Phase stabilities and surface morphologies of $(Ti_{1-x}Zr_x)Si_2$ thin films on Si(100)

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Y. Dao, D. E. Sayers and R. J. Nemanich



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Modeling of agglomeration in polycrystalline thin films: Application to TiSi₂ on a silicon substrate

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Phase stabilities and surface morphologies of $(Ti_{1-x}Zr_x)Si_2$ thin films on Si(100)

Y. Dao, D. E. Sayers, and R. J. Nemanich^{a)}

Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202

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The effects of zirconium content on the phase stabilities and the surface morphologies of Ti-Zr alloy disilicide thin films were examined. The $(Ti_{1-r}Zr_r)Si_2$ thin films were grown by codeposition of Ti and Zr alloys (200 Å) onto Si(100) surfaces in ultrahigh vacuum and followed by in situ thermal annealing at temperatures between 650 and 1000 °C. The structural properties of films were studied by in situ Raman scattering experiments and ex situ x-ray diffraction experiments. The $(Ti_{1-x}Zr_x)Si_2$ films with low Zr contents (x<0.1) initially form a base-centered orthorhombic structure (C49 phase) and transform to a face-centered orthorhombic structure (C54 phase) at higher temperatures. The C49-to-C54 phase transition temperature increases with increasing Zr content. When the Zr content, x, is higher than 0.1, the C49 phase is stable in the temperature range of 700-1000 °C, and the C49-to-C54 phase transition is not observed. We propose that increasing the Zr content in the alloy silicide films results in a decreased enthalpy difference between these two crystalline structures. An analysis based on the classical theory of nucleation indicates that the nucleation energy barrier for the formation of a C54 cluster is increased. The surface morphologies of the alloy disilicide films were studied using scanning electron microscopy, and the surface roughnesses were quantified using atomic force microscopy. Substrate coverages of the C49 $(Ti_{1-r}Zr_r)Si_2$ thin films on Si are larger compared to the C54 TiSi₂ thin films with the same thicknesses. The agglomeration of the C49 alloy silicide thin films is less severe than for the C54 TiSi₂ thin films, because the C49 $(Ti_{1-x}Zr_x)Si_2$ silicide thin films have lower surface and interface free energies than C54 TiSi2. © 1995 American Institute of Physics.

I. INTRODUCTION

As metal-oxide-semiconductor field-effect transistor (MOSFET) channel lengths decrease to submicron size, a shallow metallurgical junction is required.¹⁻⁵ Contacts to the shallow junctions are often formed by the thin film reaction of a refractory metal and silicon to form a silicide. For shallow junctions, thinner silicide layers at the source and drain regions consume less silicon. As the junction depths approach several hundred angstroms, thermal stability of the thin silicide layers also becomes of greater concern.^{6,7}

Among the metal silicides, it is known that TiSi_2 has the lowest resistivity. The Schottky barrier height of the C54 TiSi₂ on both *n*-type and *p*-type Si is relatively low (~0.6 eV), which is preferred for contacts. Therefore, the formation of TiSi₂ on Si in the multistep SALICIDE (self-aligned silicide) process is often considered for source and drain contacts in microelectronics devices.^{6,8-12}

Two different crystalline phases are observed during the Ti–Si solid state reaction: a stable C54 phase and a metastable C49 phase.¹³ The C54 phase has an orthorhombic face-centered structure, and the C49 phase has an orthorhombic base-centered structure. The metastable C49 phase is the first TiSi₂ crystalline phase to form in the Ti–Si solid state thin film reaction. After annealing at about 700 °C, the C49 TiSi₂ films transform to the stable C54 phase. The C54 TiSi₂ films are reported to have much lower resistivity and defect density than the C49 TiSi₂ films.^{14–17} Several studies of the Ti–Si solid state reaction have addressed the energetics of the C49 $\rm TiSi_2$ formation and the C49-to-C54 polymorphic transformation. 13,18,19

The thermal instability of C54 TiSi₂ thin films formed on crystalline silicon has been commonly observed at temperatures as low as 800 °C.^{10,15,20} For films produced with 200 Å of Ti or less, the agglomeration of C54 TiSi₂ results in discontinuous films and rough surface morphologies.^{7,13,18} This agglomeration significantly degrades sheet resistance and increases the leakage current.⁷ The driving force for film agglomeration has been proposed to be the tendency toward decreasing the surface-to-volume ratio of the film, which results in a decreased total free energy of the film.^{13,18} This agglomeration is less significant for films formed with greater than 400 Å of Ti on Si. However, the shallow junctions on the source and drain regions of MOSFET devices require thinner uniform silicide layers while not sacrificing the contact resistance.

To solve the thermal instability problem of C54 TiSi₂ thin films, a new approach has been recently attempted.²¹ It was observed that the addition of Zr to the Ti–Si reaction stabilized the reacted layer in the C49 phase. Both Ti and Zr are in the group IVb column in the periodic table. While Ti and Zr exhibit many similar electrical and chemical properties,²² ZrSi₂ exhibits only one stable phase, namely the C49 phase.^{22,23} The resistivity of the C49 Ti–Zr alloy silicide films formed on Si(111) was measured to be ~46 $\mu\Omega$ cm, which is higher than the ~18 $\mu\Omega$ cm observed for C54 TiSi₂.²¹ However, the Ti–Zr alloy silicide thin films were reported to have much lower surface roughness than the C54 TiSi₂ thin films after annealing at high temperatures (~900 °C).²¹ The C49 Ti–Zr alloy silicide films exhibited

^{a)}Electronic mail: robert_nemanich@ncsu.edu

improved thermal stability and lower sheet resistance at high annealing temperatures (~900 °C) compared to the C54 TiSi₂ films with similar thicknesses.

In this study, $Ti_{1-x}Zr_x$ alloy layers $(0 \le x \le 0.3)$ were deposited on Si(100) surfaces in ultrahigh vacuum (UHV). The alloy films were reacted with Si to form $(Ti_{1-x}Zr_x)Si_2$ thin films using a variety of annealing temperatures. Structural properties were examined using Raman spectroscopy and x-ray diffraction (XRD), surface morphologies were examined using scanning electron microscopy (SEM), and surface roughnesses were examined using atomic force microscopy (AFM). The effects of the Zr content on the phase stability, the C49-to-C54 phase transition temperature, and the surface morphology are the primary focus of the studies reported here.

II. EXPERIMENT

The in situ experiments described here were carried out in an integrated film growth/characterization UHV system. The three chambers from that system used in this study include the sample deposition system, a chamber with lowenergy electron diffraction (LEED) and Auger electron spectroscopy (AES) capability, and a chamber for Raman spectroscopy. The base pressure of the transfer line of the system is $\sim 1 \times 10^{-9}$ torr. Before the Ti–Zr deposition, *n*-type Si(100) substrates were cleaned by exposure to UV/ozone irradiation to remove hydrocarbon contamination from the surface, a HF-based spin etch to remove the native oxide, and followed by heat cleaning to 850 °C for 10 min in the UHV chamber to desorb hydrogen and other residues.^{24,25} The in situ LEED pattern of the cleaned substrates exhibited the 2×1 diffraction characteristic of the Si(100) reconstructed structure, and AES showed no detectable carbon or oxygen on the surface prior to the deposition. The base pressure in the UHV deposition chamber was $<5 \times 10^{-10}$ Torr. The Ti-Zr alloy films were deposited at room temperature on the atomically clean Si(100) substrates by electron beam coevaporations from the Ti and Zr sources. The thicknesses of the alloy metal films are 200 Å. The compositions of the alloy metal films were selected by controlling the deposition rates of the Ti and Zr sources. The thickness and the deposition rates of the films were monitored by quartz crystal oscillators. Feedback from the deposition monitors was used to automatically control the relative Ti and Zr deposition rates. The maximum fluctuations of the deposition rates were lower than 15%. The films were then annealed in situ at temperatures between 650 and 1000 °C. The annealing time was 20 min in each case.

It has previously been shown that Raman spectroscopy can be used to distinguish between the C49 and C54 phases of TiSi₂.^{21,26} In this study a series of *in situ* Raman experiments were carried out to identify the phases of the alloy films after the *in situ* annealing. Raman spectra were excited with ~200 mW of 514.5 nm Ar ion laser radiation. The scattered light was first filtered with a subtractive 0.32 m double monochromator and then dispersed with a 0.64 m spectrometer. The light was detected with a liquid nitrogen cooled multichannel charge-coupled device (CCD) detector. The structural properties of the $(Ti_{1-x}Zr_x)Si_2$ thin films were



FIG. 1. Raman spectra of the 200 Å $Ti_{0.9}Zr_{0.1}$ films on Si(100) annealed at temperatures from 500 to 1000 °C. The features displayed in the wave number range of 250–350 cm⁻¹ of the 600–1000 °C spectra can all be assigned to the C49 TiSi₂ structure.

also examined by a Rigaku x-ray diffractometer, which has the Bragg-Brentano configuration. The wavelengths of the incident x-ray beam are 1.5406 Å (Cu $K\alpha_1$) and 1.5444 Å (Cu $K\alpha_2$). An average x-ray wavelength (1.5419 Å), which is weighted by the intensities of the Cu $K\alpha_1$ and Cu $K\alpha_2$ lines during the averaging, is used for structual analysis of the alloy silicide thin films. Surface morphologies of the allov silicide thin films were examined using a JEOL 6400 field-emission scanning electron microscope. The surface roughnesses of the films were measured using AFM. The AFM used for this experiment was a Park Scientific SFM-BD2. The piezo scanner had a 10 μ m scanning range in both the X and Y directions and a 2.5 μ m range in the Z direction. The scan area on the sample surfaces was $\sim 4 \ \mu m \times 3.2 \ \mu m$. Sheet resistances of the films were measured using a fourpoint probe.

III. RESULTS

In situ Raman experiments were performed on 200 Å $(Ti_{0.9}Zr_{0.1})/Si(100)$ films annealed over a temperature range from 500 to 1000 °C. The results are shown in Fig. 1. The features displayed in the wave number range of 250–350 cm⁻¹ of the 600–1000 °C spectra can all be assigned to the C49 TiSi₂ structure.^{13,21} No detectable signal was observed at ~240 cm⁻¹ where features associated with the C54 phase should be located.^{13,26} However, the signal to noise ratio of the 1000 °C data is lower than that from the other samples. The sample may contain a small amount of C54 phase, which was below the detection limit of the measurement. The Raman results indicate that the transition temperature from the C49 phase to the C54 phase is greater than 900 °C for the 200 Å (Ti_{0.9}Zr_{0.1}) alloy films on Si(100). This is more



FIG. 2. X-ray diffraction scans of the 200 Å $Ti_{0.98}Zr_{0.02}$ films on Si(100) annealed at 700, 800, and 900 °C.

than 200 °C higher than the previously observed transition temperature for $TiSi_2$ films on Si(100) with similar thicknesses.¹³

To study the Zr composition effect on the C49-to-C54 phase transition, Ti-Zr alloy silicide thin film samples with various Zr compositions were prepared. XRD experiments were performed to identify the phases of these samples. The samples studied using XRD were 200 Å (Ti_{1-r}Zr_r)/Si(100) films annealed at 650–1000 °C, where x=0, 0.01, 0.015,0.02, 0.03, 0.035, 0.05, 0.1, 0.2, and 0.3. The error bar of the Zr content is $\sim \pm 0.003$, due to fluctuations of the Ti and Zr deposition rates. The XRD scans of the 200 Å ($Ti_{0.98}Zr_{0.02}$) alloy films on Si(100) annealed between 700 and 900 °C are shown in Fig. 2. In the 38°-44° two theta region, the XRD scan of the 700 °C annealed sample contains peaks corresponding to diffraction from the (060) and (131) planes of the C49 phase. The scan of the 900 °C annealed film contains peaks corresponding to diffraction from the (311) and (004)planes of the C54 phase. Peaks associated with both the C49 and the C54 phases were observed in the 800 °C annealed sample. The 800 °C annealed sample contains mixed phases, which indicates that the C49-to-C54 phase transition temperature for the $(Ti_{0.98}Zr_{0.02})Si_2$ thin films is ~800 °C. This is higher than the C49-to-C54 phase transition temperature of the TiSi₂ films of similar thickness, but lower than that of the $(Ti_{0.9}Zr_{0.1})Si_2$ thin films (as shown in Fig. 1).

The observed phases of the $(Ti_{1-x}Zr_x)Si_2$ thin film samples annealed at different temperatures are plotted in Fig. 3. For each alloy composition the phase transition boundary is identified by the sample which exhibits the presence of both phases. There is a clear trend toward an increased C49to-C54 phase transition temperature with increasing Zr content. The transition temperature increases from 650 °C for TiSi₂ to 1000 °C for $(Ti_{0.9}Zr_{0.1})Si_2$. When the Zr content is higher than 0.1, the C49 phase is stable over the temperature range of 700–1000 °C.



FIG. 3. Phase diagram of the 200 Å $Ti_{1-x}Zr_x$ films on Si(100) ($0 \le x \le 0.1$) annealed at temperatures from 650 to 1000 °C. The C49-to-C54 phase transition boundary is identified by the samples which contain both phases. There is a clear trend toward increased C49-to-C54 phase transition temperature with increasing Zr content.

The XRD scans of the $(Ti_{1-x}Zr_x)Si_2$ thin films annealed at 800 °C, with $0.01 \le x \le 0.3$, are plotted in Fig. 4. For x=0.01, the alloy silicide film is in the C54 phase. Both of the C49 and C54 phases are observed in the sample with Zr content of 0.02. The alloy silicide thin films with Zr content of 0.05 or higher are in the C49 phase. It is also observed that all the diffraction peaks shift to lower angles with increasing Zr content, indicating that the spacing of the diffraction planes increase. The spacing of the C49 (131) plane was calculated from the XRD results and plotted versus Zr content in Fig. 5. The spacing increases linearly with increasing



FIG. 4. X-ray diffraction scans of the 200 Å $Ti_{1-x}Zr_x$ films on Si annealed at 800°C, where $0.01 \le x \le 0.3$. All the diffraction peaks shift to lower angles with increasing Zr content.



FIG. 5. The *d* spacing of the (131) planes of C49 $(Ti_{1-x}Zr_x)Si_2$ thin films vs Zr content, *x*. The spacing increases linearly with increasing Zr content, which in agreement with Vegard's Law.

Zr content, which shows good agreement with Vegard's law. This suggests that Ti and Zr atoms are randomly distributed throughout the alloy silicide films.

The surface morphologies of the alloy silicide thin films were studied using scanning electron microscopy (SEM). The SEM micrographs of the 200 Å $(Ti_{1-r}Zr_r)/Si(100)$ thin films annealed at high temperatures are shown in Fig. 6 [Fig. 6(a): x=0, 800 °C; Fig. 6(b): x=0.05, 800 °C; Fig. 6(c): x=0.1, 800 °C; Fig. 6(d): x=0.1, 900 °C]. There are randomly distributed regions in the C54 TiSi₂ film annealed at 800 °C [Fig. 6(a)], where the Si substrate is exposed to the surface. These regions are typically 5–10 μ m long and ~0.5 μm wide. It is evident that the film is discontinuous. In the C49 (Ti_{0.95}Zr_{0.05})Si₂ film annealed at 800°, only pin holes, at multiple grain boundaries, were observed [Fig. 6(b)]. The film consists of many small grains. The grain sizes of the C49 (Ti_{0.95}Zr_{0.05})Si₂ film vary from ~ 0.1 to $\sim 1 \mu m$. The Si substrate is fully covered by the C49 (Ti_{0.9}Zr_{0.1})Si₂ film annealed at 800 °C [shown in Fig. 6(c)]. The average grain size of the C49 $(Ti_{0.9}Zr_{0.1})Si_2$ film is smaller than that of the lower Zr content (0.05) alloy silicide film. The surface morphology of the C49 (Ti_{0.9}Zr_{0.1})Si₂ film annealed at 900 °C is shown in Fig. 6(d). The areal coverage of the silicide decreases significantly compared to the film annealed at 800 °C with the same Zr composition. The film agglomerates more severely and the grains are more faceted.

AFM was used to measure the rms surface roughnesses of the films. A comparison of rms surface roughness results of the TiSi₂ films, the $(Ti_{0.9}Zr_{0.1})Si_2$ films, and the $(Ti_{0.8}Zr_{0.2})Si_2$ films is shown in Fig. 7. The rms surface roughnesses of the C49 $(Ti_{0.9}Zr_{0.1})Si_2$ films and the C49 $(Ti_{0.8}Zr_{0.2})Si_2$ films are smaller than those of the C54 TiSi₂ films annealed at temperatures higher than 700 °C. The alloy silicide films exhibit reduced surface roughnesses at high temperatures, due to less agglomeration.

In Fig. 8 the sheet resistances of the $TiSi_2$, the $(Ti_{0.9}Zr_{0.1})Si_2$, and the $(Ti_{0.8}Zr_{0.2})Si_2$ films annealed at different temperatures are compared. The $TiSi_2$ film exhibits a low

FIG. 6. SEM images of the 200 Å $Ti_{1-x}Zr_x/Si(100)$ thin films annealed at high temperatures. (a) x=0, 800 °C; (b) x=0.05, 800 °C; (c) x=0.1, 800 °C; and (d) x=0.1, 900 °C.

sheet resistance at 700 °C (2.4 Ω/\Box), characteristic of the C54 phase. The resistivity was calculated to be ~12 $\mu\Omega$ cm. At ~900 °C, the sheet resistance of the C54 TiSi₂ films on Si(100) increases dramatically (33.6 Ω/\Box), presumably due to the agglomeration of the C54 TiSi₂. The lowest measured



FIG. 7. The rms surface roughness vs annealing temperature for the 200 Å $Ti_{0.9}Zr_{0.1}/Si(100)$, the 200 Å $Ti_{0.8}Zr_{0.2}/Si(100)$, and the 200 Å Ti/Si(100) films. The values were obtained from AFM scans. The $Ti_{0.9}Zr_{0.1}/Si(100)$ and the $Ti_{0.8}Zr_{0.2}/Si(100)$ films exhibit reduced surface roughnesses compared to the Ti/Si(100) films at high temperatures, due to less agglomeration.

resistivity of the C49 $(Ti_{0.9}Zr_{0.1})Si_2$ films is ~51 $\mu\Omega$ cm, which is ~4.3 times the lowest value for the C54 TiSi₂ films. However, the sheet resistance of the $(Ti_{0.9}Zr_{0.1})Si_2$ thin films are relatively stable over the temperature range of 600–900 °C. At 900 °C, the alloy silicide thin films exhibit much lower sheet resistances (18.8 Ω/\Box) than the TiSi₂ films. The $(Ti_{0.9}Zr_{0.2})Si_2$ films exhibit slightly increased sheet resistances than the $(Ti_{0.9}Zr_{0.1})Si_2$ films, presumably due to the effect of scattering by the Zr atoms.

IV. DISCUSSION

A. Phase stabilities

As described above, the phase stabilities of the C49 phase and the C54 phase of $(Ti_{1-x}Zr_x)Si_2$ thin films vary



FIG. 8. Sheet resistance of the 200 Å $Ti_{0.9}Zr_{0.1}/Si(100)$, the 200 Å $Ti_{0.8}Zr_{0.2}/Si(100)$, and the 200 Å Ti/Si(100) films at different temperatures. The sheet resistances of the $Ti_{0.9}Zr_{0.1}/Si(100)$ and the $Ti_{0.8}Zr_{0.2}/Si(100)$ films exhibit reduced degradation than the Ti/Si(100) films at temperatures (~900 °C) as a result of less agglomeration.

with Zr content. The transition temperature from the C49 phase to the C54 phase increases with increasing Zr content. Furthermore, the effect occurs in the Zr content range of 0-0.1. The presence of Zr atoms in the alloy silicide thin films tends to stabilize the C49 phase. The effect of Zr content on phase stabilities will be described using a classical nucleation model.

Jeon *et al.* described the phase formation sequence in the Ti–Si solid state reaction in terms of nucleation barriers.¹³ The metastable C49 phase, which is the first TiSi₂ crystalline phase to form, has a lower surface and interface free energy compared to the final C54 phase. Therefore, the nucleation energy barrier for the C49 phase is lower despite the fact that the C49 phase of TiSi₂ has a higher bulk free energy.^{8,18}

A classical nucleation model of a new phase forming in a parent phase has been extensively explored by d'Heurle.²⁷ The nucleation energy barrier ΔG^* of a spherical nucleus of a new phase is

$$\Delta G^{*\alpha} \frac{\sigma^3}{\Delta G_1^2},\tag{1}$$

where σ is the interface energy between the new phase and the parent phase, and ΔG_1 is the bulk free energy difference between these two phases per unit volume.²⁷ For thin films, a disc-shaped nucleus model was proposed by Ma *et al.*¹⁹ In this case the surface-to-volume ratio is increased and the effect of the surface and interface energies is enhanced. Equation (1) is modified and expressed as

$$\Delta G^{*\alpha} \frac{\sigma^3}{c^2 \Delta G_1^2},\tag{2}$$

where c is a geometrical coefficient, which depends upon the shape and dimension of the nucleus.

The bulk free energy difference between the growing phase and the parent phase ΔG_1 is given by $\Delta G_1 = \Delta H - T\Delta S$. Here ΔH is the enthalpy difference of the phases, and the second term $T\Delta S$ is the entropic contribution to the free energy change. If it is assumed that the entropies of the C49 $(\text{Ti}_{1-x}\text{Zr}_x)\text{Si}_2$ and the C54 $(\text{Ti}_{1-x}\text{Zr}_x)\text{Si}_2$ are similar and the entropic contributions to the free energy change of the C49-to-C54 phase transition is much smaller compared to the enthalpic contributions,²⁸ the difference in the free energy ΔG_1 can be approximated by the difference in the enthalpies of the C49 and C54 phases of $(\text{Ti}_{1-x}\text{Zr}_x)\text{Si}_2$. Therefore, Eq. (1) can be modified as

$$\Delta G^* \propto \frac{\sigma^3}{\Delta H^2}.$$
 (3)

Here ΔH is the enthalpy difference between the C49 and C54 phases of $(Ti_{1-x}Zr_x)Si_2$.

The interface free energies of the C49 TiSi₂/Si(100), the C54 TiSi₂/Si(100), and the C49 ZrSi₂/Si(111) were estimated to be 752, 860, and 770 erg/cm², respectively by Sukow *et al.*¹⁹ and Kropman.²⁹ As shown in Fig. 5, the spacing of the C49 (Ti_{1-x}Zr_x)Si₂ (131) plane is increased by about 5%, when x is increased from 0.02 to 1. This indicates that the lattice constant of the C49 (Ti_{1-x}Zr_x)Si₂ is increased by only ~5%. Presumably the interface energy σ between the C49



FIG. 9. Schematic illustration of enthalpy changes of C49 $(Ti_{1-x}Zr_x)Si_2$ and C54 $(Ti_{1-x}Zr_x)Si_2$ with respect to the Zr content, x. The value x_c indicates the critical composition in which the driving force for the C49-to-C54 phase transition is zero.

phase and the C54 phase of $(Ti_{1-x}Zr_x)Si_2/Si$ in Eqs. (1), (2), and (3) is not strongly dependent on the Zr content, x.

The stable phase for the Ti–Si solid phase reaction is the TiSi₂ C54 phase, and the stable phase for the Zr–Si solid phase reaction is the ZrSi₂ C49 phase, although Ti and Zr share many chemical and electrical similarities.^{22,23} The calculated values of the heats of formations of the C54 TiSi₂ and C49 ZrSi₂ are -57.0 and -53.1 kJ/mol, respectively.²⁸ Presumably, the C54 TiSi₂ has a lower enthalpy than the C49 TiSi₂, and the C49 ZrSi₂ has a lower enthalpy than the C54 ZrSi₂.

The TiSi₂–ZrSi₂ pseudobinary phase diagram was studied by Kornilov *et al.*³⁰ Their results indicated that in the temperature range of our study for x > -0.5, the equilibrium phase of the $(Ti_{1-x}Zr_x)Si_2$ compound is the C49 phase; for x < -0.05, the equilibrium phase of the $(Ti_{1-x}Zr_x)Si_2$ is the C54 phase; and for x between 0.05 and 0.5, the C49 and the C54 phases coexist. The equilibrium phase of $(Ti_{1-x}Zr_x)Si_2$ is determined by the bulk free energy, G, which includes both enthalpy and entropy terms. Presumably, the C54 $(Ti_{1-x}Zr_x)Si_2$ compound has a minimum in the free energy at x = -0.05, and the C49 $(Ti_{1-x}Zr_x)Si_2$ compound has a minimum in the free energy at x = -0.5. When 0.05 < x < 0.5, Tirich C54 $(Ti_{1-y}Zr_y)Si_2$ and Zr-rich C49 $(Ti_{1-z}Zr_z)Si_2$ coexist (y < x < z), because the free energy is lower when phase segregation occurs.

In contrast, no evidence of phase segregation was observed for the $(Ti_{1-x}Zr_x)Si_2$ thin films, which were annealed up to 1000 °C (as shown in Figs. 2–5). However, mixed phases were observed at the C49-to-C54 phase transition boundary, and this was attributed to incomplete phase transformation. As we discussed above, the enthalpic term is the dorminate contribution to the bulk free energy G. We assume that the enthalpies of the C54 $(Ti_{1-x}Zr_x)Si_2/Si$ and the C49 $(Ti_{1-x}Zr_x)Si_2/Si$ thin films change linearly with respect to Zr content. The trends of the enthalpies of the C49 $(Ti_{1-x}Zr_x)Si_2$ and the C54 $(Ti_{1-x}Zr_x)Si_2$ are schematically illustrated in Fig. 9. We suggest that there must be a critical Zr content x_c between 0.05 and 0.5, where the difference in the enthalpies between the C49 $(Ti_{1-x}Zr_x)Si_2$ and the C54 $(Ti_{1-x}Zr_x)Si_2$ is equal to zero. When $x < x_c$, the C54 structure of the $(Ti_{1-x}Zr_x)Si_2$ compound has a lower enthalpy than the C49 structure, and when $x > x_c$, the C49 structure has a lower enthalpy.

Although the C54 phase has lower enthalpy when $x < x_c$, the magnitude of the enthalpy difference between the C49 phase and the C54 phase, ΔH , decreases as x approaches x_c . According to Eq. (3) the nucleation energy barrier for a C54 nucleus to form increases with decreasing ΔH . Therefore, the nucleation energy barrier would increase as the Zr content is increased from 0 to x_c , and the C49-to-C54 phase transition would be totally inhibited at $x = x_c$. Presumably, the phase transition temperature is proportional to the nucleation energy barrier. Therefore, the C49-to-C54 phase transition temperature rises with increasing Zr content, which corresponds very well with the trend shown in Fig. 3.

The $(Ti_{1-x}Zr_x)Si_2$ films with Zr contents higher than 0.1 are stable in the C49 phase over the temperature range of 700–1000 °C. The C54 phase was not observed at x>0.1, even though the TiSi₂-ZrSi₂ pseudobinary phase diagram shows mixed phases in this composition range because of the nucleation barrier.

B. Surface morphologies

Agglomeration has been a common problem of silicide thin films at high temperatures. The agglomeration process involves material transport, i.e., lateral diffusion. Slower diffusion processes result in less agglomeration at specified anneals. Zr and ZrSi₂ have higher melting points than Ti and TiSi₂, which implies that they also have higher bond energies. We suggest that $(Ti_{1-x}Zr_x)Si_2$ thin films with high Zr contents exhibit slower lateral diffusion processes and therefore results in less agglomeration. As shown in Figs. 6(a)-6(c), the substrate coverages are different, even though these alloy silicides with different Zr contents were all annealed at the same temperature (800 °C). The $(Ti_{1-x}Zr_x)Si_2$ thin films with higher Zr contents have larger substrate coverages. Comparison between Figs. 6(c) and 6(d) also demonstrates that higher annealing temperatures result in lower substrate coverages, which can be attributed to increased lateral diffusion processes at the higher temperatures. In addition, the grains of the agglomerated C49 (Ti_{0.9}Zr_{0.1})Si₂ film at 900 °C are all connected to each other. No distinct islands are observed. In contrast, discontinuous island formation was observed for C54 TiSi2 with a similar thickness and annealing temperature.7,13,18

Although the agglomeration is limited by kinetics (diffusion), the driving force for the agglomeration is related to the energetics of the system. Jeon *et al.* and Sukow *et al.* proposed a "solid state capillarity" model to explain the island structure at equilibrium.^{13,18} The shapes of islands formed on Si substrates are determined by the substrate surface free energy, the film surface free energy, and the interface free energy between the film and substrate.^{13,18} This model suggests that the driving force for the agglomeration is the tendency of the thin films toward decreasing surfaceto-volume ratio while the film is approaching its lowest energy state. The films with lower surface and interface free energies have a smaller driving force for the agglomeration and therefore would be expected to exhibit smoother surfaces and better areal coverages on the substrates.

The surface and interface free energies of the C49 TiSi₂/Si films were measured to be lower than those of the C54 TiSi₂/Si films by Sukow et al.¹⁸ and Kropman et al.²⁹ Presumably, the surface and interface free energies of the C49 $(Ti_{1-r}Zr_r)Si_2$ films with low Zr contents have almost the same values as those of the C49 TiSi₂ films. Therefore, the C49 $(Ti_{1-x}Zr_x)Si_2$ thin films have lower surface and interface free energies than the C54 TiSi2. The C49 $(Ti_{1-x}Zr_x)Si_2$ films should have a smaller driving force for the agglomeration and would be expected to exhibit smoother surfaces and increased areal coverages on Si substrates as compared to C54 TiSi2. This corresponds very well with the SEM and AFM experimental results shown above. The C49 $(Ti_{0.9}Zr_{0.1})Si_2$ films annealed at high temperatures exhibit lower rms surface roughnesses than the C54 TiSi2 films. The C54 TiSi₂ film annealed at 800 °C is discontinuous and contains regions where the Si substrate is exposed to the surface [as shown in Fig. 6(a)]. In contrast, the areal coverages of the C49 (Ti_{1-x}Zr_x)Si₂ films annealed at 800 °C [as shown in Figs. 6(b) and 6(c), where x=0.05 and 0.1] are significantly increased compared to the C54 TiSi₂ film with similar thickness.

Nolan *et al.* proposed a "grain boundary grooving" model to explain the agglomeration process in polycrystalline thin films.³¹ They suggest that the driving force for surface grooving (i.e., agglomeration) is the equilibrium between the surface energy of the film, the interface energy of the grain boundary, and the interface energy between the film and substrate. This model predicts that small grain size promotes resistance to agglomeration.³¹ This again corresponds well with the SEM micrographs of the films. It is evident that the C49 (Ti_{1-x}Zr_x)Si₂ films are polycrystalline thin films. The C49 (Ti_{1-x}Zr_x)Si₂ films consist of many small grains. There is a trend toward decreased average grain size with increasing Zr content, x [as shown in Figs. 6(a), 6(b), and 6(c)], and the film with smaller average grain size exhibits better areal coverage on the substrate.

C. Electrical properties

Most results to date have indicated that the resistivity of the C49 phase is higher than that of the C54 phase. However, the C49 $(Ti_{1-x}Zr_x)Si_2$ thin films exhibit better thermal stability than the C54 TiSi₂ films with similar film thicknesses. The C49 $(Ti_{1-x}Zr_x)Si_2$ thin films, which have better substrate coverages, may have advantages for smaller device dimensions. As shown in Fig. 6(a), there are many regions observed in the C54 TiSi₂ film on Si(100) annealed at 800 °C, where the Si substrate is exposed to the surface. The size of these Si exposed regions are often 5–10 μ m long and $\sim 0.5 \ \mu m$ wide during the initial stage of agglomeration. However, the film does not exhibit much degradation of the sheet resistance. The sheet resistance measurements were carried out using a four-point probe. The spacings between the four probes used in the sheet resistance measurements are several millimeters. Even with the exposed regions, a complete path will exist between the two probes. These micron size Si substrate exposure regions do not have a significant effect on the measured sheet resistance results. However, this effect is anticipated to be more significant when the silicide films are patterned into smaller lateral dimensions.

Films of C54 TiSi2 are currently being used as metal shunt layers at the shallow junctions as source and drain contacts in the MOSFET devices.^{2,3,12} Present feature sizes of the devices are 0.4–1.0 μ m, and for future devices the feature sizes will be 0.25 μ m and below.^{32,33} As the feature sizes of the devices are scaled down, the junction depth would be scaled down accordingly from 3500 Å for a 1 μ m devices, to 700 Å and less for 0.25 μ m and below devices.⁴ As the thickness of the C54 TiSi₂ layers at the shallow junctions approaches several hundred angstroms, agglomeration starts to be a concern and will limit the device performance. The micron size substrate exposed regions in the C54 TiSi₂ films formed at the shallow junctions will interrupt the low conduction path and the usefulness of the metal shunt layer is lost. The alloy silicide with continuous areal coverage on the substrate would be more suitable for the thin layers required at shallow junctions on the source and drain regions of MOSFET devices. In addition, when the feature sizes of the devices are scaled down, the interconnection lines are required to have compatible linewidths.⁴ For submicron interconnections, any substrate exposed region in the C54 TiSi₂ may result in a discontinuous interconnection. Therefore, C49 $(Ti_{1-x}Zr_x)Si_2$ films with continuous areal coverage should be more electrically conductive than TiSi₂ films at temperatures of 800 °C or higher.

V. CONCLUSIONS

This study has explored the phase stability and morphology of $(Ti_{1-x}Zr_x)Si_2$ thin films formed by a solid phase reaction of Ti-Zr alloy films with the underlying Si substrate. The $(Ti_{1-x}Zr_x)Si_2$ films with low Zr contents (x<0.1) initially form the C49 structure and transform to the C54 structure at higher temperatures. The C49-to-C54 phase transition temperature of the $(Ti_{1-x}Zr_x)Si_2$ thin films increases with increasing Zr content, and the alloy disilicide thin films are stable in the C49 phase at 700-1000 °C for the Zr content greater than 0.1. No evidence of phase segregation was observed for the alloy silicide thin films. The lattice constants of the C49 $(Ti_{1-x}Zr_x)Si_2$ thin films increase linearly with increasing Zr content. The $(Ti_{1-x}Zr_x)Si_2$ thin films with higher Zr contents have reduced the enthalpy difference between the C49 phase and the C54 phase for x varied from 0 to x_c . This results in the increase of nucleation energy barrier for the C54 phase.

The C49 alloy silicide thin films exhibit improved thermal stability over the C54 TiSi₂ thin films of similar thicknesses. The substrate coverages of the C49 $(Ti_{1-x}Zr_x)Si_2$ thin films are increased compared to those of the C54 TiSi₂ films. The surface roughnesses of the alloy silicide thin films are lower than those of the agglomerated C54 TiSi₂ films formed at the same temperatures. The sheet resistances of the C49 alloy silicide thin films at high temperatures (~900 °C) as a result of the reduced agglomeration. Therefore, even though

the lowest measured resistivity of the C49 $(Ti_{1-x}Zr_x)Si_2$ thin films is about 4.3 times as high as that of the C54 $TiSi_2$ thin films, we suggest that the C49 $(Ti_{1-x}Zr_x)Si_2$ thin films may have advantages in submicron dimensioned microelectronics devices.

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