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Film thickness effects in the $Ti-Si_{1-x}Ge_x$ solid phase reaction

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The effects of film thickness on the Ti–Si_{1-x}Ge_x solid phase reaction were investigated. Thin C49 TiM₂ (M=Si_{1-y}Ge_y) films were formed from the solid phase reaction of 400 Å Ti or 100 Å Ti with Si_{1-x}Ge_x alloys. It was determined that for films formed from 400 Å Ti, the nucleation barrier of the C49-to-C54 transformation decreases with increasing germanium content, for alloy compositions with up to ≈40 at. % germanium (i.e., $x \le 0.40$). It was also observed that germanium segregates out of the TiM₂ lattice, for both the C49 and C54 phases, and is replaced on the TiM₂ lattice with Si from the substrate. The germanium segregation changes the Ge index y of the Ti(Si_{1-y}Ge_y)₂. For films formed from a 100 Å Ti layer it was observed that the C54 TiSi₂ nucleation temperature was increased by ≥125 °C. The addition of germanium to the silicon increased the agglomeration of the C49 phase and caused the C54 TiM₂ nucleation barrier to increase further. The results also indicate that the increased temperature required for the transition to the C54 phase, for the 100 Å films, leads to an increased rate of germanium segregation. © *1995 American Institute of Physics*.

I. INTRODUCTION

The bilayer solid phase Ti-Si reaction usually results in the sequential formation of at least two prominent crystalline phases: C49 TiSi₂ and C54 TiSi₂.¹⁻³ Initially Ti and Si interdiffuse to form a disordered intermixed a-TiSi interface layer.^{3,4} Following the formation of the disordered layer, TiSi₂ nucleates at the *a*-TiSi/Si interface and grows laterally to form an interface layer.^{3,4} This initial $TiSi_2$ layer has a base-centered orthorhombic crystal structure (C49 TiSi₂).^{5,6} The C49 phase of TiSi₂ is not the stable TiSi₂ phase listed in the Ti-Si binary phase diagram.⁷ It has been proposed that C49 TiSi₂ has a lower nucleation barrier than C54 TiSi₂ because the TiSi2/Si and TiSi2/a-TiSi interface energies are lower for the C49 phase than for the C54 phase.^{8,9} After an interfacial layer of C49 TiSi2 forms, Si diffuses through the C49 TiSi₂ layer and the silicide grows toward the Ti surface.^{3,4} The C49 TiSi₂ grows until the Ti layer has been completely reacted. At higher annealing temperatures the TiSi₂ layer may undergo a polymorphic transformation from the C49 structure to the C54 structure (face-centered orthorhombic).^{3,6} The polymorphic transformation is driven by a small bulk free-energy difference between the two phases (C54 having the lower bulk free energy).¹⁰ Depending on the thickness of the C49 TiSi₂ layer, the C54 TiSi₂ phase can form as a continuous layer of low-resistivity C54 TiSi₂ grains (providing a low-resistance conduction path through the C54 TiSi₂ region).¹⁰⁻¹² If a continuous layer of C54 TiSi₂ is desired then the nucleation and growth of C54 TiSi₂ in C49 TiSi2 defines a lower limit to the thermal budget for Ti-Si processing.¹³

The thermal stability of C54 $TiSi_2$ determines the processing conditions which cause a continuous layer of C54 $TiSi_2$ to agglomerate and defines an upper limit to the thermal budget for Ti–Si processing. When C54 $TiSi_2$ initially forms during the solid phase reaction of Ti and Si the C54 phase may form as a continuous layer of low-resistivity C54 $TiSi_2$ grains which provide a low-resistance conduction path through the metallized layer. At high annealing temperatures the formation of grooves along the C54 $TiSi_2$ grain boundaries has been observed.^{14–16} The formation of the grooves requires mass transport which is a thermally activated process and the grooves become more rapidly prominent as the annealing temperature is increased.^{3,16} Nolan and co-workers¹⁶ have examined groove formation at both the C54 $TiSi_2$ surface and at the C54 $TiSi_2/Si$ interface and modeled the groove formation as a balance of the surface and the interface energies.

As the thermal grooves deepen, eventually the surface groove will meet the interface groove and the two neighboring grains will separate.¹⁶ When the C54 TiSi₂ grains become individual islands another energy term must be considered, the Si surface energy. The equilibrium shape of the C54 TiSi₂ grains (islands) is determined by the relative surface and interface energies of the C54 TiSi2 surface, the C54 TiSi2/Si interface, and the Si surface.^{11,17} Jeon et al.¹¹ modeled the triple junction of the TiSi2 surface, the Si surface, and the TiSi₂/Si interface as a balance between the surface and interface energies (solid-state capillary model). By measuring contact angles of TiSi₂ islands they were able to calculate values for the TiSi2 surface energy and the TiSi2/Si interface energy using a known value of the Si surface energy.^{11,17} When the low-resistance conduction path is broken by the islanding of C54 TiSi2 grains the sheet resistance of the C54 TiSi2 layer increases rapidly. A temperature processing window, for a given annealing duration, can be defined by the temperatures at which a continuous layer of C54 TiSi₂ forms (forming a continuous low-resistance conduction path) and the temperature at which the C54 TiSi₂ grains completely agglomerate (breaking the low resistance conduction path).¹³

The C49 TiSi₂ film thickness can have a profound effect on both the C49 TiSi₂-to-C54 TiSi₂ transformation and the TiSi₂ agglomeration processes. It was initially reported by van Houtum and Raaijmakers¹⁸ and later by Jeon *et al.*¹¹ that, for Ti–Si solid phase reactions, as the thickness of the

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initial Ti film was decreased the C49 TiSi_2 -to-C54 TiSi_2 transformation temperature increased. It has also been observed that, for a given annealing duration, the agglomeration temperature decreases as the film thickness decreases.^{13,19} For thin films less material transport is required for thermal grooving to result in agglomeration (i.e., for a given annealing duration agglomeration occurs in a thin film at a lower temperature than in a thick film, and for a given annealing temperature agglomeration occurs in a thin film in a shorter time than in a thick film). Therefore, as the film thickness decreases, the temperature needed to form the low-resistivity C54 TiSi_2 increases and the agglomeration temperature decreases.

Like the Ti–Si reaction the bilayer solid phase Ti–Ge reaction usually results in the formation of at least two prominent crystalline phases. The two phases usually observed in the Ti–Ge reaction are Ti_6Ge_5 and C54 TiGe₂.^{20–22} Initially, the Ti_6Ge_5 phase forms by diffusion-controlled growth from the Ti/Ge interface, through the Ti layer, to the sample surface. At higher annealing temperatures germanium diffuses into the Ti_6Ge_5 , C54 TiGe₂ nucleates, and the C54 TiGe₂ grows laterally through the Ti_6Ge_5 film.^{20.21} There is no analogy in the Ti–Si system for Ti_6Ge_5 , and C49 TiGe₂ has not been observed in the solid phase reaction of Ti–Ge bilayers. However, Hong, Barmak, and d'Heurle²³ have observed the formation of C49 TiGe₂ during the crystallization of codeposited amorphous Ti+2Ge.

Previously it has been observed that C54 Ti $(Si_{1-x}Ge_x)_2$ is the final phase of the $Ti-Si_{1-x}Ge_x$ solid phase reaction.^{24,25} In a recent study of the phase formation sequence in the $Ti-Si_{1-x}Ge_x$ solid phase reaction it was observed that for a range of silicon-rich alloys the reaction followed a "Ti-Si-like" reaction path (i.e., $Ti+Si_{1-x}Ge_x$ \Rightarrow C49 TiM₂ \Rightarrow C54 TiM₂, where M=Si_{1-y}Ge_y).⁹ The $Ti-Si_{1-x}Ge_x$ reaction was observed to follow a "Ti-Si-like" reaction path for germanium content up to 40 at. % germanium (i.e., $x \le 0.40$). In that same study⁹ it was also observed that for "Ti-Si-like" reactions the C54 TiM₂ nucleation temperature decreased with increasing germanium content. In this study the addition of germanium to the very thin-film Ti-Si solid phase reaction was investigated as a possible means of alleviating some of the C54 TiM2 nucleation difficulties associated with very thin films. Structural and compositional properties were examined using x-ray diffraction (XRD) and *in vacuo* Raman spectroscopy. The morphologies of the surfaces and interfaces were examined using scanning electron microscopy (SEM) and cross-sectional transmission electron microscopy (XTEM).

II. EXPERIMENT

The samples used in this study consisted of cleaned 1 in. Si(100) wafers on which a layer of $Si_{1-x}Ge_x$ and a layer of Ti were deposited. The silicon wafers were precleaned by the manufacturer using a standard RCA cleaning procedure. Prior to use in the laboratory the wafers were further cleaned by

(1) exposure to UV-generated ozone to remove hydrocarbons from the surface and to form a stable oxide,

- (2) spin etching with a solution of hydrofluoric acid: H₂O:ethanol (1:1:10) to remove the oxide and passivate the Si(100) surface with hydrogen, and
- (3) an *in situ* thermal desorption at >850 °C for 10 min to remove any surface contaminants which may remain.

This cleaning process has been shown to produce atomically clean surfaces.²⁶ Following the *in situ* thermal desorption at >850 °C, the substrate temperature was reduced at 40 °C/ min and held at 550 °C for the deposition of a heteroepitaxial single-crystal $Si_{1-x}Ge_x$ alloy layer. The $Si_{1-x}Ge_x$ alloy layer was not intentionally doped. Alloy compositions with x=0.00, 0.10, and 0.20 were deposited. Silicon and germanium were codeposited from two electron-beam evaporation sources. The silicon and germanium deposition rates were monitored using oscillating quartz-crystal monitors. Feedback from the deposition monitors was used to automatically control the relative silicon and germanium deposition rates. The maximum composition variation during deposition was approximately 2%. The compositions of the deposited Si_{1-r}Ge_r alloys were determined from Rutherford backscattering (RBS) and x-ray-absorption fine structure (XAFS) analysis of native $Si_{1-r}Ge_r$ layers similarly prepared.²⁴ Following deposition of the epitaxial $Si_{1-x}Ge_x$ alloy layer the sample was cooled at 40 °C/min to <150 °C and titanium was deposited from an *in situ* hot-filament titanium source. The titanium layer thickness was either 400 or 100 Å. The thickness of the preceding $Si_{1-x}Ge_x$ layer was such that the ratio of Ti-to-Si₁₋, Ge, atoms in the bilayer structure was ≈ 1 to 2. The thickness of the deposited titanium was monitored using an oscillating quartz-crystal deposition monitor. Upon completion of the titanium deposition, the sample was annealed in situ. During the annealing cycle the substrate temperature was increased at a rate of 40 °C/min, held at the desired temperature for 10 min, and decreased at a rate of 40 °C/min. Annealing temperatures ranging from 579 to 605 °C were used for the 400 Å Ti samples, and annealing temperatures ranging from 710 to 770 °C were used for the 100 Å Ti samples. The final cleaning step, the depositions, and the annealing were all performed in the same ultrahigh-vacuum (UHV) chamber to minimize the effects of contamination. The processing chamber base pressure was $\sim 1 \times 10^{-10}$ Torr, the pressure during desorption was $<5 \times 10^{-10}$ Torr, the pressure during silicon and germanium deposition was $<1 \times 10^{-8}$ Torr, the pressure during titanium deposition was $<5 \times 10^{-9}$ Torr, and the pressure during annealing was $<1 \times 10^{-9}$ Torr.

Results obtained from four Ti-Si_{0.68}Ge_{0.32} samples which have been the subject of a previous study²⁷ were also included here. These samples were produced using a procedure similar to that outlined above. However, in these samples, following the *in situ* thermal desorption at >850 °C, the substrate temperature was reduced and held at 550 °C for the deposition of a homoepitaxial silicon buffer layer (~225 Å) and a heteroepitaxial single-crystal Si_{0.68}Ge_{0.32} alloy layer (~2500 Å). Following deposition of the epitaxial Si_{0.68}Ge_{0.32} alloy layer each sample was cooled to <150 °C and 400 Å of titanium was deposited from the *in situ* hot-filament Ti source. The samples were annealed *in*



FIG. 1. The phases of TiM₂ present in the series annealed 400 Å Ti-Si_{1-x}Ge_x samples as determined by *in vacuo* Raman spectroscopy. The C54 TiM₂ Raman signal in the Ti-Si_{0.80}Ge_{0.20} sample after annealing at 579 °C was at the threshold of the Raman detectability limit. The x=0.32 samples are from a previous study of the Ti-Si_{1-x}G_x reaction (Ref. 27) and the composition of these samples was determined by XRD (as outlined in the previous study). The dashed line is drawn to guide the eye to the decrease in the C54 TiM₂ nucleation temperature with increasing Ge content.

situ at 530, 570, 660, or 700 °C for 10 min using the temperature ramp rates listed above. The complete sample preparation is outlined in a previous study.²⁷

The structural properties of the alloys were examined using a Rigaku x-ray diffractometer and *in vacuo* Raman spectroscopy. Raman spectra were excited with ~250 mW of 514.5 nm Ar-ion laser light. The scattered light was filtered and dispersed with an ISA U3000 spectrometer, and the light was detected with a LN₂-cooled charge-coupled-device (CCD) array detector. An instrument resolution of ~6 cm⁻¹ was used. The sample was held in UHV and excitation and scattered light passed through a 4-in.-diam glass window. Surface and interface morphologies were examined using a JEOL 6400 field-emission scanning electron microscope and a Topcon 002B transmission electron microscope operated at 200 kV.

III. RESULTS

A. The 400 Å Ti–Si_{1-x}Ge_x solid phase reaction

To examine the effect of $Si_{1-x}Ge_x$ alloy composition on the nucleation of C54 TiM₂ in C49 TiM₂ during the $Ti-Si_{1-x}Ge_x$ solid phase reaction, thin-film $Ti-Si_{1-x}Ge_x$ samples were prepared using 400 Å Ti and $Si_{1-x}Ge_x$ alloy compositions of x = 0.0, 0.1, and 0.2. The samples were repeatedly annealed in $\approx 9^{\circ}$ increments from 579 to 605 °C. After each anneal the composition and structure of the titanium germanosilicide were examined using in vacuo Raman spectroscopy (the samples were never exposed to pressures greater than 1×10^{-9} Torr during the annealing and Raman cycles). The C49 and C54 phases of TiM₂ were the only titanium germanosilicide phases detected, and the Raman signatures of these phases remained distinct, despite changes in alloy composition, allowing for easy detection of C54 TiM₂ nucleation. The observed phases are plotted in Fig. 1. In the Ti-Si_{0.90}Ge_{0.10} and Ti-Si_{0.80}Ge_{0.20} samples the C49 and C54 phases of TiM₂ were observed to coexist at some of the annealing temperatures. The Raman peak from the



FIG. 2. Peak position of one of the Raman active C49 TiM₂ phonon modes, plotted for each annealing temperature for which C49 TiM₂ was detected in the series annealed 400 Å Ti–Si_{1-x}Ge_x samples. The x=0.0, 0.1, and 0.2 samples are indicated by the circles, squares, and diamonds, respectively. The peak positions were correlated to the C49 TiM₂ composition, the lower the wave number of the peak the higher the Ge index of the C49 Ti(Si_{1-y}Ge_y)₂. The plot indicates that as the Ti–Si_{0.80}Ge_{0.20} sample was repeatedly annealed the composition of the C49 TiM₂ changed [i.e., the Ge content of the C49 Ti(Si_{1-y}Ge_y)₂ decreased].

Si(100) substrate was not observed in any of the Raman spectra of any of the series annealed samples indicating that initially the titanium germanosilicide formed as a continuous layer and that the layer remained continuous during the repeated annealing.

In a previous study of titanium germanides it was predicted and observed that the Raman active phonon frequencies of C54 TiGe₂ are lower than those of C54 TiSi₂.²⁸ It was anticipated that in the titanium germanosilicides the phonon frequencies of both C49 TiM2 and C54 TiM2 would decrease with increasing germanium content. To examine changes in the relative compositions of the TiM₂ samples, the phonon frequencies of the titanium germanosilicide phases were examined for each sample at each annealing temperature. Changes in phonon frequencies were examined as a function of the annealing temperature and deposited $Si_{1-x}Ge_x$ alloy composition. The position of one of the Raman active C49 TiM₂ phonon peaks was determined for each sample at each temperature where C49 TiM_2 was detected. The C49 TiM_2 peak positions are plotted in Fig. 2. If C49 Ti $(Si_{1-y}Ge_y)_2$ were to form from the $Ti-Si_{1-x}Ge_x$ reaction with the same Ge index as the $Si_{1-x}Ge_x$ alloy (i.e., y=x) then as x decreases y would also decrease and the frequency of the Raman active C49 TiM_2 phonon modes would decrease (i.e., the C49 TiM₂ Raman peaks would shift to lower wave number as Ge index increased). The phonon frequencies of the C49 TiM₂ observed in the Ti-Si_{0.90}Ge_{0.10} sample were lower than in the Ti-Si sample (as anticipated). The phonon frequencies of C49 TiM₂ observed in the Ti-Si_{0.80}Ge_{0.20} sample, after the first annealing at 579 °C, were lower than in the $Ti-Si_{0.90}Ge_{0.10}$ sample (as anticipated). However, as the Ti-Si_{0.80}Ge_{0.20} sample was repeatedly annealed the C49 TiM₂ phonon frequency increased suggesting that the composition of the C49 Ti $(Si_{1-y}Ge_y)_2$ was changing (i.e., germanium was being replaced by silicon on the C49 $Ti(Si_{1-y}Ge_y)_2$ lattice, $y=0.2 \Rightarrow 0.0$).

TABLE I. The phases and compositions of the titanium germanosilicides and the Si_{1-z}Ge_z precipitates formed in the 400 Å Ti-Si_{0.68}Ge_{0.32} samples. The phases and compositions were determined by XRD and depth profile Auger electron spectroscopy (DPAES) analysis. The error in the determined y values is ± 0.02 , and the error in the determined z values is ± 0.04 .

Annealing temperature	$Ti(Si_{1-y}Ge_y)_2$		Si. Ge precipitate
	Phase	Composition	composition
530	C49	y=0.30	z=1.00, 0.87
570	C54	y=0.32	none
660	C54	y=0.29	z = 0.60
700	C54	y=0.26	z=0.59

Following the series annealing and Raman analysis, the 400 Å Ti-Si_{1-x}Ge_x samples were examined using XRD. The XRD analysis was used to determine the final state of the samples and to corroborate the Raman analysis. In the XRD scans of the Ti-Si and Ti-Si_{0.90}Ge_{0.10} samples, the only diffraction peaks observed were due to C54 TiM2 and the Si(100) substrate, indicating that the TiM_2 had completely converted to the C54 phase during the series annealing (in good agreement with the final Raman spectra of the samples). In the XRD scan of the Ti-Si_{0.80}Ge_{0.20} sample, diffraction peaks due to both C49 TiM_2 and C54 TiM_2 were observed. The presence of both the C49 and C54 phases suggests that the growth (not the nucleation) of the C54 phase is being retarded by the presence of germanium. Also observed in the XRD scan of the Ti-Si_{0.80}Ge_{0.20} sample were diffraction peaks corresponding to the (400) diffractions from both Si(100) and Si_{1-z}Ge_z(100). Using Vegard's law to estimate the composition of the observed $Si_{1-z}Ge_z$ alloy a composition of $Si_{0.74}Ge_{0.26}$ was determined.²⁹ The thickness of the initially deposited Si_{0.80}Ge_{0.20} layer was such that it should have been completely consumed during the formation of C49 TiM₂ and the presence of Si_{0.74}Ge_{0.26} in the Ti-Si_{0.80}Ge_{0.20} sample after repeated annealing suggests that following the initial formation of TiM₂, germanium segregation out of the titanium germanosilicide led to the formation of Si_{1-} , Ge. alloy (z>0.20). The germanium segregation may play a role in retarding of the growth of the C54 phase.

In a previous study²⁷ the phases and compositions of the titanium germanosilicides present in the 400 Å Ti-Si_{0.68}Ge_{0.32} samples were determined using XRD and depth-profiled Auger electron spectroscopy; the results are listed in Table I. In some of the samples the segregation of germanium out of the titanium germanosilicide was observed. Formation of Ge and germanium-rich Si_{1-z}Ge_z precipitates corresponded with the observed germanium segregation. XRD was also used to determine the composition of the precipitates (also listed in Table I).

B. The 100 Å Ti–Si_{1-x}Ge_x solid phase reaction

To study the effects of decreased film thickness and added germanium on the C49 $TiSi_2$ -to-C54 $TiSi_2$ phase transformation in the Ti-Si solid phase reaction, $Ti-Si_{1-x}Ge_x$ samples were produced using 100 Å layers of Ti and $Si_{1-x}Ge_x$ alloy compositions of x=0.00 and 0.10. In the $Ti-Si_{0.90}Ge_{0.10}$ samples the thickness of the deposited

Annealing temperature	Ti-Si reaction	Ti-Si _{0.90} Ge _{0.10} reaction		
	TiSi ₂ phase	$\frac{\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2}{\text{phase}}$	$Si_{1-z}Ge_z$ precipitate composition	
770	C49 & C54	C49	z=0.30	
750	C49 & C54	C49	z = 0.32	
730	C49	•••	•••	
710	C49	•••	•••	

 $Si_{0.90}Ge_{0.10}$ was such that it would be completely consumed during the formation of TiM₂. Individual samples were produced for each alloy composition and each annealing temperature. Four Ti–Si samples were produced using annealing temperatures of 710, 730, 750, and 770 °C. Two Ti–Si_{0.90}Ge_{0.10} samples were produced using annealing temperatures of 750 and 770 °C. Following the UHV deposition and annealing the samples were removed from vacuum, and the compositions and morphologies of the samples were examined.

XRD was used to identify the titanium germanosilicide phases present in the 100 Å $Ti-Si_{1-x}Ge_x$ samples. The XRD scans of the Ti-Si samples annealed at 710 and 730 °C contained diffraction peaks corresponding to only C49 TiSi2 and the Si(100) substrate. The XRD scans of the Ti-Si samples annealed at 750 and 770 °C indicated that both C49 TiSi2 and C54 TiSi2 were present in these samples. The XRD scans of the Ti-Si_{0.90}Ge_{0.10} samples annealed at 750 and 770 °C indicated that C49 TiM₂ was the only titanium germanosilicide phase present in these samples. A diffraction peak corresponding to the (400) diffraction from a Si_{1-} , Ge, alloy (z>0.1) was also present in the XRD scans of both Ti-Si_{0.90}Ge_{0.10} samples. Vegard's law was used to estimate the composition of the $Si_{1-z}Ge_z$ alloy.²⁹ The phases of the titanium germanosilicides and compositions of the Si1-, Ge, alloy precipitates are listed in Table II.

The morphologies of the four Ti-Si and two Ti-Si_{0.90}Ge_{0.10} samples were examined using SEM. A micrograph of the Ti-Si sample annealed at 770 °C, which contains both C49 TiSi₂ and C54 TiSi₂, appears in Fig. 3. The C49 regions consist of small TiSi2 grains and the C54 regions consist of large TiSi₂ grains. Figure 4 contains micrographs of the C49 regions of the Ti-Si samples annealed at 710, 750, and 770 °C. In Fig. 4 it can be seen that as the annealing temperature increases the small C49 TiSi₂ grains begin to agglomerate into individual islands. Figure 5 contains SEM micrographs of the C49 TiM₂ found in the Ti-Si_{0.90}Ge_{0.10} samples annealed at 750 and 770 °C. In the Ti-Si_{0.90}Ge_{0.10} samples the agglomeration is more severe than in the corresponding Ti-Si samples. In the Ti-Si_{0.90}Ge_{0.10} sample annealed at 770 °C the agglomeration of the C49 TiM₂ grains into distinct islands is clearly visible [Fig. 5(b)].



FIG. 3. Scanning electron micrograph of a 100 Å Ti–Si sample annealed at 770 °C for 10 min. Both of the C49 and C54 phases of TiSi₂ were detected by XRD. The regions of C49 TiSi₂ and C54 TiSi₂ have distinctly different surface morphology and are clearly visible in the micrograph. The C49 TiSi₂ consists of small grains which give the surface a rough appearance (a generally cloudy appearance in the micrograph). The C54 TiSi₂ has a large grain structure which gives the surface of the C54 TiSi₂ a very smooth appearance (the regions of uniform contrast in the micrograph).

IV. DISCUSSION

A. Energetics of the C49 TiSi₂-to-C54 TiSi₂ polymorphic transformation

From classical nucleation theory the free-energy change which accompanies the nucleation of a new phase can be written as

$$\Delta G(r) = Br^2 \sigma - Ar^3 \Delta G_1, \tag{1}$$

where Br^2 is the interface area of the interface between the parent phase and the product phase, σ is the energy per unit area of the interface formed between the parent phase and the product phase, Ar^3 is the volume of the nucleus of the product phase, and ΔG_1 is the free-energy difference per unit volume between the two phases.³⁰ In the C49 TiSi₂-to-C54 TiSi2 transformation C49 TiSi2 is the parent phase and C54 TiSi2 is the product phase. For a nucleus of C54 TiSi2 to form and grow in C49 TiSi₂, $\Delta G(r)$ must decrease as the C54 TiSi₂ nucleus size increases (i.e., as r increases). If σ and ΔG_1 are both positive values then $\Delta G(r)$ may initially increase and then decrease as the nucleus size increases. The nucleus size at which $\Delta G(r)$ is a maximum represents a critical nucleus size above which the nucleus will grow and below which the nucleus will not be stable. The critical nucleus size r^* and the nucleation barrier ΔG^* for a spherical nucleus can be derived from Eq. (1),

$$r^* = 2\sigma/\Delta G_1,\tag{2}$$

$$\Delta G^* = \Delta G(r^*) = (16 \pi/3) (\sigma^3 / \Delta G_1^2), \tag{3}$$

where ΔG^* is the energy required to form a stable nucleus (i.e., the nucleation barrier). Equation (3) represents the nucleation barrier for a very simple case (the formation of a spherical nucleus with the formation of only one new interface) but it does give an indication of the strong dependence of the nucleation barrier on the energy of the new interface that forms. For nucleation at a surface or at an interface Eq.



FIG. 4. A comparison of the morphologies of C49 TiSi₂ formed in three 100 Å Ti–Si samples annealed at (a) 710 °C, (b) 750 °C, and (c) 770 °C. The small grain structure of the C49 TiSi₂ is apparent in the sample annealed at (a) 710 °C. The C49 TiSi₂ layer is still relatively continuous following the 710 °C anneal and the underlying Si substrate is only slightly exposed. It appears that during the 750 °C anneal the C49 TiSi₂ grains agglomerated slightly more than during the 710 °C anneal and small discontinuous areas of exposed Si are clearly visible [(b)]. During the 770 °C anneal the C49 TiSi₂ grains agglomerated significantly and in (c) the rounded shape of the grains can be seen. Following the 770 °C anneal the areas of exposed Si are similar in size to the C49 TiSi₂ grains. While significant agglomeration has occurred during the 770 °C anneal it appears that many of the C49 TiSi₂ grains are still in contact with neighboring grains

(1) becomes more complicated with the addition of surface energy terms and/or more interface energy terms.

In Eq. (1) the driving force for the nucleation event is the bulk free-energy change (volume term) and the retarding force is the energy of the new interface that forms (area term). In the simple two-phase case the interface energy is assumed to be isotropic and the nucleus of the product phase



FIG. 5. A comparison of the morphologies of C49 TiM_2 formed in two 100 Å Ti-Si_{0.90}Ge_{0.10} samples annealed at (a) 750 °C and (b) 770 °C. During the 750 °C anneal the C49 TiM₂ grains agglomerated significantly. In (a) it can be seen that many of the exposed Si areas between C49 TiM₂ grains are connected, isolating groups of C49 TiM₂ grains. Following the 770 °C anneal the C49 TiM₂ grains are nearly completely agglomerated into individual islands and very few C49 TiM₂ grain boundaries remain.

is a sphere. The spherical shape minimizes the surface-tovolume ratio of the nucleus (i.e., it minimizes ΔG^*). For nuclei of different shapes the surface-to-volume ratio increases causing both the critical nucleus size and the nucleation barrier to increase.

In a study of the Ti–Si reaction by Ma and Allen¹⁰ it was observed that the formation of C54 TiSi₂ occurred along the C49 TiSi₂ grain boundaries and grain edges. By nucleating and growing along a C49 TiSi₂ grain boundary the C54 TiSi₂ nucleus eliminates some of the C49 TiSi₂ grain boundary. The energy from the eliminated C49 TiSi₂ grain boundary adds to the driving force for the C54 TiSi₂ nucleation and growth (i.e., along the C49 grain boundaries the activation energy for nucleation of C54 is reduced).

In this study it was observed that in the Ti–Si solid phase reaction, decreasing the Ti layer thickness from 400 to 100 Å caused an increase of >125 °C in the temperature required to nucleate C54 TiSi₂ from C49 TiSi₂. This effect of the film thickness has been observed previously by van Houtum and Raaijmakers¹⁸ and by Jeon *et al.*¹¹ In the study by Jeon *et al.* it was proposed that the observed increase in C54 TiSi₂ nucleation temperature with decreasing film thickness may be attributable to an increase of the surface-to-volume ratio of the C54 TiSi₂ nucleus caused by the decreasing film thickness. If the equilibrium shape of the C54 TiSi₂ nucleus changes then the surface-to-volume ratio of the nucleus will increase causing the nucleation barrier to also increase. In a study by Ma and Allen¹⁰ several possible nucleus shapes were examined.

B. Effects of germanium on the nucleation of C54 TiSi_2 from C49 TiSi_2

In the 400 Å Ti–Si_{1-x}Ge_x samples it was observed that the C54 TiM₂ nucleation temperature decreased with increasing germanium content (Fig. 1). Presumably, the decrease in the C54 TiM₂ nucleation temperature indicates that the presence of the germanium decreases the C54 TiM₂ nucleation barrier. The nucleation barrier [Eq. (3)] could decrease if

- (1) the C54 $TiM_2/C49 TiM_2$ interface energy decreases and/or
- (2) the ΔG_1 of the C49 TiM₂-to-C54 TiM₂ transition increases.

In a previous study by Aldrich *et al.*⁹ it was proposed that the C54 TiM₂/C49 TiM₂ interface energy decreases slightly as the Ge index varies from x=0.00 to x=1.00, and the ΔG_1 for the transition increases slightly as the germanium content increases.

Also observed in the 400 Å Ti-Si_{1-x}Ge_x samples was the segregation of germanium out of both the C49 and C54 phases of TiM₂. A previous study of the thermal stability of C54 TiM₂ reported on the germanium segregation out of C54 TiM₂ which occurred during the Ti-Si_{0.68}Ge_{0.32} solid phase reaction (the same Ti-Si_{0.68}Ge_{0.32} samples examined in this study).²⁷ In that study it was observed that, at the C54 formation temperature, the C54 Ti(Si_{1-y}Ge_y)₂ formed with $y\approx 0.32$. At higher annealing temperatures it was observed that the Ge index y of the C54 Ti(Si_{1-y}Ge_y)₂ decreased (y <0.32) and that Si_{1-z}Ge_z ($z \geq 0.32$) nucleated along the C54 TiM₂ grain boundaries and grain edges. It was suggested that following the initial formation of the C54 TiM₂

- (1) silicon and germanium diffused into the C54 TiM₂ (from the underlying $Si_{0.68}Ge_{0.32}$ layer),
- (2) some of the silicon replaced germanium on the C54 lattice causing the decrease in the Ge index of the C54 TiM₂ (y≤x), and
- (3) the remaining silicon and the excess germanium diffused to the C54 grain boundaries where it precipitated as the Si_{1-z}Ge_z (z>x).

Because the solubility of silicon and germanium in C54 TiM₂ is limited, both the replacement of germanium with silicon in the C54 TiM₂ and the growth of the grain-boundary decorations continues concurrently. The driving force for the germanium segregation was modeled as a decrease in the C54 TiM₂ crystal energy that accompanied the composition change of the C54 TiM.²⁷ The driving force was modeled in terms of the crystal energy of C54 Ti(Si_{1-v}Ge_v)₂ as

$$\Delta H_{C54}(y) = \Delta H_{C54}(0) - y^* [\Delta H_{C54}(0) - \Delta H_{C54}(1)], \quad (4)$$

where $\Delta H_{C54}(0)$ is the heat of formation of C54 TiSi₂, $\Delta H_{C54}(1)$ is the heat of formation of C54 TiGe₂, and $\Delta H_{C54}(y)$ is the heat of formation of C54 Ti(Si_{1-y}Ge_y)₂. Since C54 TiSi₂ has a lower heat of formation than C54 TiGe₂,³¹ the heat of formation of C54 Ti(Si_{1-y}Ge_y)₂ decreases as y decreases (i.e., as germanium is replaced by Si in C54 TiM₂ the crystal energy of the C54 TiM₂ decreases).²⁷ While the first-order approximation of the C54 crystal energy [Eq. (4)] is sufficient to understand the segregation effects addressed in this study, higher-order terms, including entropy of mixing, will determine the true equilibrium structures. Studies are in progress to explore these contributions.

From the results of this study it appears that germanium also segregates from the C49 phase of TiSi₂. During the Ti-Si_{0.68}Ge_{0.32} reaction, segregation of germanium from C49 TiM₂ was observed after annealing at 530 °C, but the segregation of germanium from C54 TiM₂ was not detected until after annealing at >570 °C (Table I). This suggests that the driving force for germanium segregation is greater for the C49 phase and/or the mobility of silicon and germanium is greater in the C49 phase. In a recent study of the phase formation sequences in $Ti-Si_{1-x}Ge_x$ solid phase reactions it was proposed that the difference in crystal energies between C49 TiSi₂ and C49 TiGe₂ is greater than the difference in crystal energies between C54 TiSi₂ and C54 TiGe₂.⁹ In a study by Motakef et al.³² it was observed that silicon is more mobile in the C49 phase of TiSi₂ than in the C54 phase. Such differences in the crystal energies and mobilities could cause the segregation of germanium out of the C49 phase of TiM₂ at lower temperatures than required for similar germanium segregation out of the C54 phase. By analogy to germanium segregation from C54 TiM₂ it is assumed that the germanium segregating out of C49 TiM_2 accumulates in the C49 TiM_2 grain boundaries.

C. Effects of film thickness on the nucleation of C54 TiM_2 from C49 TiM_2

In the 400 Å Ti–Si_{1-x}Ge_x samples it was observed that the C54 TiM₂ nucleation barrier decreased with increasing Ge index x. If the only effect of germanium in the Ti–Si reaction is a reduction of the C54 TiM₂ nucleation barrier then the effect observed in the 400 Å Ti–Si_{1-x}Ge_x samples should also be observed in the 100 Å Ti–Si_{1-x}Ge_x samples. In the 100 Å Ti–Si samples annealed at 710, 730, 750, and 770 °C the lowest temperature at which C54 TiSi₂ was detected was 750 °C. An examination of the two 100 Å Ti–Si_{0.90}Ge_{0.10} samples annealed at 750 and 770 °C indicated that C49 TiM₂ was the only titanium germanosilicide phase present, suggesting that the germanium was responsible for more than just a reduction in the C54 TiM₂ nucleation barrier.

The delayed formation of the C54 phase observed as a result of adding germanium to samples prepared from titanium layers 100 Å thick may be due to two effects. The first of these effects is increased thermal grooving and agglomeration of the C49 phase prior to the nucleation of the C54 phase. The increased agglomeration decreases the number of preferred C54 nucleation sites along the C49 grain boundaries, and the increased thermal grooving along the remaining C49 TiM₂ grain boundaries may interfere with the nucleation C54 TiM₂ at these remaining sites. The agglomeration of the C49 phase also limits the growth of the C54 phase

(i.e., the C54 phase can only grow laterally through connected C49 grains, and the growth of the C54 is terminated where the C49 has agglomerated).

The second effect is the precipitation of a germaniumrich alloy in the grain boundaries of the C49 phase, also prior to the nucleation of the C54 phase. The formation of grainboundary precipitates may destroy some or most of the preferred nucleation sites in the grain boundary. For a C54 TiM_2 nucleus to form, centered on a C49 TiM_2 grain boundary, any excess silicon and germanium in the C49 TiM_2 grain boundary would either

- (1) have to be forced out of the C49 $TiSi_2$ grain boundary before or during the C54 $TiSi_2$ nucleation and growth or
- (2) be dissolved in the C54 TiM_2 , increasing the C54 TiM_2 crystal energy.

Both thermal grooving (agglomeration) and germanium segregation are related to the mobility of the atomic species (i.e., both are thermally activated processes requiring material transport).^{3,16,27} The effects of these two process are more evident in thin films because increased annealing temperatures are required to overcome the C54 TiM₂ nucleation barrier as film thickness decreases (independent of the effects of germanium). Rapid thermal annealing techniques make it possible to use high annealing temperatures (required to activate the rapid C49-to-C54 transformation) and short annealing durations (which minimizes the effects of agglomeration and germanium segregation). If the C49-to-C54 transformation can be activated in the Ti-Si₁₋, Ge, samples prior to the onset of agglomeration or germanium segregation then the reduced C54 TiM2 nucleation barrier caused by the presence of germanium may actually reduce the annealing temperature and duration needed to completely transform the C49 TiM_2 to C54 TiM_2 .

V. CONCLUSIONS

The addition of germanium to the silicon in the titanium-silicon solid phase reaction affects the reaction in several ways. The addition of germanium decreases the C49 TiM_2 -to-C54 TiM_2 nucleation barrier. Following the formation of $Ti(Si_{1-x}Ge_x)_2$ (in either the C49 or C54 phase) germanium segregates out of the titanium germanosilicide, if silicon is available to replace it, and germanium-rich Si-Ge alloy precipitates at the TiM_2 grain boundaries. The addition of germanium also increases the rate at which TiM_2 agglomerates. Both agglomeration and germanium segregation require material transport, and the rates of these processes increase with annealing temperature.

The initial Ti film thickness also has a significant effect on the Ti–Si_{1-x}Ge_x reaction. In the Ti–Si reaction, decreasing the titanium film thickness from 400 to 100 Å causes the C49-to-C54 nucleation barrier to increase. At the increased annealing temperature needed to overcome the increased C54 nucleation barrier, the agglomeration of the C49 TiM₂ and the germanium segregation from the C49 TiM₂ become limiting factors to the nucleation of C54 TiM₂ in the 100 Å Ti–Si_{1-x}Ge_x reaction. In thin films the advantage of lowering the C49-to-C54 nucleation barrier may be partially (or completely) offset by the segregation of germanium and the increase in agglomeration. However, if rapid thermal processing can be used to nucleate and grow the C54 phase, prior to the onset of the limiting effects of agglomeration and germanium segregation, then the technological use of such thin films may be possible.

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