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# Electrical and structural properties of zirconium germanosilicide formed by a bilayer solid state reaction of Zr with strained $Si_{1-x}Ge_x$ alloys

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The effects of alloy composition on the electrical and structural properties of zirconium germanosilicide (Zr-Si-Ge) films formed during the  $Zr/Si_{1-x}Ge_x$  solid state reaction were investigated. Thin films of  $Zr(Si_{1-v}Ge_v)$  and C49  $Zr(Si_{1-v}Ge_v)_2$  were formed from the solid phase reaction of Zr and  $Si_{1-x}Ge_x$  bilayer structures. The thicknesses of the Zr and  $Si_{1-x}Ge_x$  layers were 100 and 500 Å, respectively. It was observed that Zr reacts uniformly with the Si<sub>1-x</sub>Ge<sub>x</sub> alloy and that C49  $Zr(Si_{1-y}Ge_y)_2$  with y = x is the final phase of the  $Zr/Si_{1-x}Ge_x$  solid phase reaction for all compositions examined. The sheet resistance of the  $Zr(Si_{1-v}Ge_v)_2$  thin films was higher than the sheet resistance of similarly prepared ZrSi<sub>2</sub> films. The stability of  $Zr(Si_{1-\nu}Ge_{\nu})_2$  in contact with  $Si_{1-x}Ge_x$  was investigated and compared to the stability of  $Ti(Si_{1-y}Ge_y)_2$  in contact with  $Si_{1-x}Ge_x$ . The  $Ti(Si_{1-y}Ge_y)_2/Si_{1-x}Ge_x$  structure is unstable when annealed for 10 min at 700 °C, with Ge segregating from  $Ti(Si_{1-y}Ge_y)_2$  and forming Ge-rich  $Si_{1-z}Ge_z$  precipitates at grain boundaries. In contrast, no Ge segregation was detected in the  $Zr(Si_{1-v}Ge_v)_2/Si_{1-x}Ge_x$  structures. We attribute the stability of the Zr-based structure to a smaller thermodynamic driving force for germanium segregation and stronger atomic bonding in C49  $Zr(Si_{1-y}Ge_y)_2$ . Classical thermodynamics were used to calculate  $Zr(Si_{1-\nu}Ge_{\nu})_2 - Si_{1-\nu}Ge_{\nu}$  tie lines in the Zr-Si-Ge ternary phase diagram. The calculations were compared with previously calculated  $Ti(Si_{1-\nu}Ge_{\nu})_2 - Si_{1-\nu}Ge_{\nu}$  tie lines. © 1997 American Institute of Physics. [S0021-8979(97)00617-8]

### I. INTRODUCTION

The potential incorporation of  $Si_{1-x}Ge_x$  alloys into Sibased devices has motivated many investigations on the metallization of  $Si_{1-x}Ge_x$  alloys.<sup>1-20</sup> Metal germanosilicides may be used for making metallic contacts with  $Si_{1-x}Ge_x$  alloys, and knowledge about the formation and stability of thin metal germanosilicide films is essential for such applications. The thermally induced metal/ $Si_{1-x}Ge_x$  reaction has previously been studied in Pt,<sup>5-7</sup> Pd,<sup>7,8</sup> W,<sup>9</sup> Ni,<sup>10</sup> Ti,<sup>11-15</sup> and Co.<sup>16-20</sup> Various degrees of germanium segregation and/or the formation of segregated layered structures were observed in the reactions of these metal/ $Si_{1-x}Ge_x$  systems.

The  $Ti/Si_{1-x}Ge_x$  system is of particular interest. Due to its low resistivity TiSi2 is widely used in the semiconductor industry. In recent studies it has been observed that the final phase of the Ti/Si<sub>1-x</sub>Ge<sub>x</sub> solid phase reaction is C54  $Ti(Si_{1-\nu}Ge_{\nu})_2$  and that the properties of the resulting C54 material (morphology, stability, and electrical characteristics) are strongly dependent on composition.<sup>21</sup> In a study of the Ti/Si<sub>1-r</sub>Ge<sub>r</sub> reaction by Aldrich *et al.*<sup>22</sup> it was observed that C54 Ti(Si<sub>1-v</sub>Ge<sub>v</sub>)<sub>2</sub> forms such that initially y = x. However, during further annealing there is a net segregation of germanium out of the C54 Ti $(Si_{1-v}Ge_v)_2$  which is accompanied by the formation of germanium-rich  $Si_{1-z}Ge_z$  precipitates along the C54  $Ti(Si_{1-y}Ge_y)_2$  grain boundaries. Both the morphology and sheet resistance of the films are affected by the germanium segregation. In the study by Aldrich et al.<sup>22</sup> the driving force for germanium segregation

Since Zr and Ti have many common physical and chemical characteristics<sup>23</sup> and ZrSi<sub>2</sub> and ZrGe<sub>2</sub> share the same C49 crystal structure, similar results may be anticipated for the  $Zr/Si_{1-r}Ge_r$  reaction. The average enthalpy of formation of C54 TiSi<sub>2</sub> and C54 TiGe<sub>2</sub> is 51 kJ (mole atoms)<sup>-1</sup> for and the driving force segregation  $\sim 8 \text{ kJ} \text{ (mole atoms)}^{-1}$ .<sup>24</sup> In the Zr–Si–Ge system the average enthalpy of formation of C49 ZrSi2 and ZrGe2 is 81 kJ (mole atoms)<sup>-1</sup> and the driving force for segregation is  $\sim$  5 kJ (mole atoms)<sup>-1</sup>.<sup>24</sup> The mobility of Si and Ge in the C49 and C54 structures will also play a role in the germanium segregation process. It has been reported that the mobility of Si is lower in C49 ZrSi<sub>2</sub> than in C49 TiSi<sub>2</sub>.<sup>23</sup> If the mobility of Ge is also lower then this may provide an additional barrier against Ge segregation in the Zr-Si-Ge system. Because the driving force for Ge segregation is lower in the Zr-Si-Ge system than in the Ti-Si-Ge system, one might anticipate that C49  $Zr(Si_{1-x}Ge_x)_2$  would be stable to higher temperatures and/or longer annealing times. Previous work has also determined that ZrSi<sub>2</sub> does not exhibit a persistent tendency for surface roughening and islanding like TiSi<sub>2</sub>, which results in comparable sheet and contact resistance in the Ti-Si and Zr-Si systems.<sup>23</sup> These results suggest that Zr may be more attractive than Ti as a contact material in SiGe-based applications.

was modeled in terms of the enthalpy of formation of C54  $Ti(Si_{1-y}Ge_y)_2$ . The enthalpy of formation of  $TiSi_2$  is lower than that of  $TiGe_2$  and it was proposed that, after formation, the C54  $Ti(Si_{1-y}Ge_y)_2$  changes composition to decrease the total energy of the system.

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In this study we investigated issues relating to (1) the formation of C49  $Zr(Si_{1-y}Ge_y)_2$  from the solid phase reaction of Zr with  $Si_{1-x}Ge_x$  alloys and (2) the stability of the C49  $Zr(Si_{1-y}Ge_y)_2/Si_{1-x}Ge_x$  bilayer structure, where the stability of a system only refers to the stability with respect to elemental segregation. The zirconium germanosilicide phases formed during the reactions were identified using x-ray diffraction (XRD) and extended x-ray absorption fine structure spectroscopy (EXAFS). The surface morphology and grain structure were examined with scanning electron microscopy (SEM). The electrical characteristics of the zirconium germanosilicide films were measured with a four-point probe.

# **II. EXPERIMENT**

The samples used in this study consisted of clean 25 mm Si (100) wafers on which a layer of  $Si_{1-x}Ge_x$  and a layer of Zr were deposited. The silicon wafers were precleaned by the manufacturer using a standard RCA cleaning procedure. Prior to use in the laboratory the wafers were further cleaned by (1) exposure to UV generated ozone to remove hydrocarbons from the surface and to form a stable oxide, (2) spin etching with a solution of hydrofluoric acid: H<sub>2</sub>O: ethanol (1:1:10) to remove the oxide and passivate the Si (100) surface with hydrogen, and (3) an in situ thermal desorption at >850 °C for 10 min to remove any surface contaminants which may remain. This cleaning process has been shown to produce atomically clean surfaces.<sup>25</sup> Following the in situ thermal desorption at >850 °C, the substrate temperature was reduced at 40 °C/min and held at 550 °C for the deposition of a 200 Å homoepitaxial single crystal Si buffer layer and a strained 500 Å heteroepitaxial single crystal  $Si_{1-r}Ge_r$  alloy layer. The Si and  $Si_{1-r}Ge_r$  alloy layers were not intentionally doped. Alloy compositions with x = 0, 0.20,0.32, and 0.50 were deposited. Silicon and germanium were codeposited from two electron beam evaporation sources in a UHV chamber with a base pressure of  $\sim 1 \times 10^{-10}$  Torr. The pressure during silicon and germanium deposition was <1 $\times 10^{-8}$  Torr. 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 silicon and germanium deposition rates. The maximum composition variation during deposition was approximately 2%. The compositions of the deposited  $Si_{1-r}Ge_r$  alloys were determined from Rutherford backscattering and x-ray absorption fine structure (XAFS) analysis of native  $Si_{1-r}Ge_r$  layers similarly prepared.<sup>26</sup> Following deposition of the epitaxial  $Si_{1-x}Ge_x$  alloy layer the sample was cooled at 40 °C/min to room temperature. Low energy electron diffraction (LEED) was used to examine the surface of these  $Si_{1-r}Ge_r$  samples. Sharp 2×1 LEED patterns were observed which indicted that the surfaces of these samples were well ordered. The samples were then removed from vacuum for transport to a second deposition system.

Prior to Zr deposition each  $Si_{1-x}Ge_x$  sample was cleaned by the same process used for the initial cleaning of the Si wafer, except that in the second deposition chamber a thermal desorption temperature of 700 °C was used. Following thermal desorption the substrate temperature was reduced

and the surface was examined with Auger electron spectroscopy (AES) and LEED. The O and C Auger signals were below the detection limits of AES. Diffuse  $2 \times 1$  LEED patterns were observed, which indicated that the surfaces of these SiGe samples were partially disordered after the cleaning process. An electron beam evaporation source was then used to deposit 100 Å thick Zr films at a rate of 0.2 Å/s. The thickness of the Zr films was monitored with an oscillating quartz crystal monitor. During deposition the chamber pressure was  $< 8 \times 10^{-10}$  Torr. Following deposition of Zr the samples were annealed in situ. The temperature was increased at a rate of 60 °C/min, held at the desired temperature for 20 min or 100 min, and decreased at a rate of 60  $^{\circ}\text{C}/$ min. Annealing temperatures of 500, 600, and 700 °C were used. The thicknesses of the Zr and  $Si_{1-x}Ge_x$  alloy layers were chosen such that the  $Zr/Si_{1-x}Ge_x$  reaction would not completely consume the  $Si_{1-x}Ge_x$  alloy, and the reaction products would be in contact with the remaining  $Si_{1-r}Ge_r$ alloy.

A Rigaku x-ray diffractometer (monochromatic Cu  $K\alpha$ radiation) was used for XRD experiments. A JEOL 6400 field-emission scanning electron microscope was used for SEM imaging. Sheet resistance was measured with a Magne-Tron Instruments Model M-700 resistivity/conductivity test system. EXAFS data were collected at beamline X-11A at the National Synchrotron Light Source (NSLS). The x-ray energy was defined with a variable-exit monochromator using two flat Si (111) crystals. Harmonics were rejected by detuning the second monochromator crystal. EXAFS data were collected at room temperature at the Zr K-edge in a low-angle total electron yield configuration.<sup>27</sup> Background subtraction and Fourier filtering were performed with a modified version of the University of Washington-Naval Research Labs package.<sup>28</sup> Local structural information about Zr was obtained by nonlinear least-squares fitting of the experimental data with theoretical EXAFS functions. The theoretical EXAFS functions were generated by FEFF5,<sup>29</sup> and the curve fitting was performed with FEFFIT.<sup>30</sup> EXAFS data were analyzed according to the recommendations of the International Committee on XAFS Standards and Criteria.<sup>31</sup> Curve



FIG. 1. X-ray diffraction scans of  $Zr/Si_{1-x}Ge_x$  samples (x=0, 0.20, 0.32, and 0.50) annealed at 700 °C for 20 min.



FIG. 2. Fourier transforms of Zr *K*-edge  $k^2$ -weighted EXAFS of Zr/Si<sub>1-x</sub>Ge<sub>x</sub> samples (x=0, 0.20, 0.32, 0.50) annealed at 700 °C for 20 min (without phase correction). The transform range is 2.8–10.0 Å<sup>-1</sup>.

fitting was performed in r space over the range 1.0–4.2 Å with nine variable parameters per data set.

#### III. RESULTS

In order to examine the effect of  $Si_{1-x}Ge_x$  alloy composition on the structure and stability of  $Zr(Si_{1-y}Ge_y)_2$  formed during the  $Zr/Si_{1-x}Ge_x$  solid phase reaction, samples were prepared with alloy compositions of x=0, 0.20, 0.32, and 0.50. The samples were annealed at 700 °C for 20 min. The XRD scans of these samples are shown in Fig. 1. All peaks in the scans of the  $Zr/Si_{1-x}Ge_x$  samples can be directly correlated to peaks in the C49  $ZrSi_2$  standard. This correlation indicates that the final zirconium germanosilicide phase is C49  $Zr(Si_{1-y}Ge_y)_2$  regardless of the initial  $Si_{1-x}Ge_x$  alloy composition for  $0.0 \le \times \le 0.50$ , and suggests that C49  $Zr(Si_{1-y}Ge_y)_2$  is the final phase for the complete alloy composition range.

The effect of composition on the crystal structure of C49  $ZrM_2(M=Si_{1-x}Ge_x)$  was also examined using EXAFS analysis. The C49  $Zr(Si_{1-y}Ge_y)_2$  crystal structure consists of a Zr sublattice and a semiconductor (Si–Ge) sublattice. As the Si/Ge ratio in the C49  $Zr(Si_{1-y}Ge_y)_2$  changes, the composition of the semiconductor sublattice will change. Zirconium *K*-edge EXAFS analysis was used to examine the local structure in the vicinity of the Zr atoms, and to correlate changes in structure to changes in the composition of the semiconductor sublattice. EXAFS analysis provides both qualitative and quantitative information about the C49 crys-

tal structure. The Fourier transformed EXAFS spectra of the  $Zr/Si_{1-x}Ge_x$  samples are shown in Fig. 2. The x=0 spectrum is for the C49  $ZrSi_2$  standard. The similarities between the x=0 spectrum and spectra for  $x\neq 0$  confirm that Zr atoms exist in a C49-type structure for all samples examined here.

Quantitative crystal structure information was obtained by fitting the experimental EXAFS data with theoretically generated EXAFS functions. For Zr K-edge EXAFS analysis the local structural parameters determined from the fitting include: (1) the number N and type of the atoms that surround central Zr atom; (2) the distance, R, between the central Zr atom and the neighboring atoms; and (3) a measure of the disorder in the local structure, quantified as a Debye-Waller factor,  $\sigma^2$ . In C49 ZrSi<sub>2</sub> the first coordination shell consists of ten Si atoms at an average Zr-Si distance of 2.73 Å, and the second coordination shell consists of six Zr atoms at an average Zr-Zr distance of 3.67 Å. For the C49  $Zr(Si_{1-v}Ge_v)_2$  EXAFS data, the first shell was split into two subshells to account for the fact that both Si and Ge atoms are contained in the first shell. Fitting results are given in Table I. From the EXAFS fitting results it is possible to calculate the Ge index y of the C49  $Zr(Si_{1-y}Ge_y)_2$  alloy:

$$y = N_{Zr-Ge} / (N_{Zr-Ge} + N_{Zr-Si}).$$

$$\tag{1}$$

The compositions calculated from the EXAFS analysis and Eq. (1) suggest that the C49  $Zr(Si_{1-y}Ge_y)_2$  formed in the  $Zr/Si_{1-x}Ge_x$  reaction is such that the Ge index *y* is the same as in the underlying  $Si_{1-x}Ge_x$ . Also, the increase in the Zr–Zr bond length  $R_{Zr-Zr}$  with Ge content of the compound indicates that the C49 unit cell expands uniformly with Ge content.

It must be noted here that Eq. (1) is an approximation that will give identical results for a "true"  $Zr(Si_{1-y}Ge_y)_2$ alloy, and for a physical mixture consisting of y parts  $ZrGe_2$ and (1-y) parts  $ZrSi_2$ . The correct expression for calculating the Ge index of a  $R(Si_{1-x}Ge_x)_2(R=Zr,Ti)$  compound requires knowledge of both the average number of Si near neighbors around Ge  $N_{Ge-Si}$ , and the average number of Ge near neighbors around Si  $N_{Si-Ge}$ :

$$y = N_{\text{Ge-Si}} / (N_{\text{Ge-Si}} + N_{\text{Si-Ge}}).$$
<sup>(2)</sup>

However, XRD measurements discussed in the following paragraphs do not show any evidence for phase segregation in these samples, which justifies the use of Eq. (1) in place of Eq. (2).

TABLE I. Coordination number *N*, bond length *R*, and Debye–Waller factor  $\sigma^2$  determined by EXAFS analysis of the Zr/Si<sub>1-x</sub>Ge<sub>x</sub> samples (x = 0, 0.20, 0.32, 0.50) annealed at 700 °C for 20 min.

	First shell Zr-Si			First shell Zr-Ge			Second shell Zr-Zr		
Sample $Zr/Si_{1-x}Ge_x$	$N \pm 1.0$	$\begin{array}{c} R  (\text{\AA}) \\ \pm 0.02 \end{array}$	$\sigma^2 (\times 10^{-4} \text{ Å}^2) \\ \pm 10$	$N \pm 1.0$	$\begin{array}{c} R  (\text{\AA}) \\ \pm 0.02 \end{array}$	$\sigma^2 ( imes 10^{-4} \text{ Å}^2) \\ \pm 10$	$N \pm 1.0$	$\begin{array}{c} R  (\text{\AA}) \\ \pm 0.02 \end{array}$	$\sigma^2 ( imes 10^{-4} \text{ Å}^2) \\ \pm 10$
x = 0.00	10.0	2.73	78	-	-	-	6.0	3.67	82
x = 0.20	8.1	2.73	60	2.0	2.78	60	5.9	3.68	97
x = 0.32	7.1	2.73	67	2.7	2.80	62	5.8	3.69	96
x = 0.50	4.6	2.71	75	4.4	2.78	76	5.4	3.72	96



FIG. 3. Plane spacing for the C49  $Zr(Si_{1-x}Ge_x)_2$  (131) and (002) planes calculated from x-ray diffraction patterns for  $Zr/Si_{1-x}Ge_x$  samples (x=0, 0.20, 0.32, 0.50) annealed at 700 °C for 20 min. The dashed line is Vegard's law.

Further analysis of the XRD data in Fig. 1 gives another indication of the effect of composition on the C49 ZrM<sub>2</sub> crystal structure. In Fig. 1 it can be seen that the diffraction peaks corresponding to the C49 Zr-Si-Ge compounds are located at angles lower than those of C49 ZrSi<sub>2</sub> and that the diffraction angles decrease with increasing Ge composition. These shifts in the diffraction angle are due to the expansion of the corresponding lattice planes. The plane spacings, d, were calculated for both the  $ZrM_2$  (131) and (002) planes of these samples and are plotted in Fig. 3. The calculated dspacings are plotted versus the  $Si_{1-x}Ge_x$  substrate compositions. The d spacings for C49 ZrSi<sub>2</sub> and C49 ZrGe<sub>2</sub> are also plotted in Fig. 3 and the line connecting these two points represents Vegard's law. It has been observed that Vegard's law is valid for  $TiM_2$ ,<sup>32</sup> and since the bonding in  $ZrM_2$  is very similar to the bonding in TiM2 we assume that Vegard's law is valid for C49  $Zr(Si_{1-y}Ge_y)_2$ . If  $Zr(Si_{1-y}Ge_y)_2$  forms from  $Zr/Si_{1-x}Ge_x$  such that y=x (as indicated by the EX-AFS results) then all of the points in Fig. 3 should fall on the line defined by Vegard's law. As seen in Fig. 3 this is indeed the case.

During studies of the Ti/Si<sub>1-x</sub>Ge<sub>x</sub> reaction it was observed that Ge segregates out of Ti(Si<sub>1-y</sub>Ge<sub>y</sub>)<sub>2</sub> and precipitates as Ge-rich Si<sub>1-z</sub>Ge<sub>z</sub> along the Ti(Si<sub>1-y</sub>Ge<sub>y</sub>)<sub>2</sub> grain boundaries.<sup>22</sup> XRD scans of the angular range containing the (400) diffraction peaks of Ge, Si, and the Si<sub>1-x</sub>Ge<sub>x</sub> alloy ( $60^{\circ} \le 2 \theta \le 70^{\circ}$ ) detected only Si and Si<sub>1-x</sub>Ge<sub>x</sub> peaks due to the substrate and the unreacted Si<sub>1-x</sub>Ge<sub>x</sub> layer, respectively. This suggests that Ge segregation did not occur or was below the detection limit, and supports the conclusion that the only product of the Zr/Si<sub>1-x</sub>Ge<sub>x</sub> reaction is C49 Zr(Si<sub>1-y</sub>Ge<sub>y</sub>)<sub>2</sub> with y=x.

In a previous study Ge segregation was observed in  $Ti/Si_{1-x}Ge_x$  samples annealed for 10 min at 700 °C.<sup>22</sup> However, in the  $Zr/Si_{1-x}Ge_x$  samples annealed for 20 min at 700 °C no Ge segregation occurs. To further test the stability of the C49  $Zr(Si_{1-y}Ge_y)_2/Si_{1-x}Ge_x$  bilayer structure, a  $Zr/Si_{0.68}Ge_{0.32}$  sample was annealed at 700 °C for 100 min. The x-ray diffraction pattern of this sample is identical to



FIG. 4. X-ray diffraction scans of  $Zr/Si_{0.68}Ge_{0.32}$  samples annealed at 500, 600, and 700  $^{\circ}C.$ 

that of the Zr/Si<sub>0.68</sub>Ge<sub>0.32</sub> sample annealed for 20 min, indicating that no Ge segregation had occurred (within the detection limit of the experiment). This suggests that C49 Zr(Si<sub>1-x</sub>Ge<sub>x</sub>)<sub>2</sub> is more stable than C54 Ti(Si<sub>1-x</sub>Ge<sub>x</sub>)<sub>2</sub> when in contact with Si<sub>1-x</sub>Ge<sub>x</sub>.

To examine the phase formation sequence during the  $Zr/Si_{1-x}Ge_x$  bilayer solid state reaction, the crystal structures of the two  $Zr/Si_{0.68}Ge_{0.32}$  samples annealed at 500 and 600 °C, respectively, were characterized with XRD. The x-ray diffraction patterns of these two samples of these two samples are shown in Fig. 4, together with the pattern for the sample annealed at 700 °C. The lack of the expected C49 peaks in the  $2\theta$  range between  $37^{\circ}$  and  $50^{\circ}$  indicates that



FIG. 5. SEM micrographs of  $Zr(Si_{0.68}Ge_{0.32})_2$  thin film samples annealed at 700 °C for (a) 20 min, and (b) 100 min. Agglomeration is visible in the sample annealed for 100 min.

TABLE II. Sheet resistance of the  $Zr/Si_{1-x}Ge_x$  samples used in this study.

Sample $Zr/Si_{1-x}Ge_x$	Annealing temperature and time	Sheet resistance $(\Omega/sq)$
x = 0.00	700 °C, 20 min	20.0
x = 0.20	700 °C, 20 min	26.7
x = 0.32	500 °C, 20 min	57.0
	600 °C, 20 min	33.0
	700 °C, 20 min	32.8
	700 °C, 100 min	44.5
x = 0.50	700 °C, 20 min	44.2

Zr(Si<sub>1-x</sub>Ge<sub>x</sub>)<sub>2</sub> has not yet been formed in the sample annealed at 500 °C. The broad diffraction peak at  $2\theta \approx 36^{\circ}$  may be due to diffraction from the (102) plane of a ZrSi-type structure. However, the data is not sufficient to identify the actual crystal structure of this sample. Previous studies of the reaction sequence of the Zr–Si system have shown an amorphous Zr–Si interlayer forms initially, followed by the formation of crystalline ZrSi and ZrSi<sub>2</sub> phases.<sup>32,23</sup> Thus, in parallel with the Zr/Si system, one may speculate that at 500 °C the material formed is small-grained Zr(Si<sub>1-x</sub>Ge<sub>x</sub>). The diffraction pattern of the sample annealed at 600 °C indicates that part of the reacted layer has been converted to C49 Zr(Si<sub>1-x</sub>Ge<sub>x</sub>)<sub>2</sub>, and that two phases, Zr(Si<sub>1-x</sub>Ge<sub>x</sub>)<sub>2</sub> coexist in the reacted layer. At 700 °C the entire reacted layer has transformed to C49 Zr(Si<sub>1-x</sub>Ge<sub>x</sub>)<sub>2</sub>.

Four-point probe and SEM measurements were used to examine the effects of composition and annealing on the electrical and morphological properties of the C49  $Zr(Si_{1-\nu}Ge_{\nu})_2$  films. The SEM images revealed that the C49 ZrM<sub>2</sub> films formed by annealing at 700 °C for 20 min are continuous films consisting of  $Zr(Si_{1-\nu}Ge_{\nu})_2$  grains, similar to C49 ZrSi<sub>2</sub>. However, an annealing duration of 100 min produced islanded films. SEM micrographs of two of the Zr/Si<sub>0.68</sub>Ge<sub>0.32</sub> samples are shown in Fig. 5. In Fig. 5(a) the continuous layer of grains formed during the 20 min anneal at 700 °C is visible. In Fig. 5(b) the islanding of the grains which occurred during the 100 min anneal at 700 °C can be observed. The islanding is most likely due to the energy difference between bulk and surface. Longer annealing gives atoms enough energy and time to minimize the energy of the system by forming small islands. The sheet resistances measured for the C49  $Zr(Si_{1-v}Ge_v)_2$  films are listed in Table II. The sheet resistance of the  $Zr(Si_{1-\nu}Ge_{\nu})_2$  thin films increases with increasing Ge composition y, from 22  $\Omega$ /sq for y=0 to 44  $\Omega/sq$  for y=0.50. A similar trend was observed in the dependence of the sheet resistance of C54  $Ti(Si_{1-y}Ge_y)_2$  on the Ge index y.<sup>33</sup> The effect was attributed to alloy scattering. The Zr/Si<sub>0.68</sub>Ge<sub>0.32</sub> sample annealed for 100 min has a higher sheet resistance than the sample annealed for 20 min at the same temperature. This increase can be attributed to the observed islanding of the ZrM<sub>2</sub> thin film during the long duration anneal (see Fig. 5).

#### **IV. DISCUSSION**

Both XRD and EXAFS analyses indicate that when a  $Zr/Si_{1-x}Ge_x$  bilayer structure is annealed at a temperature



FIG. 6. Calculated tie lines at 700 °C for (a) the C49  $Zr(Si_{1-y}Ge_y)_2$ - $Si_{1-x}Ge_x$  system; and (b) the C54  $Ti(Si_{1-y}Ge_y)_2$ - $Si_{1-x}Ge_x$  system. The numbers in the figure indicate the initial composition of the SiGe alloy corresponding to each tie line. Note that the tie lines in the Zr system are less inclined towards the silicide than in the Ti system, indicating a lower thermodynamic driving force for Ge segregation in Zr-Si-Ge than in Ti-Si-Ge.

sufficient to form C49  $Zr(Si_{1-y}Ge_y)_2$ , the C49  $Zr(Si_{1-y}Ge_y)_2$  forms with a composition y=x. This is similar to the Ti/Si<sub>1-x</sub>Ge<sub>x</sub> reaction, in which C54 Ti(Si<sub>1-y</sub>Ge<sub>y</sub>)<sub>2</sub> initially forms with y=x. Although both Zr and Ti react uniformly with  $Si_{1-x}Ge_x$ , the resulting C49  $Zr(Si_{1-y}Ge_y)_2$  appears to be more stable than the resulting C54 Ti(Si<sub>1-y</sub>Ge<sub>y</sub>)<sub>2</sub>. For the Ti(Si<sub>1-x</sub>Ge<sub>x</sub>)<sub>2</sub>/Si<sub>1-x</sub>Ge<sub>x</sub> system it was observed that Ge segregated from the initial Ti(Si<sub>1-x</sub>Ge<sub>x</sub>)<sub>2</sub> compound after a 10 min anneal at 700 °C, resulting in a Ti(Si<sub>1-y</sub>Ge<sub>y</sub>)<sub>2</sub>/Si<sub>1-x</sub>Ge<sub>x</sub> system appears to be stable against Ge segregation for annealing duration as long as 100 min.

In a study by Aldrich *et al.*<sup>34</sup> the energetics of the C54 Ti(Si<sub>1-y</sub>Ge<sub>y</sub>)<sub>2</sub>/Si<sub>1-x</sub>Ge<sub>x</sub> system were examined, and C54 Ti(Si<sub>1-y</sub>Ge<sub>y</sub>)<sub>2</sub>-Si<sub>1-x</sub>Ge<sub>x</sub> tie lines were calculated with classical thermodynamics. It was determined that C54 Ti(Si<sub>1-y</sub>Ge<sub>y</sub>)<sub>2</sub> is stable in contact with Si<sub>1-x</sub>Ge<sub>x</sub> only when y < x. The dynamics of the C54 Ti(Si<sub>1-y</sub>Ge<sub>y</sub>)<sub>2</sub>/Si<sub>1-x</sub>Ge<sub>x</sub> interface instability were modeled in terms of the calculated tie lines and the kinetics of the silicon and germanium atoms in both materials. Initially, the driving force for the forma-

TABLE III. Comparison of theoretical and experimental differences in enthalpies of formatiion for a series of Ti and Zr silicides. All values are from Ref. 24, and  $\Delta H$  is the difference in the heats of formation between "Material 1" and "Material 2." The average value for the experimental heat of formation was used whenever multiple measurements were available, and the quoted uncertainties were calculated as standard deviations of the experimental values.

Material 1	Material 2	$\Delta H_{\rm exp}  {\rm kJ}$ (mole atoms) <sup>-1</sup>	$\Delta H_{\text{theory}}  \text{kJ}$ (mole atoms) <sup>-1</sup>
TiSi <sub>2</sub>	TiSi	$+19\pm17$	+19
TiSi <sub>2</sub>	Ti <sub>5</sub> Si <sub>3</sub>	$+19\pm12$	+13
TiSi	Ti <sub>5</sub> Si <sub>3</sub>	$0 \pm 11$	-6
$ZrSi_2$	ZrSi	$+34\pm22$	+18
$ZrSi_2$	Zr <sub>5</sub> Si <sub>3</sub>	$+21\pm 4$	+4
ZrSi	Zr <sub>5</sub> Si <sub>3</sub>	$-13\pm 26$	-14

tion of  $Ti(Si_{1-y}Ge_y)_2$  from  $Ti/Si_{1-x}Ge_x$  is greater than the driving force for the segregation of germanium, and  $Ti(Si_{1-\nu}Ge_{\nu})_2$  forms with a Ge concentration similar to that of the underlying  $Si_{1-x}Ge_x$  substrate (i.e., y=x). The average enthalpy of formation of C54 TiSi2 and C54 TiGe2 is 51 kJ/mol, and the driving force for segregation is  $\sim 8$  kJ/mol.<sup>23</sup> In the Zr-Si-Ge system the average enthalpy of formation of C49 ZrSi<sub>2</sub> and ZrGe<sub>2</sub> is 81 kJ/mol and the driving force for segregation is  $\sim$  5 kJ/mol.<sup>24</sup> From a comparison of these values it is reasonable to expect that C49  $Zr(Si_{1-y}Ge_y)_2$  will form from the Zr/Si<sub>1-x</sub>Ge<sub>x</sub> reaction with y = x (prior to any segregation which may occur). Also, the larger average enthalpy of formation of C49 ZrM<sub>2</sub> with respect to C54 TiM<sub>2</sub> suggests that the atomic bonding is stronger in the Zr-Si-Ge system. This can lead to a reduced atomic mobility, as observed by Sukow et al.23 A combination of lower atomic mobility and a lower driving force may make C49  $Zr(Si_{1-y}Ge_y)_2$  more stable to germanium segregation than C54 Ti $(Si_{1-v}Ge_v)_2$ .

Tie lines of C49  $Zr(Si_{1-y}Ge_y)_2-Si_{1-x}Ge_x$  were calculated with the same method used to calculate C54  $Ti(Si_{1-y}Ge_y)_2-Si_{1-x}Ge_x$  tie lines.<sup>35</sup> The calculated tie lines for both systems are plotted in Fig. 6. These tie lines indicate that  $Zr(Si_{1-y}Ge_y)_2$  is thermodynamically stable in contact with  $Si_{1-x}Ge_x$  only when y < x. However, a comparison of the tie lines of these two systems indicates that for a given  $Si_{1-x}Ge_x$  alloy composition C54  $Ti(Si_{1-x}Ge_x)_2$  will have to expel more Ge to reach its equilibrium composition than will C49  $Zr(Si_{1-x}Ge_x)_2$ . For example, the compositions of the TiM<sub>2</sub> and  $ZrM_2$  alloys in equilibrium with  $Si_{0.70}Ge_{0.30}$  at 700 °C will be  $Ti(Si_{0.91}Ge_{0.09})_2$  and  $Zr(Si_{0.85}Ge_{0.15})_2$ , respectively. As discussed earlier, the reduced mobility of Si and Ge in C49  $Zr(Si_{1-x}Ge_x)_2$  will tend to suppress further the driving force for Ge segregation in the Zr-Si-Ge system.

It must be noted that, to the best of our knowledge, no experimental values exist for the enthalpies of formation of TiGe<sub>2</sub> and ZrGe<sub>2</sub>. We have therefore used the theoretical values from Ref. 24 throughout this work. However, comparison of the theoretical and experimental heats of formation of ZrSi<sub>2</sub>, 83 kJ (mole atoms)<sup>-1</sup> and 53 kJ (mole atoms)<sup>-1</sup>, respectively, reveals a substantial discrepancy, which raises the possibility that the thermodynamic driving

force for Ge segregation may be larger in Zr/SiGe than in Ti/SiGe. While the reliability of the absolute magnitude of the theoretical estimates may be questioned, comparison to available experimental values in de Boer *et al.*,<sup>24</sup> shown in Table III, indicates that the theoretical calculations faithfully represent trends in the differences in the heats of formation. Since our calculations are not used to make any quantitative conclusions but merely as a qualitative indication of the trend of the reaction, we feel that in the absence of experimental results for the enthalpy of formation of ZrGe<sub>2</sub> we are justified in using theoretical values.<sup>35,36</sup>

# **V. CONCLUSIONS**

We have investigated the structural properties and stability of zirconium germanosilicide films formed by the solid state reaction of  $Zr/Si_{1-x}Ge_x$  bilayer structures. The results indicate that C49  $Zr(Si_{1-y}Ge_y)_2$  is the final phase of the reaction, independent of the initial  $Si_{1-x}Ge_x$  alloy composition. A small-grained  $Zr(Si_{1-y}Ge_y)$  phase may be formed in samples annealed at 500 °C. This may be an intermediate phase prior to the formation of C49  $Zr(Si_{1-\nu}Ge_{\nu})_2$ . When  $Zr/Si_{1-r}Ge_r$  structures are annealed at 700 °C, a uniform ternary compound,  $Zr(Si_{1-y}Ge_y)_2$ , was formed with the same Ge index y as the underlying  $Si_{1-x}Ge_x$  substrate. The  $Zr(Si_{1-v}Ge_v)_2$  films consisted of grains which islanded when annealed at 700 °C for 100 min. The sheet resistance of the C49  $Zr(Si_{1-y}Ge_y)_2$  films were higher than the sheet resistance of a similarly prepared C49 ZrSi<sub>2</sub> film, possibly due to alloy scattering in the ternary compound.

After initial formation, the C49  $\operatorname{Zr}(\operatorname{Si}_{1-y}\operatorname{Ge}_y)_2$  layer contact with the unreacted  $\operatorname{Si}_{1-x}\operatorname{Ge}_x$  alloy was stable to 700 °C. Unlike C54  $\operatorname{Ti}(\operatorname{Si}_{1-y}\operatorname{Ge}_y)_2$ , the composition of the C49  $\operatorname{Zr}(\operatorname{Si}_{1-y}\operatorname{Ge}_y)_2$  did not change upon further annealing at 700 °C (up to 100 min). The  $\operatorname{Zr}(\operatorname{Si}_{1-x}\operatorname{Ge}_x)_2/\operatorname{Si}_{1-x}\operatorname{Ge}_x$  system appears to be stable with respect to Ge segregation from the metal germanosilicide. We suggest that this is due to the combination of a smaller thermodynamic driving force, lower mobility, and a higher barrier for Ge segregation in the C49  $\operatorname{Zr}(\operatorname{Si}_{1-x}\operatorname{Ge}_x)_2$  alloys than in the C54  $\operatorname{Ti}(\operatorname{Si}_{1-x}\operatorname{Ge}_x)_2$  alloys.

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