Effect of composition on phase formation and morphology in $Ti-Si_{1-x}Ge_x$ solid phase reactions

D. B. Aldrich^{a)}, Y. L. Chen, D. E. Sayers, and R. J. Nemanich Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202

S.P. Ashburn and M.C. Öztürk

Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina 27695-7911

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The effects of $Si_{1-x}Ge_x$ alloy composition on the $Ti-Si_{1-x}Ge_x$ solid phase reaction have been examined. Specifically, effects on the titanium germanosilicide phase formation sequence, C54 Ti $(Si_{1-v}Ge_v)_2$ nucleation temperature, and C54 Ti $(Si_{1-v}Ge_v)_2$ morphology were examined. It was determined that the $Ti-Si_{1-x}Ge_x$ reaction follows a "Ti-Si-like" reaction path for Si-rich $Si_{1-x}Ge_x$ alloys and follows a "Ti–Ge-like" reaction path for Ge-rich $Si_{1-x}Ge_x$ alloys. The coexistence of multiple titanium germanosilicide phases was observed during Ti-Si_{1-x}Ge_x reactions for Si_{1-x}Ge_x alloys in an intermediate composition range. The morphology and stability of the resulting C54 germanosilicides were directly correlated to the $Ti-Si_{1-x}Ge_x$ reaction path. Smooth continuous C54 titanium germanosilicide was formed for samples with $Si_{1-x}Ge_x$ compositions in the "Ti-Si-like" regime. Discontinuous islanded C54 germanosilicides were formed for samples with $Si_{1-x}Ge_x$ compositions in the mixed phase and "Ti-Ge-like" regimes. Using rapid thermal annealing techniques, it was found that the C54 titanium germanosilicides were stable to higher temperatures. This indicated that the morphological degradation occurs after C54 phase formation. The C54 Ti(Si_{1-x}Ge_x)₂ formation temperature was examined as a function of alloy composition and was found to decrease by ≈ 70 °C as the composition approached $x \approx 0.5$. An optimum Si_{1-x}Ge_x alloy composition range of $0 \le x \le 0.36$ was determined for the formation of stable-continuous-low-resistivity-C54 titanium germanosilicide films from the solid phase reaction of Ti and $Si_{1-x}Ge_x$ alloy. The results were described in terms of the relevant nucleation processes.

I. INTRODUCTION

The C54 phase of titanium disilicide (TiSi₂) is often used in microelectronics for interconnects and source and drain contacts. The C54 phase of TiSi₂ has a low resistivity (13–25 $\mu\Omega$ cm) and exhibits a low Schottky barrier with both p- and n-type silicon (~0.60 eV).¹ The C54 phase of TiSi2 is usually formed by the solid phase reaction of Ti and Si in the multistep SALICIDE (self-aligned silicide) process.¹ The high temperature solid phase reaction of Ti with Ge can also result in the formation of a low resistivity C54 TiGe₂. The C54 phase of TiGe₂ forms at temperatures comparable to the C54 TiSi₂ formation temperature.^{2,3} We have shown previously that C54 $Ti(Si_{1-v}Ge_v)_2$, isomorphic with C54 TiSi₂, results from the high temperature solid phase reaction of Ti and $Si_{1-x}Ge_x$ over the entire alloy composition range $(0.0 \le x \le 1.0)^4$ Recently, selective deposition of $Si_{1-x}Ge_x$ prior to the solid phase Ti metallization reaction has been developed as a technique for raised source and drain contacts.⁵⁻⁷ This novel application and the potential use of $Si_{1-x}Ge_x$ in device structures motivates the search for information about the metallization of this material.⁸⁻¹¹

The bilayer solid phase Ti–Si reaction usually results in the formation of at least two prominent crystalline phases: C49 TiSi₂ and C54 TiSi₂.^{1,12,13} Initially Ti and Si interdiffuse to form a disordered intermixed *a*-Ti–Si interface layer.^{13,14} Following the formation of the disordered layer, TiSi₂ nucleates at the *a*–Ti–Si/Si interface.^{13,14} The TiSi₂ nucleates in the metastable C49 phase (base-centered orthorhombic¹⁵), which is not the stable C54 TiSi₂ phase listed in the Ti–Si binary phase diagram.^{16,17} After an interfacial layer of C49 TiSi₂ forms, Si diffuses through the C49 TiSi₂ layer and the silicide grows toward the Ti surface.^{13,14} The C49 TiSi₂ grows until the Ti layer has been completely reacted. This planar growth of C49 TiSi₂ from the Ti/Si

^{a)}Current address: Texas Inst., Inc., SPDC, P.O. Box 655012, MS461, Dallas, Texas 75265.

interface to the Ti surface can result in a relatively smooth C49 TiSi₂ surface. The lower crystal energy of the C54 phase of TiSi₂ provides a driving force for the polymorphic C49 to C54 transformation of the TiSi₂ layer, and at higher temperatures the silicide film may transform to C54 TiSi₂. Contamination in the Ti film and at the Ti/Si interface can have a profound effect on the reaction.^{13,18} The presence of contamination at the Ti/Si interface can limit the diffusion of Si into Ti and cause the formation of titanium silicide phases richer in Ti than TiSi₂. In a study of such reactions by Berti *et al.*,¹⁸ the formation of Ti₅Si₃ and Ti₅Si₄ was observed.

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 solid phase reaction are Ti₆Ge₅ and C54 TiGe₂.^{3,19,20} Initially, the Ti₆Ge₅ phase forms by diffusion-controlled growth from the Ti-Ge interface, through the Ti layer, to the sample surface. As in the Ti-Si system, the planar growth of this first phase results in a relatively smooth titanium germanide surface.²¹ At higher annealing temperatures Ge diffuses into the Ti₆Ge₅ and C54 TiGe₂ nucleates as columns extending from the Ti_6Ge_5/Ge interface to the Ti₆Ge₅ surface. The TiGe₂ regions then grow laterally through the Ti_6Ge_5 film.^{3,19} As in other nucleationcontrolled solid-state reactions, a roughening of the germanide surface accompanies the Ti₆Ge₅ to C54 TiGe₂ transition.^{19,22,23} (It is more correct to write this reaction as 7Ge + Ti₆Ge₅ \rightarrow 6TiGe₂.)

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.^{4,21} Several other studies have investigated properties of the $Ti-Si_{1-r}Ge_r$ reaction, ^{21,22,24,25} including the formation and agglomeration of low resistance C54 titanium germanosilicide thin films and intermediate phase formation during the Ti-Si_{1-r}Ge_r solid phase reaction. In a study by Thomas *et al.*,²¹ the titanium germanosilicide phase formation sequences that occur during $Ti-Si_{1-x}Ge_x$ solid phase reactions were investigated. The formation of C49 TiM_2 (M = Si_{1-v}Ge_v) was observed during the Ti-Si_{0.8}Ge_{0.2} reaction, the formation of Ti₆M₅ during the Ti-Si_{0.25}Ge_{0.75} reaction, and both C49 TiM2 and Ti₆M5 during the Ti-Si_{0.5}Ge_{0.5} reaction. In the Ti-Si and Ti-Ge solid phase reactions, the primary diffusing species are Si and Ge, respectively.^{13,21} The initial crystalline phases in both systems experience diffusion-controlled growth, and it is anticipated that the relative diffusion rates of Si and Ge in the $Ti-Si_{1-r}Ge_r$ reaction may effect the composition of the intermediate phases that form. Contamination at the $Ti/Si_{1-x}Ge_x$ interface may also affect the phase formation sequence. The surface, interface, and crystal energies of $Si_{1-x}Ge_x$, Ti, and the various titanium germanosilicide phases will determine the nucleation barriers for the formation of the titanium germanosilicide phases.²³ The nucleation barriers will, in turn, determine which phases form during the $Ti-Si_{1-x}Ge_x$ reaction.

In this study the $Ti-Si_{1-x}Ge_x$ reaction was investigated. The effect of alloy composition on the phase formation sequence, relative reaction rates, and C54 TiM_2 formation and stability were examined. Samples for this study were produced by reacting Ti with a wide range of $Si_{1-x}Ge_x$ alloy compositions (x = 0.00, 0.33, 0.41, 0.55, 0.58, 0.65, 0.72, and 1.00).Several different annealing temperatures and durations were used. Structural and compositional properties were examined using x-ray diffraction (XRD) and depth profile Auger electron spectroscopy (DPAES). The morphologies of the surfaces and interfaces were examined using scanning electron microscopy (SEM) and cross-sectional transmission electron microscopy (XTEM). The sheet resistances of the samples were determined using four-point probe measurements.

II. EXPERIMENTAL

Samples annealed for 10 min were used to study the effect of alloy composition on the titanium germanosilicide phase formation sequence. Ultrahigh vacuum (UHV) cleaning, deposition, and annealing techniques were used during the preparation of the 10 min annealed samples to minimize the effects of contamination on the $Ti-Si_{1-x}Ge_x$ solid phase reaction. Samples annealed for 10 min at high temperatures were used to study the nucleation temperature, morphology, and thermal stability of C54 TiM₂ (the low resistivity titanium germanosilicide phase). To study the effects of annealing duration on titanium germanosilicide formation and stability, several sets of samples were produced using an annealing duration of 10 s. To produce the short duration annealed samples, rapid thermal chemical vapor deposition (RTCVD) and rapid thermal annealing (RTA) techniques were used.

The one inch diameter Si(100) wafers used in preparation of the UHV processed samples were precleaned by the manufacturer using a standard RCA cleaning procedure prior to shipment. In the laboratory the wafers were cleaned prior to use by (i) exposure to UV generated ozone to remove hydrocarbons from the surface and to form a stable oxide, (ii) spin etching with a solution of hydrofluoric acid: H₂O: ethanol (1:1:10) to remove the oxide and passivate the surface with hydrogen, and (iii) an *in situ* thermal desorption at >850 °C for 10 min to remove any surface contaminants that might 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 and held at 550 °C for the deposition of a homoepitaxial silicon buffer layer $(\approx 225 \text{ Å})$ and a heteroepitaxial single crystal Si_{1-x}Ge_x allow layer (2000 Å–2500 Å). Alloy compositions of x = 0.33, 0.41, 0.58, 0.65, and 0.72 were deposited. The Si buffer layer and $Si_{1-x}Ge_x$ layers were not intentionally doped. Silicon and germanium were codeposited from two electron beam evaporation sources. The Si and Ge deposition rates were monitored using oscillating quartz crystal monitors. Feedback from the deposition monitors was used to automatically control the relative Si and Ge deposition rates, and the maximum composition variation during deposition was approximately 2%. The compositions of the deposited $Si_{1-x}Ge_x$ alloys were determined from Rutherford backscattering (RBS) and x-ray absorption fine structure (XAFS) analysis of native $Si_{1-x}Ge_x$ layers similarly prepared.²⁷ Following deposition of the epitaxial $Si_{1-x}Ge_x$ alloy layer, each sample was cooled to <150 °C and 400 Å of titanium was deposited from an in situ hot-filament Ti source. The thickness of the deposited Ti was also monitored using an oscillating quartz crystal deposition monitor. Upon completion of the titanium deposition, the samples were annealed *in situ* at temperatures of 530 °C, 570 °C, 615 °C, 660 °C, or 700 °C. During annealing 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. 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 Si and Ge deposition was $< 1 \times 10^{-8}$ Torr, the pressure during Ti deposition was $<5 \times 10^{-9}$ Torr, and the pressure during annealing was $< 1 \times 10^{-9}$ Torr.

The in situ heater used to anneal the UHV processed samples consists of a tungsten coil and a thermocouple which are positioned $\approx 2 \text{ mm}$ from the backside of the Si wafer during processing. The heater thermocouple was calibrated using a clean Si(100)substrate and a Minolta/Land Cyclops 52 optical pyrometer to measure the Si surface temperature at the face of the Si wafer. The optical pyrometer was positioned normal to the substrate surface at a distance of 1 m. The optical pyrometer was focused on the substrate through a quartz viewport, and an emissivity setting of 0.4 was used. The viewport was positioned on the deposition system such that it would receive minimum deposition from the Si, Ge, and Ti deposition sources (i.e., no direct line of sight between any of the sources and the viewport). The substrate temperature was varied from 500 °C to 1000 °C in 50 °C steps and optical pyrometer readings were recorded at each step. A function for the temperature, as measured by the optical pyrometer, as a function of heater setting was determined, and the optical pyrometer temperatures

are the annealing temperatures reported in this study. To facilitate the comparison of the results of this study with the results of other studies, Ti–Si samples were prepared and studied to determine the relative C54 TiSi₂ nucleation temperature. The Ti–Si samples were prepared by UHV deposition and annealing, as outlined above, using ≈ 9 °C annealing temperature steps. The nucleation of C54 TiSi₂ from C49 TiSi₂ was observed following a 10 min anneal in UHV at 605 °C, but not at 596 °C. The C54 TiSi₂ nucleation temperature measured in this study can be used to renormalize the annealing temperatures listed when comparing the results of this study with other studies.

The samples prepared using RTA consisted of 3000 Å of Si_{0.45}Ge_{0.55}, Si_{0.35}Ge_{0.65}, or Ge deposited by RTCVD on a chemically cleaned 4 in. Si(100) substrate²⁸ (a bare Si wafer was included as a reference for the Ti–Si reaction). A 300 Å Ti layer was subsequently sputter-deposited. Each 4 in. wafer was then cleaved into 1 cm² pieces which were RTA processed in an argon ambient at atmospheric pressure for 10 s at different temperatures. Annealing temperatures ranged from 300 °C to 850 °C in 50 °C steps. This technique ensured that all the samples for each Si_{1-x}Ge_x alloy composition indeed had the same Si_{1-x}Ge_x alloy composition. A more detailed description of the sample preparation process has been reported previously.²⁵

The structural properties of the alloys were examined using a Rigaku x-ray diffractometer. Surface and interface morphologies were examined using a JEOL 6400 field-emission scanning electron microscope and a Topcon 002B transmission electron microscope. Both the JEOL 6400 and the Topcon 002B electron microscopes were equipped with energy-dispersive x-ray spectrometers. Depth profiled Auger electron spectroscopy was used to examine compositional changes as a function of the depth in the sample. Depth profile composition measurements were performed with a JEOL JAMP-30 Auger electron microprobe system. The Auger microprobe was positioned using SEM. Auger data collection and sample sputtering were cycled until the composition of the region of interest was determined. The C, O, Ti, Si, and Ge Auger signals were monitored. In the UHV prepared samples C or O contamination was detected only at the surface of the samples, apparently due to the exposure of the samples to atmosphere after removal from the UHV deposition system. Standard Si, Ge, Ti, and $Si_{1-x}Ge_x$ samples were used to check the relative Si, Ge, and Ti Auger sensitivities.

III. RESULTS

A. Titanium germanosilicide phase formation

X-ray diffraction was used to determine the titanium germanosilicide phases present after 10 min annealing of

the $Ti-Si_{1-x}Ge_x$ bilayer films. X-ray diffraction scans of the samples were compared with XRD scans of four thin film standards: C49 TiSi₂, C54 TiSi₂, Ti₆Ge₅, and C54 TiGe₂. For all of the samples the peak patterns in the XRD scans matched the standards, with some peak shifting (which was anticipated because the samples contained both Si and Ge). In Fig. 1 the titanium germanosilicide phases observed in the samples are plotted for all of the $Si_{1-x}Ge_x$ alloy compositions and annealing temperatures used. All the samples annealed at, or above, 650 °C contained the C54 phase of TiM_2 . All the samples, with 0.0 < x < 1.0, annealed at 570 °C and 615 °C also contained the C54 phase of TiM2. After annealing at 530 °C the formation of Ti₆M₅ was observed for Ge-rich Si_{1-x}Ge_x alloy compositions $x \ge$ 0.65, and the formation of C49 TiM_2 was observed for the Si-rich alloy composition of x = 0.33. In the intermediate composition range, $0.41 \le x \le 0.58$, mixed phases were observed following a 530 °C anneal. For x = 0.41 the formation of both Ti₆M₅ and C49 TiM₂ was observed, and for x = 0.58 the formation of both Ti_6M_5 and C54 TiM_2 was observed.

Cross-sectional transmission electron microscopy (XTEM) and EDXS were used to further examine the two samples which contained multiple titanium germanosilicide phases (x = 0.41 and x = 0.58, both annealed at 530 °C). Micrographs of the two samples appear in Fig. 2. The XTEM micrograph of the



FIG. 1. The titanium germanosilicide phases present in the Ti + Si_{1-x}Ge_x samples following 10 min UHV annealing were examined using XRD. The XRD scans of each of the samples were compared with XRD scans from similarly prepared C54 TiSi₂, C54 TiGe₂, C49 TiSi₂, and Ti₆Ge₅ thin film standards. In all cases the peaks were identified and the titanium germanosilicide phases present were determined. The titanium germanosilicide phases observed are plotted for all of the Si_{1-x}Ge_x alloy compositions and annealing temperatures used. In two of the samples (x = 0.41 and x = 0.58, both annealed at 530 °C) multiple titanium germanosilicide phases were detected.



FIG. 2. The two UHV processed Ti-Si_{1-x}Ge_x samples (x = 0.41 and x = 0.58, both annealed at 530 °C) in which multiple titanium germanosilicide phases were detected were examined using XTEM and EDXS. In the XTEM micrograph of the x = 0.41 sample (a) it can be seen that the two titanium germanosilicide phases formed as layers. The surface layer is the phase richest in Ti (Ti₆M₅) and the underlaying layer is the phase richest in Si-Ge (TiM₂), as identified using EDXS analysis. Small regions of Ti₆M₅ were identified in the C49 TiM₂ layer. In the XTEM micrograph of the x = 0.58 sample (b) lateral segregation of the two titanium germanosilicide phases can be seen. The specific phases were identified using EDXS and are labeled appropriately in the micrograph.

x = 0.58 sample [Fig. 2(b)] reveals that the two titanium germanosilicide phases present are laterally segregated. Using EDXS (20 nm probe) the specific phases were identified as Ti₆M₅ and TiM₂ and are labeled appropriately in the figure. The XTEM micrograph of the x = 0.41 sample [Fig. 2(a)] reveals that the two titanium germanosilicide phases present in this sample have formed in layers. Again the phases were identified using EDXS, and it was determined that the surface layer consisted of the more Ti-rich germanosilicide phase (Ti₆M₅) and the underlying layer consisted of the more Si–Ge-rich germanosilicide phase (TiM_2) . It appears that in this sample (i) Ti_6M_5 may have initially grown as Si and Ge diffused into the Ti layer, and (ii) C49 TiM₂ grew as Si and Ge diffused into the Ti₆M₅ layer. In Fig. 2(a) it also appears that the C49 TiM_2 layer may be discontinuous. At varying intervals across the C49 TiM₂ layer, Ti_6M_5 islands are observed. In the

XTEM micrograph the difference in contrast between the Ti₆(Si_{1-y}Ge_y)₅ surface layer and the Ti₆(Si_{1-z}Ge_z)₅ islands suggests that the surface layer and islands may have different compositions (i.e., $z \neq y$) or different crystal orientations. It appears that the Ti₆(Si_{1-z}Ge_z)₅ regions resisted transformation to C49 TiM₂ as the C49 TiM₂ layer grew from the initial Ti₆(Si_{1-y}Ge_y)₅/ Si_{1-x}Ge_x interface toward the Ti₆(Si_{1-y}Ge_y)₅ surface.

In a previous study of the stability of C54 TiM_2 , it was observed that at high annealing temperatures $(\geq 660 \text{ °C})$ Ge segregates out of the C54 TiM₂ during 10 min annealing. Depth profiled Auger spectroscopy (DPAES) was used to examine the compositions of the samples annealed at 530 °C, 570 °C, and 615 °C to determine if segregation occurs in this temperature range. The DPAES analysis was also used to determine which titanium germanosilicide phases were present, as a check to the XRD analysis. The DPAES analysis could not distinguish between the C49 and C54 structures of the TiM_2 phase, but it could distinguish between the TiM_2 and Ti_6M_5 phases. For all the sample examined, the DPAES analysis was in agreement with the XRD analysis. Within the errors of the measurements, the measured Ge indices (y) of the $Ti(Si_{1-y}Ge_y)_2$ and $Ti_6(Si_{1-y}Ge_y)_5$ titanium germanosilicides were in good agreement with the Ge indices (x) of the deposited $Si_{1-x}Ge_x$ alloys, indicating that little, if any, segregation had occurred during the reactions.

B. C54 Ti(Si_{1-v}Ge_v)₂ morphology

It is possible to form C54 TiSi₂ with a relatively smooth surface, but the surface of C54 TiGe₂ formed during Ti–Ge solid phase reactions is very rough.^{3,21,23} Both of these types of C54 TiM₂ morphology can be seen in an SEM micrograph of the Ti–Si_{0,35}Ge_{0,65} sample which was UHV annealed at 570 °C for 10 min [Fig. 3(a)]. The tilted cross-sectional SEM micrographs in Figs. 3(b) and 3(c) reveal that the two different morphologies correspond to two different C54 TiM₂ grain structures. The smooth morphology occurs in regions where large grain C54 TiM₂ has formed [Fig. 3(b)], and the rough morphology occurs in regions where small grain C54 TiM₂ has formed [Fig. 3(c)].

To examine the high temperature stability of C54 Ti(Si_{1-y}Ge_y)₂, four Ti-Si_{1-x}Ge_x samples (x = 0.33, 0.41, 0.58, and 0.65) were UHV annealed at 700 °C for 10 min. The SEM micrographs of the C54 titanium germanosilicide morphologies are shown in Fig. 4. In the x = 0.33 sample a continuous layer of large grain C54 TiM₂ has formed [Fig. 4(a)]. The effect of Ge segregation, which occurs at high annealing temperatures, can be seen in the x = 0.33 sample as the formation of grain boundary decorations along the large C54 titanium germanosilicide grain boundaries. The Ge





and tilted cross section SEM micrographs of the smooth (b) and rough (c) regions revealed that the morphology was correlated to the C54 TiM₂ grain structure. The regions with smooth surface morphology consisted of large grain C54 TiM₂ and the regions with rough morphology consisted of small grain C54 TiM₂.

segregation has been the subject of a previous study.²⁹ In the Ti–Si_{0.59}Ge_{0.41} sample, areas of smooth and rough morphology are observed [Fig. 4(b)]. Close inspection



FIG. 4. Samples containing C54 Ti(Si_{1-y}Ge_y)₂ were produced by UHV annealing Ti-Si_{1-x}Ge_x samples at 700 °C for 10 min. The alloy compositions of x = 0.33 (a), x = 0.41 (b), x = 0.58 (c), and x = 0.65 (d) were used. The resulting surface morphologies were examined using SEM. For the x = 0.33 alloy composition the formation of large continuous C54 TiM₂ grains is observed (a). The formation of grain boundary decorations is attributable to Ge segregation which occurs after C54 titanium germanosilicide formation.²⁹ In the other samples, x = 0.41, 0.58, and 0.65, the formation of discontinuous small faceted C54 TiM₂ islands is also observed. The areal coverage of the islanded morphology increases with increasing Ge index.

of the rough morphology revealed that the C54 TiM₂ had formed small faceted islands with regions of exposed Si_{1-x}Ge_x (Fig. 5). The faceted C54 TiM₂ islands are discontinuous across the surface of the underlying Si_{1-x}Ge_x layer and may represent a degradation of the desired continuous C54 TiM₂ layer. In the x = 0.41, 0.58, and 0.65 samples, the areal coverage of the faceted island morphology increases with increasing Ge index [Figs. 4(b), 4(c), and 4(d)].

From a comparison of the Ti-Si_{0.35}Ge_{0.65} samples which were UHV annealed for 10 min at 570 °C (Fig. 3) and 700 °C [Figs. 4(d) and 5], it appears that the large grain C54 TiM₂ is more stable to agglomeration at high temperatures than the small grain C54 TiM₂. After the 570 °C anneal there are clearly distinct regions of large and small grain C54 TiM₂ [Fig. 3(a)], and both regions are continuous. After the 700 °C anneal the small grain C54 TiM₂ appear to have agglomerated and the grains have become faceted islands (Fig. 5). After the 700 °C anneal the morphology of the large grain C54 TiM₂ remains relatively unaffected, and the only observable change is the formation of Si_{1-z}Ge_z decorations along the C54 TiM₂ grain boundaries [Fig. 4(d)].

C. Rapid thermal annealing

In a previous study of the stability of C54 TiM_2 , it was observed that by limiting the annealing duration, the segregation of Ge out of C54 TiM₂ could be limited.²⁹ In this study RTA was used to reduce the annealing duration from 10 min to 10 s to examine the affect of annealing duration on the stability of C54 Ti(Si_{1-v}Ge_v)₂ (i.e., the islanding observed in some of the samples which were annealed for 10 min). The agglomeration of C54 TiM₂ after annealing at 700 °C for 10 min was observed for alloy compositions of x = 0.41, 0.58, and 0.65. Samples annealed for 10 s using RTA processing were produced using $Si_{1-x}Ge_x$ alloy compositions of x = 0.55 and 0.65 (x = 0.0 and 1.0 were included for comparison). The sheet resistances, measured as a function of annealing temperature, are plotted in Fig. 6 for each of the $Si_{1-x}Ge_x$ alloy compositions used. During the $Ti-Si_{1-x}Ge_x$ reaction, the formation of a continuous layer of low resistivity C54 Ti $(Si_{1-y}Ge_y)_2$ is marked by the drop in the sheet resistance to its lowest value. As can be seen in Fig. 6 the temperatures at which the continuous C54 TiM₂ layers formed during the 10 s anneals appear to increase with increasing Ge index. From the



FIG. 5. Scanning electron micrograph of a C54 TiM₂ sample which shows the formation of small faceted islands of C54 TiM₂ on the partially exposed underlying $Si_{1-x}Ge_x$ layer. Along the edge of the sample three of the faceted islands were dislodged (during cleaving), revealing that both the C54 TiM₂ surface and C54 TiM₂/Si interface are faceted. Areas of exposed $Si_{1-x}Ge_x$ are clearly visible between the pits from the dislodged C54 TiM₂ islands (see label in figure).



FIG. 6. The sheet resistances of $Ti-Si_{1-x}Ge_x$ bilayer structures which were annealed for 10 s were measured for a range of annealing temperatures. The sheet resistances are plotted for the alloy compositions of x = 0.00, 0.55, 0.65, and 1.00. For each alloy composition the drop in the measured sheet resistance to the lowest value indicates the formation of a continuous layer of low resistivity C54 titanium germanosilicide.

data plotted in Fig. 6, it appears that for a 10 s annealing duration the C54 TiM₂ layers in the x = 0.55 and 0.65 samples are stable to temperatures greater than 850 °C. This is 150 °C above the temperature at which agglomeration was observed in the C54 TiM₂ layers which were annealed for 10 min.

IV. DISCUSSION

Investigations of the Ti–Si and Ti–Ge reaction paths have repeatedly reported Ti–Si \rightarrow C49 TiSi₂ \rightarrow C54 TiSi₂ and Ti–Ge \rightarrow Ti₆Ge₅ \rightarrow C54 TiGe₂, respectively, for contamination-free solid phase reactions.^{3,13,19,30} In the following discussion it is assumed that C49 TiM_2 , Ti_6M_5 , and C54 TiM_2 (M = $Si_{1-y}Ge_y$) are the predominant crystalline titanium germanosilicide phases that form during the $Ti-Si_{1-x}Ge_x$ solid phase reaction (the presence of small amounts of other titanium germanosilicides formed at random or at defect nucleation sites will not affect the analysis). The lattice parameters of C49 and C54 structures of $TiSi_2$ and $TiGe_2$ are known^{4,15,31,32} and for both the C49 and C54 structures the change in the lattice parameters between TiSi2 and TiGe2 is less than 6%, well within the 15% limit of the Hume-Rothery rule for solubility between elements.³³ In this study it is assumed that all three titanium germanosilicide phases considered (Ti₆M₅, C49 TiM₂, and C54 TiM₂) are stable (or metastable) over the entire alloy composition range $(0 \le x \le 1).$

A. Effect of $Si_{1-x}Ge_x$ alloy composition on the $Ti-Si_{1-x}Ge_x$ reaction path

For the $Si_{1-x}Ge_x$ alloy compositions examined, the formation of C54 TiM₂ during the Ti-Si_{1-x}Ge_x solid phase reaction was always preceded by the formation of Ti₆M₅ and/or C49 TiM₂. From the observed titanium germanosilicide phase formations the $Ti-Si_{1-x}Ge_x$ reaction can be divided, by $Si_{1-x}Ge_x$ alloy composition, into three regimes based on the phase formation sequence. During the solid phase Ti-Si_{0.67}Ge_{0.33} reaction the formation of C49 TiM₂ was observed prior to C54 TiM₂ formation, and it is assumed that for a range of Si-rich $Si_{1-x}Ge_x$ alloys (including x = 0.33) the $Ti-Si_{1-x}Ge_x$ reaction will follow a "Ti-Si-like" reaction path (i.e., $Ti-Si_{1-x}Ge_x \rightarrow C49 TiM_2 \rightarrow C54 TiM_2$). During the solid phase Ti-Si_{0.28}Ge_{0.72} reaction, Ti₆M₅ was the only titanium germanosilicide phase observed prior to the formation of C54 TiM₂, and presumably the reaction of Ti with Ge-rich $Si_{1-x}Ge_x$ alloys follows a "Ti–Ge-like" reaction path (i.e., Ti–Si_{1-x}Ge_x \rightarrow $Ti_6M_5 \rightarrow C54 TiM_2$).

The experimental results indicate that between the "Ti–Si-like" and "Ti–Ge-like" regimes there is a mixed phase regime where both C49 TiM₂ and Ti₆M₅ may form during the Ti–Si_{1-x}Ge_x solid phase reaction. In the solid phase reaction of Ti with Si_{0.59}Ge_{0.41} both Ti₆M₅ and C49 TiM₂ were observed to coexist and precede the formation of C54 TiM₂. A XTEM micrograph of the sample containing both Ti₆(Si_{1-y}Ge_y)₅ and C49 TiM₂ appears in Fig. 2(a). In the micrograph there are two prominent layers: a Ti₆(Si_{1-y}Ge_y)₅ surface layer and an underlying C49 TiM₂ layer. Since Ti is the limiting element in the reactions being studied here, it is expected that the Ti richest phase [Ti₆(Si_{1-y}Ge_y)₅] formed prior to the Si–Ge richest phase (C49 TiM₂). Presumably, as in the "Ti–Ge-like" reactions, the Ti₆(Si_{1-y}Ge_y)₅ layer

initially formed by diffusion-controlled growth, from the Ti/Si_{0.59}Ge_{0.41} interface, resulting in the relatively smooth germanosilicide surface apparent in the XTEM micrograph [Fig. 2(a)]. The growth of the Ti₆(Si_{1-y}Ge_y)₅ layer was apparently followed by the nucleation of C49 TiM₂ and the diffusion-controlled growth of the C49 TiM₂ from the Ti₆(Si_{1-y}Ge_y)₅/Si_{0.59}Ge_{0.41} interface through the Ti₆(Si_{1-y}Ge_y)₅ layer.

Also observable in Fig. 2(a) is the presence of a $Ti_6(Si_{1-z}Ge_z)_5$ region in the C49 TiM_2 layer. The interface between the $Ti_6(Si_{1-y}Ge_y)_5$ surface layer and both the underlying C49 TiM₂ and Ti₆(Si_{1-z}Ge_z)₅ regions is continuous. The continuity of the interface suggests that both the C49 TiM₂ and Ti₆(Si_{1-z}Ge_z)₅ regions grow vertically toward the surface of the $Ti_6(Si_{1-y}Ge_y)_5$ surface layer. Parallel growth of the two regions, would, when the vertical growth is complete, result in the lateral segregation of the titanium germanosilicide film into C49 TiM₂ and Ti₆(Si_{1-z}Ge_z)₅ regions. If the lateral segregation is maintained during the transition of the titanium germanosilicide film to C54 Ti M_2 , then the resulting morphology of the C54 TiM₂ film may give an indication of the degree of lateral segregation.

In the "Ti-Si-like" $Ti-Si_{1-x}Ge_x$ reaction, the formation of a smooth C49 TiM₂ film is followed by the polymorphic transformation of the film to C54 TiM₂, and the surface remains relatively smooth. In the "Ti-Gelike" reaction the formation of a smooth Ti₆M₅ layer is followed by the lateral growth of C54 TiM₂, which causes severe roughening of the titanium germanosilicide surface. If a correlation is established between the type of C54 TiM₂ formation reaction (C49 TiM₂ \rightarrow C54 TiM_2 or $Ti_6M_5 \rightarrow C54 TiM_2$) and the morphology of the resulting C54 TiM₂ (smooth or rough, respectively), then the morphologies of the C54 TiM₂ samples can provide insight into the $Ti-Si_{1-x}Ge_x$ reactions which proceeded the formation of C54 TiM_2 . The morphology of C54 TiM₂ formed from the Ti-Si_{0.35}Ge_{0.65} solid phase reaction at 570 °C is shown in Fig. 3(a). Both smooth and rough surface morphologies are observed, suggesting that both C49 TiM2 and Ti6M5, respectively, were present in the titanium germanosilicide layer prior to the transformation of the layer to C54 TiM₂. Figures 3(b) and 3(c) reveal that the smooth regions consist of relatively large C54 TiM₂ grains and the rough regions consist of relatively small C54 TiM₂ grains. This is consistent with observations of Ashburn et al.25 that C54 TiSi₂ grains formed during the Ti-Si solid phase reaction (C49 TiSi₂ \rightarrow C54 TiSi₂) are much larger than the C54 TiGe₂ grains formed during the Ti-Ge solid phase reaction (Ti₆M₅ \rightarrow C54 TiGe₂).

At higher annealing temperatures the two C54 TiM_2 morphologies become more distinct. Annealing at 700 °C causes the rough small grain C54 TiM_2 regions to

island (Fig. 5), but the smooth large grain regions remain relatively unchanged. The C54 TiM₂ morphologies of four $Ti-Si_{1-x}Ge_x$ samples (x = 0.33, 0.41, 0.58, 0.65) annealed at 700 °C for 10 min are shown in Figs. 4(a)-4(d). As noted above, the $Ti-Si_{0.67}Ge_{0.33}$ solid phase reaction follows a "Ti-Si-like" reaction path and the resulting C54 TiM₂ layer was formed by the polymorphic transformation of a C49 TiM₂ precursor layer. Following the 700 °C anneal the C54 TiM₂ layer still maintains a relatively smooth large grain structure [Fig. 4(a)]. During the Ti-Si_{0.59}Ge_{0.41} solid phase reaction the formation of both C49 TiM₂ and Ti_6M_5 was observed after annealing at 530 °C [Fig. 3(a)] and the formation of both smooth and rough regions of C54 TiM₂ is observed after annealing at 700 °C [Fig. 4(b)]. In the higher Ge content samples (x = 0.58and 0.65) the formation of discrete regions of C54 TiM_2 with smooth morphology is observed [Figs. 4(c) and 4(d), respectively]. Comparing the morphologies of the x = 0.41, 0.58, and 0.65 samples [Figs. 4(b), 4(c),and 4(d)], the size of the smooth C54 TiM₂ regions appears to decrease as the Ge index x increases. This observation suggests that the size of the C49 TiM₂ regions which form in the Ti₆M₅ layer (prior to the formation of C54 TiM_2) decreases with increasing Ge index.

The Ti-Si_{0.42}Ge_{0.58} reactions suggest that the transition to C54 TiM₂ begins with the polymorphic transformation of the C49 TiM₂ regions followed by the lateral growth of C54 TiM₂ through the Ti₆M₅ regions. The morphology of the Ti-Si_{0.42}Ge_{0.58} sample, which was UHV annealed at 700 °C for 10 min [Fig. 4(c)], indicates that both regions of Ti₆M₅ and C49 TiM₂ existed prior to the formation of C54 TiM₂. In the Ti-Si_{0.42}Ge_{0.58} sample that was UHV annealed at 530 °C for 10 min laterally segregated regions of Ti₅M₅ and C54 TiM₂ were observed [Fig. 2(b)]. The absence of C49 TiM₂ and the large grain structure of the C54 TiM₂ suggest that during the 530 °C annealing cycle the C49 TiM_2 regions formed and transformed to C54 TiM_2 . The lateral segregation of Ti_6M_5 and C54 TiM_2 suggests that following the polymorphic C49 Ti M_2 to C54 Ti M_2 transformation the C54 TiM₂ grows laterally through the Ti_6M_5 regions.

In the Ti-Si_{1-x}Ge_x solid phase reactions, the morphology of C54 TiM₂, formed at 700 °C, indicates the ranges of alloy compositions where the Ti-Si_{1-x}Ge_x reaction follows a "Ti-Si-like", "Ti-Ge-like", or mixed phase reaction path. The range of compositions for which both smooth and rough C54 TiM₂ morphologies were observed (i.e., both Ti₆M₅ and C49 TiM₂ formation) is $0.41 \le x \le 0.65$. The sample with the next lowest Ge index is x = 0.33, which suggests that the "boundary" between the "Ti-Si-like" and mixed phase reaction regimes is between x = 0.33 and x = 0.41. The sample

with the next highest Ge index, above the mixed phase regime, is x = 0.72, which suggests that the "boundary" between the mixed phase and "Ti-Ge-like" reaction regimes is between x = 0.65 and x = 0.72. Values of x = 0.37 and x = 0.66 were roughly designated for the divisions among the three reaction regimes. In Fig. 1 vertical dashed lines have been drawn to indicate the approximate ranges of the three reaction regimes. The composition ranges and the titanium germanosilicide phase formation sequences are summarized in Table I.

B. Nucleation, rate of formation, morphology, and stability of C54 TiM_2

The nucleation temperature, rate of formation, morphology, and stability of C54 TiM₂ formed during the $Ti-Si_{1-x}Ge_x$ solid phase reaction all appear to be correlated to the $Si_{1-x}Ge_x$ alloy composition. To correlate these properties an estimate was made of the dependence of the C54 TiM_2 nucleation temperature on both the alloy composition and the phase formation sequence. The C54 TiM₂ nucleation temperature, for a given alloy composition, is assumed to be between the highest annealing temperature where C54 TiM₂ formation was not observed and the lowest annealing temperature where C54 TiM₂ formation was observed. In Fig. 1 it appears that the C54 TiM₂ nucleation temperature decreases with increasing Ge index in the "Ti-Si-like" reaction regime. In the "Ti-Si-like" regime, the C54 TiM₂ forms directly from C49 TiM₂. This would indicate that the nucleation barrier for the formation of C54 TiM₂ from C49 TiM₂ decreases with increasing Ge index. In a study by Hong et al.,³² the C49 TiGe₂ to C54 TiGe₂ phase transition, not normally observed in the Ti-Ge solid phase reaction,

TABLE I. The solid phase $Ti-Si_{1-x}Ge_x$ reaction can be divided into three regions, by $Si_{1-x}Ge_x$ alloy composition, based on the titanium germanosilicide phase formation sequence. The observed phase formation sequences and the predicted $Si_{1-x}Ge_x$ alloy composition ranges in which these sequences occur are listed.

| $Si_{1-x}Ge_x$ alloy (composition range) | Model phase formation sequence | | |
|---|--------------------------------|----------------------|----------------------|
| | Ti ₆ M ₅ | C49 TiM ₂ | C54 TiM ₂ |
| x = 0.00 (Ti - Si) | | 1 | 2 |
| $0.00 \le x \le 0.37$ | | 1 | 2 |
| $0.37 \le x \le 0.66$ | 1 | 2 | 3 |
| $0.66 \le x \le 1.00$ | 1 | | 2 |
| x = 1.00 (Ti–Ge) | 1 | | 2 |

The known phase formation sequences for the Ti–Si and Ti–Ge solid phase reactions are listed for comparison. The "boundary" between the "Ti–Si-like" and mixed phase (3 phase) reaction regimes was observed to be between x = 0.33 and x = 0.41 (a value of x = 0.37 was arbitrarily chosen). The "boundary" between the mixed phase (3 phase) and "Ti–Gelike" reaction regimes was observed to be between x = 0.65 and x = 0.72(a value of x = 0.66 was arbitrarily chosen). was examined for thin films of codeposited Ti + 2Ge. In that study sheet resistance measurements were used to determine when a continuous layer of C54 TiGe₂ formed; however, the data also suggest a temperature at which the C54 phase first nucleated. The results of Hong *et al.*³² suggest that C54 TiGe₂ nucleates in C49 TiGe₂ at \approx 500 °C, in good agreement with the trend in the C54 TiM₂ nucleation temperatures observed in the "Ti–Si-like" reaction regime.

The relative C49 TiM_2 to C54 TiM_2 and Ti_6M_5 to C54 TiM₂ transition rates appear to be different. From the sheet resistance measurements of the RTA processed $Ti-Si_{1-x}Ge_x$ samples, the nucleation and formation of C54 TiM₂ can be examined. In Fig. 6 the measured sheet resistances of the Ti-Si-Ge layers initially increase as the annealing temperature is increased. As the annealing temperature is increased further, the sheet resistances decrease and plateau before decreasing, again, to minimum values. The plateaus correspond to the formation of precursor phases prior to the formation of C54 TiM₂ (in Fig. 6 the formation of C49 TiM₂ in the Ti-Si reaction is indicated by the decrease in the sheet resistance at 350 °C, and the formation of Ti₆Ge₅ in the Ti-Ge reaction is indicated by the decrease in the sheet resistance at 400 °C). A decrease in the sheet resistance from the plateau value indicates the initial nucleation of C54 TiM2. If, at the C54 nucleation temperature, the transition to C54 TiM₂ is very rapid and the entire layer transforms to C54 TiM₂ during the 10 s annealing cycle, then the sheet resistance will drop from the plateau value to the minimum value when the annealing temperature is at or above the C54 nucleation temperature. If, at the C54 nucleation temperature, the transition to C54 TiM₂ is relatively slow, then higher annealing temperatures may be required to increase the reaction rate such that the transition of the entire layer to C54 Ti M_2 can be completed during one annealing cycle. The sheet resistances plotted in Fig. 6 indicate that after annealing Ti-Si at 550 °C the titanium silicide is in the C49 phase of TiSi₂, and that after annealing at 600 °C a continuous layer of C54 TiM2 has formed (i.e., the C49 Ti M_2 to C54 Ti M_2 transition is relatively rapid). The transition from Ti₆Ge₅ to TiGe₂ begins at ≈ 650 °C, but a continuous layer of C54 TiGe₂ does not form during the 10 s anneal until the annealing temperature is increased to ≥ 850 °C (i.e., the Ti₆Ge₅ to C54 TiGe₂ transition rate at the C54 TiGe₂ nucleation temperature is relatively slow). The RTA results indicate that, at a given temperature, the transformation of the "silicide layer" from C49 TiSi₂ to C54 TiSi₂ occurs more rapidly than the transformation of the "germanide layer" from Ti₆Ge₅ to C54 TiGe₂.

In the Ti–Si reaction the initial C49 TiSi₂ layer grows vertically followed by a rapid C49 TiSi₂ to C54 TiSi₂ polymorphic transformation (only the first step requires the transport of material). In the Ti-Ge reaction the initial layer of Ti_6M_5 grows vertically followed by the lateral growth of C54 TiM_2 through the Ti_6M_5 layer (both steps require the transport of material). In the Ti-Si reaction only one of the phase transitions requires the transport of material, while in the Ti-Ge reaction both phase transitions require the transport of material. We suggest that the material transport necessary for the Ti₆Ge₅ to C54 TiGe₂ transition may make this phase transition slower than the C49 TiSi2 to C54 TiSi2 polymorphic transformation phase transition. In the $Ti-Si_{1-x}Ge_x$ reactions there is a wide range of compositions for which the Ti₆M₅ phase forms during the reaction, and the formation of this phase may affect the reaction rates of the titanium germanosilicides. For comparison, the plot in Fig. 7 contains: (i) the temperatures at which the nucleation of C54 TiM₂ was observed in the samples annealed for 10 min ("C54 nucleation temperature"), (ii) the temperatures required to produce continuous layers of low resistivity C54 TiM_2 in the samples annealed for 10 s ("C54 layer formation temperature"), and (iii) the division of the $Si_{1-x}Ge_x$ alloy composition range into three regions based on the phase formation sequence of the $Ti-Si_{1-x}Ge_x$ reaction (the same divisions as in Fig. 1).

The C54 layer formation temperatures (RTA temperatures) for the x = 0.55, 0.65, and 1.00 samples are much greater than the estimated C54 nucleation temperatures (10 min anneal temperatures). If the C54 layer formation temperatures for the x = 0.55, 0.65,and 1.00 samples are fit to a line, and the fit is extrapolated to lower Ge content alloys, then the point at which the extrapolated C54 layer formation temperature intersects the estimated C54 nucleation temperature is in the neighborhood of the division between the "Ti-Silike" and mixed phase reaction regimes. The relationship between the C54 nucleation temperature and the C54 layer formation temperature is different in the three sections of Fig. 7. In the "Ti-Ge-like" reaction regime of Fig. 7 the estimated C54 nucleation temperature and the estimated C54 layer formation temperature are separated by more than 100 °C. In the mixed phase reaction regime of Fig. 7 the estimated C54 nucleation temperature and the estimated C54 layer formation temperature converge as the Ge index decreases. Although there were no RTA samples produced with alloy compositions in the "Ti-Si-like" reaction regime $(0 < x \le 0.37)$, we anticipate that in this regime the C54 layer formation temperature may be only slightly higher than the C54 nucleation temperature.

For alloy compositions in the "Ti–Ge-like" reaction regime (right side of Fig. 7), C54 TiM₂ forms directly from the initial Ti₆M₅ layer. If the C54 TiM₂ grows laterally across the Ti₆M₅ layer, then by analogy to the Ti–Ge reaction the Ti₆M₅ to C54 TiM₂ transition will



FIG. 7. Comparison of the estimated C54 TiM₂ nucleation temperatures and the C54 TiM₂ layer formation temperatures (the annealing temperatures required to form continuous layers of low resistivity C54 TiM₂ in samples annealed for 10 s). The estimated C54 nucleation temperatures (solid circles and solid line) were estimated from the data plotted in Fig. 1. The C54 TiM₂ layer formation temperatures were determined from the data plotted in Fig. 6. The C54 TiM₂ layer formation temperatures are indicated by the open squares. The dashed line represents a linear fit of the C54 TiM₂ layer formation temperatures for x = 0.55, 0.65 and 1.00.

be relatively slow. A slow Ti₆M₅ to C54 TiM₂ transition rate would account for the large temperature difference between the C54 nucleation temperature and the C54 layer formation temperature in this region (i.e., for short annealing durations a higher annealing temperature is needed to increase the reaction rate such that a continuous layer of C54 TiM₂ can form during the annealing cycle). In the "Ti-Si-like" reaction regime (the high Si content alloys) C49 TiM₂ is the only phase that precedes the C54 TiM2 phase. It is anticipated that, analogous to the Ti-Si reaction, the C49 TiM₂ to C54 TiM₂ polymorphic transformation will be relatively rapid and that in the "Ti-Si-like" reaction regime the C54 layer formation temperature will be only slightly greater than the C54 nucleation temperature. In the mixed phase regime (middle section of Fig. 7), the formation of both Ti₆M₅ and C49 TiM₂ complicates the formation of C54 TiM₂.

In some of the samples it was observed that both Ti_6M_5 and C49 TiM_2 coexisted prior to the formation of C54 TiM_2 . It was speculated that the coexistence of the two intermediate phases would occur for alloy compositions in the 0.37 < x < 0.66 range. For these mixed phase samples (which contain coexisting Ti_6M_5 and C49 TiM_2) to transform to C54 TiM_2 , two types of transitions must occur: the C49 TiM_2 to C54 TiM_2 polymorphic transformation and the Ti_6M_5 to C54 TiM_2 transition. Above, it was shown that, at the C54 TiM_2 nucleation temperature, the C49 $TiSi_2$ to C54 $TiSi_2$ polymorphic transformation occurs much more rapidly than the Ti₆Ge₅ to C54 TiGe₂ phase transition (presumably due to both thermodynamic and kinetic factors). If the relative transitions rates in the Ti–Si and Ti–Ge reactions are extended to the Ti–Si_{1-x}Ge_x reaction, then, for the samples which contain both Ti₆M₅ and C49 TiM₂, it can be assumed that these two types of regions will transform to C54 TiM₂ at different rates.

In the previous section it was observed that as the Ge index was increased, for samples in the mixed phase regime (0.37 < x < 0.66), the size of the Ti₆M₅ regions increased and the size of the C49 TiM₂ regions decreased. Assuming that the Ti₆M₅ to C54 TiM₂ and C49 TiM₂ to C54 TiM₂ transition rates are independent of composition, then the formation of a layer of C54 TiM₂ from a mixed layer (containing both Ti₆M₅ and C49 TiM₂) can be written as:

$$\begin{pmatrix} C54 \text{ TiM}_2 \text{ layer} \\ \text{formation time} \end{pmatrix} = \begin{pmatrix} \text{volume of } \text{Ti}_6\text{M}_5 \\ \hline \text{Ti}_6\text{M}_5 \rightarrow \text{C54 } \text{TiM}_2 \\ \text{transition rate} \end{pmatrix} + \begin{pmatrix} \text{volume of } \text{C49 } \text{TiM}_2 \\ \hline \text{C49 } \text{TiM}_2 \rightarrow \text{C54 } \text{TiM}_2 \\ \text{transition rate} \end{pmatrix}.$$
(1)

We suggest that the C49 TiM_2 to C54 TiM_2 transformation rate is much greater than the Ti_6M_5 to C54 TiM_2 transition rate. Therefore, as the Ge index of the alloy is increased (i.e., as the volume of Ti₆M₅ increases and the volume of the C49 TiM_2 decreases), the C54 layer formation time will also increase. For short duration annealing the increasing C54 layer formation time is reflected in an increase in the C54 layer formation temperature (i.e., as the volume of the Ti₆M₅ region increases, the temperature necessary to transform the Ti_6M_5 to C54 TiM_2 , within the duration of the RTA cycle, also increases). This effect may be responsible for the effect shown in Fig. 7 where, in the mixed phase regime, the C54 nucleation temperature and the C54 layer formation temperature diverge as the Ge index of the alloy increases.

C. Nucleation model of Ti-Si-Ge phase formation

1. Nucleation of TiSi2

Previously, modeling of nucleation barriers has been used to explain the phase formation sequence in the Ti–Si solid phase reaction. In the Ti–Si solid phase reaction, the C49 phase of TiSi₂ is the first crystalline phase to form despite the fact that the C54 phase of TiSi₂ has a lower crystal energy. In a study by Jeon and Nemanich,³⁴ the formation of C49 TiSi₂ during the solid phase Ti–Si reaction was modeled in terms of the relative nucleation barriers for the two TiSi₂ phases. In the classical model of nucleation, the nucleation barrier for the formation of a spherical nucleus of a new phase is

$$\Delta G^* \alpha \, \frac{\sigma^3}{\Delta H^2} \,, \tag{2}$$

where ΔG^* is the magnitude of the nucleation barrier, σ is the interface energy between the old phase and the forming phase, and ΔH is the free energy difference between the two phases.²³ For the formation of TiSi₂, ΔH_{C54} is greater than ΔH_{C49} , and Jeon and Nemanich proposed that σ_{C49} is less than σ_{C54} such that the nucleation barrier of C49 TiSi₂ is less than the nucleation barrier of C54 TiSi₂.³⁴

Estimates of the relative interface and crystal energies of the C49 and C54 phases of TiSi₂ can be made from the results of several recent studies. Jeon et al.³⁵ proposed that by measuring the contact angles of TiSi2 islands on a Si substrate the relative surface and interface energies could be determined. In studies by Sukow and Nemanich³⁶ and Kropman,³⁷ this model was used to determine the relative TiSi₂/Si interface and TiSi₂ surface energies for both the C49 and C54 phases of TiSi₂. In those studies of the values of 752 ergs/cm² and 860 ergs/cm² were determined for the C49 TiSi₂/Si and C54 TiSi2/Si interface energies, respectively, for TiSi₂ formed on Si(100). If it is assumed that the $TiSi_2/a$ -TiSi interface energies are similar to the $TiSi_2/Si$ interface energies, then the measured TiSi2/Si interface energies can be used in Eq. (2) for calculating the relative nucleation barriers for the formation of C49 TiSi₂ and C54 TiSi₂ at the a-TiSi/Si interface (i.e., $\sigma_{\rm C49} \approx 752 \ {\rm ergs/cm^2}$ and $\sigma_{\rm C54} \approx 860 \ {\rm ergs/cm^2}$).

In Eq. (2) the ΔH term represents the difference in the crystal energies between the initial phase and the final phase of a nucleation process. If it is assumed that the entropies of the titanium silicide phases are the same, then the difference in the crystal energies of the phases can be approximated by the difference in the heats of formation of the phases (i.e., $\Delta H = crystal$ energy change \approx difference in the heats of formation). The heat of formation of C54 TiSi2 has been determined (-57.0 kJ/mole).³⁸ Based on reported values of 1 kJ/mole to 3 kJ/mole for polymorphic transformations in other intermetallic compounds, a value of 2 kJ/mole was used for the silicide transformation, and an estimated heat of formation of -55.0 kJ/mole was determined for C49 TiSi₂.³⁹ The values of -55.0 kJ/mole and -57.0 kJ/mole for the heats of formation of C49 TiSi₂ and C54 TiSi₂ are based on a Ti + Si \rightarrow TiSi₂ reaction. In the Ti-Si solid phase reaction a-TiSi forms prior to the formation of TiSi2 (which forms at the a-TiSi/Si interface). For the formation of TiSi₂, the ΔH term in Eq. (2) represents the crystal energy (heat of formation) difference between the a-TiSi and the TiSi₂ phases.

In a study by DeAvillez et al.,40 the heat of formation of C49 TiSi₂ formed at the a-TiSi/Si interface was determined to be -25.8 kJ/mole (i.e., $\Delta H_{a\text{-TiSi-to-C49}} = -25.8 \text{ kJ/mole}$). The heat of formation of C49 TiSi₂ formed from Ti + Si was estimated (in the previous paragraph) to be -55.0 kJ/mole. The difference between these two values (-29.2 kJ/mole) is an approximation of the heat of formation of the initial a-TiSi phase. Using this value the heat of formation of C54 TiSi₂ formed at the *a*-TiSi/Si interface can be deduced ($\Delta H_{a-\text{TiSi-to-C54}} = -27.8 \text{ kJ/mole}$). Using Eq. (2) the relative nucleation barriers were calculated from the values of σ and ΔH . The ratio of the calculated nucleation barriers is $\Delta G_{C49}^* / \Delta G_{C54}^* \approx 0.78$. The calculated nucleation barriers of the TiSi2 phases indicate that, despite the lower crystal energy of the C54 phase, the lower interface energy of the C49 phase causes the C49 TiSi₂ to have a lower nucleation barrier (in agreement with the model of Jeon and Nemanich³⁴).

The Ti₆Si₅ phase does not appear in the Ti–Si binary phase diagram and no heat of formation or surface/ interface energy could be found for this compound. Neglecting the effects of entropy, the heat of formation of Ti₆Si₅ must be smaller than -141.8 kJ per mole of Ti atoms to preclude the appearance of this phase in the Ti–Si binary alloy phase diagram. For this model a value of -140 kJ per mole of Ti atoms was chosen for the heat of formation of Ti₆Si₅ (i.e., 2 kJ less than the -141.8 kJ limit). The known and estimated heats of formation of the silicide phases are listed in Table II.

2. Nucleation of TiGe₂

In the Ti–Ge solid phase reaction, the Ti_6Ge_5 germanide phase forms first followed by the formation of C54 TiGe₂. It has been observed that, similar to

TABLE II. The known and estimated heats of formation of the Ti_6M_5 , C49 TiM_2 , and C54 TiM_2 phases of titanium silicide and titanium germanide.

| Silicide-germanide phase | Heat of formation (kJ/mole of Ti) | | |
|--------------------------------|-----------------------------------|-----------|--|
| | Silicide | Germanide | |
| Ti ₆ M ₅ | -140.0 | -117.9* | |
| C49 TiM ₂ | -165.0 | -135.0 | |
| C54 TiM ₂ | -171.0* | -142.5* | |

All the "known" heats of formation (denoted with an "*") are from a study by Pretorius, Marais, and Theron (Ref. 38). The estimated heats of formation are based on previous analytical studies and phenomena observed in the Ti–Si and Ti–Ge solid phase reactions (Refs. 3, 32, 39, and 44). It is assumed that the heats of formation of the titanium germanosilicides phases vary linearly with alloy composition between the silicide and germanide values.

the growth of C49 TiSi₂, Ti₆Ge₅ initially forms at the Ti/Ge interface and grows vertically through the Ti layer by diffusion-controlled growth.² Apparently, at the Ti/Ge interface, Ti₆Ge₅ has the lowest nucleation barrier of the germanide phases. The heats of formation of Ti₆Ge₅ and C54 TiGe₂ are known³⁸ and the heat of formation of C49 TiGe₂ can be estimated. (The same argument used to estimate the heat of formation of C49 TiSi₂ can be used to estimate the heat of formation of C49 TiGe₂). The known and estimated heats of formation of the germanide phases are listed in Table II.

3. Nucleation of Ti(SiGe)₂

For the Ti–Si_{1–x}Ge_x reactions the first phase to form is either C49 TiM₂ or Ti₆M₅. Based on the alloy composition ranges where the two phases were observed to form first, effective nucleation barriers were estimated and drawn schematically in Fig. 8(a). In Fig. 8(a) the magnitude of the C49 TiM₂ nucleation barrier increases with increasing Ge index because C49 TiGe₂ is not observed in the Ti–Ge solid phase reaction. Presumably as the Ge index of C49 TiM₂ is increased, the nucleation barrier for the formation of C49 TiM₂ also increases. Likewise, the inverse is true of the nucleation barrier of the Ti₆M₅ phase.

Once the Ti layer has been completely reacted to form the initial crystalline titanium germanosilicide phase (Ti_6M_5 or C49 TiM_2), there are three possible phase transitions that can follow. If the initial phase is C49 TiM₂ then it is not possible for a phase richer in Ti (like Ti_6M_5) to form, and the only allowable phase transition is the C49 TiM₂ to C54 TiM₂ transformation. If the initial phase is Ti_6Ge_5 then there are two possible phase transitions/reactions which may follow: Ti₆M₅ to C49 TiM₂ or Ti₆M₅ to C54 TiM₂. Using Eq. (2) it is possible to estimate the relative nucleation barriers for the formation of the second (and third) titanium germanosilicide phases, as a function of alloy composition. In this study it is assumed that the Ti_6M_5 , C49 TiM_2 , and C54 TiM2 phases can form over the entire alloy composition range and that the heats of formation of these phases vary linearly with composition between the silicide and germanide values.

To estimate the effect of alloy compositions on the titanium germanosilicide interface energies, the Ge–Ge and Si–Si diatomic bond strengths and the TiSi₂ and TiGe₂ lattice parameters were examined. The diatomic bond strength of Ge–Ge is $\approx 19\%$ less than the diatomic bond strength of Si–Si (263.5 kJ/mole and 326.8 kJ/mole, respectively) and the lattice parameters of Ge, C49 TiGe₂, and C54 TiGe₂ are $\approx 4\%$ larger than the lattice parameters of Si, C49 TiSi₂, and C54 TiSi₂, respectively.^{15,27,32,41,42} We assume that the germanide interface energies (and the germanide/germanium interface)



FIG. 8. The effective nucleation barriers for the titanium germanosilicide phases were estimated at various stages during the $Ti-Si_{1-x}Ge_x$ solid phase reactions. The nucleation barriers of C49 TiM_2 (----) and Ti_6M_5 (....) were estimated for first crystalline phase formation (a). The nucleation barriers for the formation of C49 TiM_2 (----) and C54 TiM_2 (----) in Ti_6M_5 were estimated (b). The nucleation barrier for the nucleation of C54 TiM_2 in C49 TiM_2 was estimated (c).

energy) are approximately 10% lower than the corresponding silicide interface energies (and the silicide/ silicon interface energy). Based on previous studies of Si_{1-x}Ge_x and C54 TiM₂, it is assumed that the lattice parameters of the titanium germanosilicides vary linearly with alloy composition (Vergard's law)^{27,43} and that the interface energies between the different germanosilicide phases also vary linearly with alloy composition. Estimates of the relative Ti₆M₅/C49 TiM₂, Ti₆M₅/ C54 TiM₂, and C49 TiM₂/C54 TiM₂ interface energies were made by comparing phenomena observed in the Ti–Si, Ti–Ge, and Ti–Si_{1-x}Ge_x solid phase reactions. The estimated interface energies are listed in Table III.

If C49 TiM₂ is the initial phase to form, then the only allowable phase transition is the C49 TiM₂ to C54 TiM₂ transformation. Using the estimated interface and bulk crystal energies, the relative C49 TiM₂ to C54 TiM₂ nucleation barrier was calculated, as a function of alloy composition, using Eq. (2) and is shown schematically in Fig. 8(c). In the previous section it was observed that the C54 TiM₂ nucleation temperature decreases with increasing Ge index when the C54 TiM₂ is nucleating from C49 TiM₂. The decreasing C54 TiM₂ nucleation temperature indicates that $\Delta G^*_{C49-C54}$ is decreasing. The slope of the estimated C49 TiM₂ to C54 TiM₂ nucleation barrier shown in Fig. 8(c) is in good agreement with this experimental observation.

If Ti_6M_5 is the first phase to form, TiM_2 may subsequently form (in either the C49 or C54 phase). In the previous section it was noted that following the formation of Ti_6M_5 , C49 TiM_2 would nucleate for alloy compositions in the mixed phase reaction regime and C54 TiM_2 would nucleate for alloy compositions in

TABLE III. Estimated relative *a*-TiSi/silicide, silicide/Si(100), and silicide/silicide interface energies.

| Interface(s) | Estimated interface energy (ergs/cm ²) |
|---|--|
| a-TiSi/C49 TiSi ₂ and C49 TiSi ₂ /Si(100) | 752 |
| a-TiSi/C54 TiSi2 and C54 TiSi2/Si(100) | 860 |
| $Ti_6Si_5/C49 TiSi_2$ | 281 |
| $Ti_6Si_5/C54 TiSi_2$ | 339 |
| C49 TiSi ₂ /C54 TiSi ₂ | 125 |

The estimates are based on phenomena observed in the Ti–Si, Ti–Ge, and Ti–Si_{1-x}Ge_x solid phase reactions. It is assumed that the *a*-TiSi/germanide, germanide/Ge(100), and germanide/germanide interface energies are 10% less than the corresponding interface energies in the Ti–Si system. It is also assumed that the interface energies vary linearly with alloy composition between the Ti–Si and Ti–Ge values. The relative magnitudes of the interface energies are consistent with the anticipated coherence of the different interfaces. For interfaces between dissimilar materials (e.g., silicide/Si(100) and *a*-TiSi/silicide), relatively high interface energies are expected. For interfaces between different silicide phases (e.g., Ti₆Si₅/C49 TiSi₂ and Ti₆Si₅/C54 TiSi₂), interface energies lower than for dissimilar materials are expected. For an interface between two silicides with similar structure (e.g., C49 TiSi₂/C54 TiSi₂, base-centered orthorhombic and face-centered orthorhombic, respectively, Ref. 15), a relatively small interface energy is expected. the "Ti-Ge-like" reaction regime. For this to occur the nucleation barrier for the Ti₆Ge₅ to C49 TiM₂ transition must be the lowest for the mixed phase reaction regime, and the nucleation barrier for the $T_{16}M_5$ to C54 TiM₂ transition must be the lowest for the "Ti-Gelike" reaction regime. The effect of composition on the Ti₆M₅ to C49 TiM₂ transition temperature was not directly observed; however, from the plot in Fig. 1 it does appear that the Ti_6M_5 to C54 TiM_2 transition temperature increases with increasing Ge index (i.e., the Ti_6M_5 to C54 TiM_2 nucleation barrier is increasing with increasing Ge index). In this case the Ti₆M₅ to C49 TiM₂ would also have to increase with Ge index, but at a higher rate than the Ti_6M_5 to C54 TiM_2 nucleation barrier. Based on the estimated interface and bulk crystal energies, the relative Ti_6M_5 to C49 TiM_2 and Ti_6M_5 to C54 TiM₂ nucleation barriers were calculated and are shown schematically in Fig. 8(b). As can be seen in Fig. 8(b) the phase formation sequence predicted by the estimated nucleation barriers is consistent with the experimental observations.

V. CONCLUSIONS

In this study five distinct observations were reported. First, the nucleation temperature of C54 $Ti(Si_{1-x}Ge_x)_2$ decreases as *x* approaches ≈ 0.5 . Second, the $Ti-Si_{1-x}Ge_x$ reaction can be divided, by alloy composition, into three regions based on the phase formation sequence:

$$Ti-M \rightarrow C49 \ TiM_2 \rightarrow C54 \ TiM_2$$

for $0.00 \le x \le 0.37$, (3)
$$Ti-M \rightarrow Ti_6M_5 \rightarrow C49 \ TiM_2 \rightarrow C54 \ TiM_2$$

for $0.37 \le x \le 0.66$, (4)

$$\text{Ti}-\text{M} \rightarrow \text{Ti}_6\text{M}_5 \rightarrow \text{C54 Ti}\text{M}_2 \text{ for } 0.66 \leq x \leq 1.00$$
. (5)

Third, the observed effects of composition on both the nucleation barriers and phase formation sequences can be modeled using a simple nucleation barrier model. Fourth, the formation of Ti_6M_5 during the $Ti-Si_{1-x}Ge_x$ reaction appears to decrease the rate of formation of C54 TiM_2 . Fifth, the formation of Ti_6M_5 during the $Ti-Si_{1-x}Ge_x$ leads to the formation of C54 TiM_2 which has reduced high temperature stability.

It was observed that during the $Ti-Si_{1-x}Ge_x$ solid phase reaction the first phase to form nucleated at the $Ti/Si_{1-x}Ge_x$ interface and grew by diffusion-controlled growth through the Ti. If the first phase to form was C49 TiM₂, then the second phase to form was C54 TiM₂. It was observed that the temperature required to nucleate C54 TiM₂ in C49 TiM₂ decreased with increasing Ge index. If the first phase to form was Ti₆Ge₅, then the second phase to form was TiM₂ (either the C49 phase of the C54 phase). If C49 TiM₂ followed the formation of Ti₆M₅, then the C49 TiM₂ formed only in limited regions of the Ti₆M₅ layer and the size of the C49 TiM₂ regions decreased as the Ge index increased. Following the formation of Ti₆M₅ and C49 TiM₂ (or just Ti₆M₅ for high Ge index alloys), the titanium germanosilicide film transformed to C54 TiM₂. Using a simple nucleation barrier model and estimates of surface, interface, and bulk free energies, it was possible to model analytically the experimentally observed effects of composition on both the nucleation barriers and phase formation sequences.

The properties of C54 TiM_2 were correlated to the $Ti-Si_{1-x}Ge_x$ reaction path. It was observed that the Ti₆Ge₅ to C54 TiM₂ transition proceeds at a slower rate than the C49 TiM_2 to C54 TiM_2 transformation. As the annealing duration is reduced, the presence of Ti_6M_5 in the titanium germanosilicide layer necessitates the use of higher annealing temperatures to completely transform the Ti_6M_5 layer to C54 TiM_2 during the annealing cycle. The Ti₆M₅ to C54 TiM₂ transition caused the formation of small grain C54 TiM₂ which was unstable at high temperatures. The C49 TiM₂ to C54 TiM₂ transformation caused the formation of large grain C54 TiM₂ which was more stable at high temperatures. Reducing the annealing duration from 10 min to 10 s improved the stability of the C54 TiM₂, indicating that the agglomeration of the C54 TiM₂ was related to material transport in the layer, possibly related to previously reported Ge segregation.²⁹

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