thicknesses have been measured using a x-ray rocking curve technique. From the strains measured, the critical thickness for pseudomorphic growth is determined to be about 30 nm for a

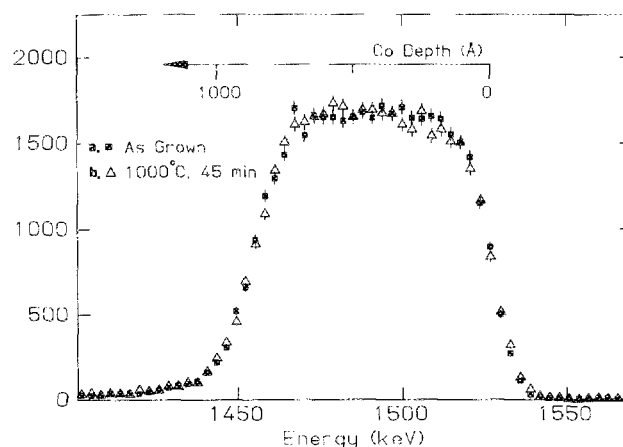


FIG. 5. Random backscattering spectra of the Co profiles of a 94-nm thick CoSi<sub>2</sub> film before and after thermal treatment. (a) As grown, and (b) annealed at 1000 °C for 45 min.

growth temperature of 550 °C. The commensurate nature of growth is confirmed by TEM. For thicker films studied, the strain is found to relax to an intermediate value and complete relaxation of strain does not happen. Progressive strain relaxation of these samples is observed after thermal annealing up to 850 °C. The samples after 1000 °C annealing show an increase in strain. It is suggested that energy relaxation expected during annealing is accommodated by pinhole formation. The RBS data show that there is little change in the Co concentration profile after thermal treatment up to 1000 °C. The channeling data along the  $\langle 111 \rangle$  axis on CoSi<sub>2</sub>/Si samples show a low  $\chi_m$  value regardless the presence of misfit dislocations and pinholes.

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