Transient Phase Formation During the Growth of Epitaxial CoSi₂
by Annealing of CoTi Bi-Layers on (100) Si*

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Phase evolution during the annealing of Co/Ti bi-layers on (100) Si has been studied by x-ray diffraction and analytical electron microscopy. X-ray diffraction performed in situ during annealing revealed a reaction pathway involving the formation of a transient phase when epitaxial CoSi2 films were grown. Analytical electron microscopy was used to identify this phase as a spinel-related phase, isostructural with Co2TiO4. This phase grows as a result of the presence of the Ti interlayer and a small amount of oxygen from the annealing ambient. Annealing in vacuum or other purified inert gases yielded polycrystalline CoSi2 films which form via a different reaction pathway that does not involve a spinel phase. This spinel phase may serve both to reduce the native oxide from the underlying Si substrate and to control interdiffusion between Si and Co during the reaction, thereby promoting epitaxial growth.

INTRODUCTION

The growth of epitaxial CoSi2 films on (100) Si substrates has attracted considerable interest over the past few years. While epitaxial films have been grown using a variety of methods, most have required rather complicated processing or UHV techniques.[1-5] However, one technique reported by Lawrence, et al.[6] has proven successful in promoting epitaxial growth of CoSi2 on (100) Si substrates using a simple post-deposition annealing procedure. In this technique, a thin Ti layer is first deposited onto the Si substrate, followed by deposition of the Co layer. Annealing of such a bi-layer sample in a nitrogen atmosphere yields <100> oriented epitaxial films of CoSi2. In that work, the authors suggested that one of the key roles of the Ti interlayer was in reducing the native oxide. More recently, several investigators have reported similar results, also using Co/Ti bi-layer films.[7-11]

In spite of the attention devoted to the factors which control epitaxial growth in this system, the specific role of the Ti interlayer remains unclear. Most of the studies seem to agree that the Ti interlayer must play some role in reducing the native oxide as well as in controlling the diffusion of Co to the Si substrate. For example, Vantomme, et al. [7] studied the reaction of Co/Ti bi-layer films on (100) Si in reactive and non-reactive atmospheres. They reported the formation of a polycrystalline Co0.25Ti0.75Si2 film that restricted the supply of Co, resulting in epitaxial growth of CoSi2. Similarly, Ogawa, et al. [10] observed a thin layer claimed to moderate diffusion during annealing of Co/Ti bi-layers. In this work,
we have studied the role of the Ti interlayer in forming a transient phase which may both scavenge oxygen and control interdiffusion.

EXPERIMENT

Si(001) substrates were cleaned, stripped of their native oxide, hydrogen terminated and then immediately inserted into the deposition chamber. Films were deposited by sputtering 50 Å Ti followed by 300 Å Co without breaking vacuum. In situ x-ray diffraction (XRD) was performed in a hot cell mounted on a fast powder diffractometer, which is described in detail elsewhere.[12] Samples were mounted on a Ta strip heater and a flow of 99.9995% N₂ (water vapor specified to 2 ppm) was maintained throughout the process. Diffraction data (θ-2θ) was acquired continuously as the temperature was ramped at rates of 10-30 °C/min. Companion samples were annealed in a conventional tube furnace using a flowing N₂ atmosphere. Most samples were heated continuously until the reaction was completed, but selected samples were quenched from various points for more detailed study. Transmission electron microscopy (TEM) was carried out using a Philips CM30 microscope equipped with a thin window energy dispersive spectrometer (EDS) for compositional analyses. Cross-sectional samples were prepared by conventional techniques involving grinding, dimpling, and ion milling at 77K to final perforation.

RESULTS

In situ XRD was performed on a large number of samples under a variety of conditions. Details of those experiments are reported elsewhere.[11,13] In short, the results showed that annealing in N₂ yielded epitaxial CoSi₂ films while annealing in vacuum or otherwise inert environments yielded polycrystalline films. Samples which were annealed to yield epitaxial films always showed the emergence of a transient phase (M) which preceded the nucleation and growth of the epitaxial silicide whereas samples which were annealed in vacuum or otherwise protected from oxygen contamination (and yielded polycrystalline films) showed little or none of this transient phase. In those cases the formation of CoSi₂ was generally preceded by growth of CoSi. Typical XRD patterns which illustrate this behavior are shown in Fig. 1. The XRD patterns from a film annealed in N₂ but with a TiN cap layer (Fig. 1a) or in vacuum (1b) show strong peaks from misoriented CoSi₂ as well as peaks from CoSi. In contrast, the film annealed in N₂ (Fig. 1c) shows no evidence of CoSi and significantly less intense peaks from misoriented CoSi₂. However, additional peaks associated with the transient phase, marked as "M", are evident. During in situ XRD experiments, additional peaks were also observed occasionally as the peaks from the M phase began to diminish. This slight splitting of the peaks associated with the M phase suggests a decomposition reaction. Companion samples annealed in a tube furnace and analyzed by post-annealing, ex situ XRD also showed evidence of the transient M phase. Thus, in these experiments, the growth of epitaxial CoSi₂ was always associated with the formation of this transient phase.
In order to identify this transient phase, samples that contained a large fraction of the M phase were prepared by holding at an intermediate temperature (≈650°C), based on the in situ XRD results. An XRD pattern from such a sample is shown in Fig. 2 in which a series of strong peaks associated with the M phase are evident as marked. The peaks could not be indexed based on any of the reported binary or ternary silicide phases reported for this system, so analytical electron microscopy was used to identify this phase. The results of these analyses are shown in Fig. 3. The bright-field micrograph in Fig. 3a shows a nearly single-phase film on top of the Si substrate, separated by a thin layer of amorphous oxide. The oxide layer reflects the higher level of background oxygen present during annealing of this sample, but the XRD results indicate the M phase forms even when the oxygen level is lower. The EDS spectrum shown in Fig. 3b was collected from the film and reveals the presence of Co, Ti, and Si. More significantly, however, the spectrum also shows a large peak due to oxygen. Microdiffraction patterns collected from various zone axes are shown in Fig. 3c. These patterns could be indexed consistently, as marked, according to a face-centered cubic unit cell with $a_0 \approx 8.43\,\text{Å}$. Together with the compositional data
Figure 2 XRD spectrum from a sample annealed to yield a nearly phase pure film of the transient phase. The peaks from the transient phase are labeled as "M."

from EDS, this diffraction information allows the identification of the transient M phase as a spinel-like phase, isostructural with Co2TiO4. Based upon this identification, the additional peaks observed by XRD as the M phase began to diminish were indexed according to a defect spinel isostructural with CoTiO3.

DISCUSSION

It is clear from the many reports in the literature that a Ti interlayer plays some special role in promoting epitaxial <100> growth of CoSi2. The most commonly proposed mechanisms suggest that the Ti layer plays some role in reducing the native oxide as well as in controlling the diffusion of Co to the Si substrate. It is likely that the specific manner by which this is achieved may vary somewhat based on the experimental details. In this work, the identification of a transient spinel which was always observed to precede epitaxial growth of CoSi2 is consistent with these proposed mechanisms. Firstly, the formation of an oxide-based spinel provides a natural sink for oxygen from the substrate surface. Secondly, the ordered structure and the different cation sites (octahedrally and tetrahedrally coordinated) provide a natural mechanism for a moderated flux of Co arriving at the substrate and likewise limit the diffusion of Si out into the film. A growth mechanism based on epitaxial CoSi2 growth moderated by this spinel-like phase is not necessarily inconsistent with other reports in the literature. For example, Vantomme, et al.[7] reported improved quality of epitaxial films, smoother interfaces, and fewer misoriented grains in bi-layer films annealed in N2 compared
to films annealed in \((N_2 + H_2)\) or in vacuum. They attributed the controlled epitaxial growth to an intermediate \(\text{Co}_{0.25}\text{Ti}_{0.75}\text{Si}_2\) layer which moderates diffusion. In films annealed in \(N_2\)-based atmospheres, the Ti ultimately resides in a top layer in the form of oxide and/or nitride compounds while for samples annealed in vacuum the ternary silicide remains stable. Although the \(\text{Co}_{0.25}\text{Ti}_{0.75}\text{Si}_2\) phase was clearly identified, the increasing interface roughness and misorientation and the outward diffusion of Si associated with reducing atmospheres are also consistent with a reaction that proceeds by diffusion across a spinel layer. The reducing atmosphere could result in the partial disruption of this layer yielding films with more misoriented grains and rougher interfaces as observed in those experiments. Furthermore, transformation of the spinel from one isostructural with \(\text{Co}_2\text{TiO}_4\) to one isostructural with \(\text{CoTiO}_3\) during growth is consistent with a mechanism in which Co diffusion is controlled by the spinel until the supply of Co is diminished.

Figure 3  (a) Bright-field TEM image of a film annealed to yield a nearly phase pure film of the transient phase. (b) EDS spectrum from the transient "M" phase. (c) Microdiffraction patterns from the transient "M" phase indexed according to \(\text{Co}_2\text{TiO}_4\).
CONCLUSIONS

Phase evolution during the annealing of Co/Ti bi-layers on (100) Si has been studied by x-ray diffraction and analytical electron microscopy. The growth of epitaxial CoSi2 films was always associated with the formation of a spinel structurally related to Co2TiO4. Annealing in vacuum or other inert environments yielded polycrystalline CoSi2 films which form via a different reaction pathway that does not involve a spinel phase. The presence of such an oxide layer and the progression of phases that develop, in particular the sequence of Co2TiO4 to CoTiO3, suggests that this spinel phase may serve both to reduce the native oxide from the underlying Si substrate and to control interdiffusion between Si and Co during the reaction, thereby promoting epitaxial growth.

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