

Interface stability of $\text{Ti}(\text{SiGe})_2$ and SiGe alloys: Tie lines in the ternary equilibrium diagram

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The C54 phases of TiSi_2 and TiGe_2 are known to be completely miscible, however, we have observed that thin films of C54 $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2$ are not stable in contact with $\text{Si}_{1-x}\text{Ge}_x$ when $y=x$. In this study it is shown that this interface instability can be related to the composition-dependent energetics that determine the Ti-Si-Ge ternary equilibrium diagram. Tie lines of the $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2$ to $\text{Si}_{1-x}\text{Ge}_x$ system were calculated on the basis of classical thermodynamics. The calculations indicate that for C54 $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2$ to be stable in contact with $\text{Si}_{1-x}\text{Ge}_x$ the compositions of the two phases must be such that $y < x$. The specific compositions of the two phases in equilibrium depend on the temperature and the relative quantities of the two phases. The dynamics of the interface reactions of C54 $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2$ on $\text{Si}_{1-x}\text{Ge}_x$ are related to the calculated tie lines, and the diffusion kinetics of the materials. Experimental results are presented that quantitatively support the model calculations. [S0163-1829(96)04920-X]

The formation of stable metal-semiconductor interfaces is a key aspect in all semiconductor technologies. The reactions of metals with Si to form a silicide-silicon interface have proven to be an important process for integrated circuits, and also a demonstration materials system for the study of reactive interface formation. Recently, advanced high-performance device structures have employed SiGe layers, and in advanced integrated circuit technologies, SiGe layers are being considered for channel engineering¹ and raised source-drain contacts.² Metal junctions to these layers may prove essential for the advancement of the technology. The interface reactions between a metal and a two-component semiconductor will be substantially more complex, and to date, most results have relied on an empirical approach. In the reaction of thin-film Ti with silicon or germanium, the final phases that form are C54 TiSi_2 and C54 TiGe_2 , respectively. Both Si-Ge and TiSi_2 - TiGe_2 form continuous solid solutions, making this a model ternary system for the study of reactive interface formation. This paper relates the unexpected morphological and compositional inhomogeneities that develop in the reaction of Ti and SiGe alloys. A model guided by thermodynamic arguments is presented to describe the dynamics of the interface reactions, and new results indicate quantitative agreement.

In the course of studying the interaction between Ti and Si-Ge solid solutions, unexpected phenomena were observed.^{3,4} Upon reaction of Ti with a $\text{Si}_{1-x}\text{Ge}_x$ alloy (with a Ge concentration of x) one obtains a compound with the formula $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2$ and a C54 (orthorhombic) crystal structure. Initially, the composition of the compound is such that $y=x$ (as anticipated). Once the compound is formed, upon further heating at a constant temperature, the grain boundaries of the compound become decorated with a nearly continuous precipitate of an $\text{Si}_{1-x}\text{Ge}_x$ alloy rich in Ge, and

containing no detectable Ti, as shown in Fig. 1. As this precipitation occurs, the compound composition changes to values of y smaller than the original $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2$ (i.e., $y \rightarrow y < x$). It is clear that this phenomenon is caused by the larger enthalpy of formation of TiSi_2 (-55 kJ per mole) as compared to that of TiGe_2 (-47 kJ per mole).⁵ This effect has been observed for other similar compounds: e.g., it has been found, for example, that Si reduces Cu_3Ge to Cu_3Si with precipitation of Ge.⁶ In the system of interest here, since TiGe_2 and TiSi_2 have the same crystal structure and nearly the same lattice parameters, they form continuous solid solutions,⁷⁻⁹ so that there cannot be formation of new compounds. With Si available from the underlying Si-Ge alloy

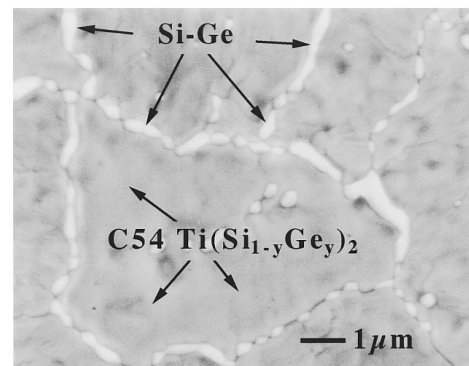


FIG. 1. Micrograph of the surface morphology of a film of C54 $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2$ on $\text{Si}_{1-x}\text{Ge}_x$. The C54 TiM_2 film was formed by reacting 400 \AA of Ti with $\approx 2200 \text{ \AA}$ of $\text{Si}_{0.67}\text{Ge}_{0.33}$ at 700°C . Upon heating, the formation of $\text{Ti}(\text{Si}_{0.67}\text{Ge}_{0.33})_2$ is observed initially. During further annealing the composition of the compound changes and germanium-rich Si-Ge alloy precipitates form along the grain boundaries of the compound (Ref. 3).

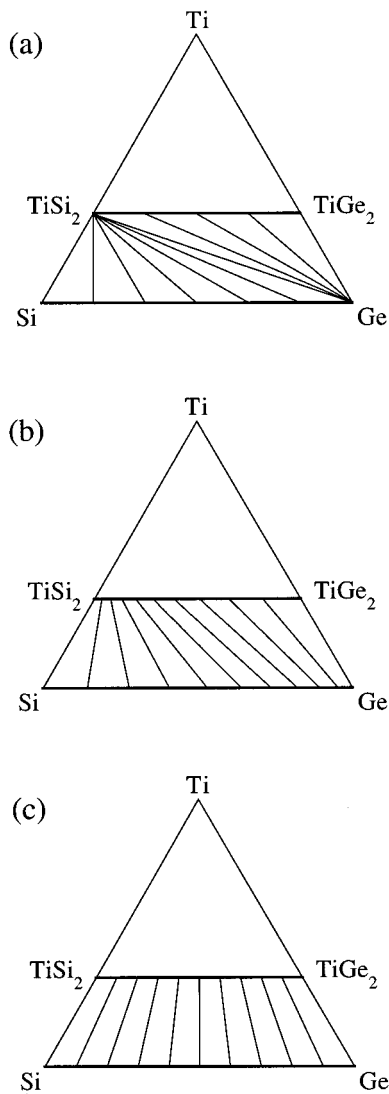


FIG. 2. Calculated C54 $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2\text{-Si}_{1-x}\text{Ge}_x$ tie lines for 1 mole of C54 $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2$ in contact with 1 mole of $\text{Si}_{1-x}\text{Ge}_x$. The C54 TiSi_2 -C54 TiGe_2 boundary and the Si-Ge boundary are indicated by thick solid lines. The C54 $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2\text{-Si}_{1-x}\text{Ge}_x$ tie lines are indicated by the lines extending between the boundaries. Tie lines were determined by minimizing the total energy of both the C54 $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2$ compound and $\text{Si}_{1-x}\text{Ge}_x$ alloy. Calculations were performed for temperatures of (a) 0 K and (b) 700 °C using starting compositions of $y=x=0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, \text{ and } 0.90$. For comparison, in (c), tie lines are drawn for $y=x$ (i.e., for the compound and Si-Ge alloy with the same Ge concentrations), which represents the high-temperature limit.

there is a tendency to form a Si-rich compound. Given that the quantity of Ti is finite, that cannot happen without some precipitation of Ge, or of a Ge-rich alloy. It will be shown below that this, at first unanticipated observation, is quite in keeping with an understanding of the ternary equilibrium diagram of the Ti-Si-Ge system.

For the present purpose attention will be focused entirely on the area bound by the compounds TiSi_2 , TiGe_2 , Si, and Ge (see Fig. 2). The Ti-rich part of the diagram will not be discussed here. The line from Si to Ge defines the solid solution alloy (one phase). In reality it should have a finite thickness, but since the solubility of Ti in Si, Ge, or their

alloys is presumed to be extremely small the width of this one phase field can be neglected. The TiSi_2 - TiGe_2 line likewise defines the compound solid solution, extending from one end to the other. This one phase domain should have a finite width, and as with the Si-Ge solid solution considered first, this single phase will be assumed to have no width. Thus the domain of interest in the ternary diagrams is a two-phase domain limited by a Si-Ge solid solution on the bottom and the compound solid solution at the top. Like all two-phase domains in a ternary equilibrium diagram, this domain should show true tie lines that indicate the compositions of the two phases that are in equilibrium with each other. That is not an arbitrary matter, the phase rule (see Ref. 10) dictates that in a ternary system at constant pressure and temperature in any two-phase domain, one phase with a chosen composition can only be in equilibrium with the other phase at a specific composition. This should be shown by tie lines. The straight lines that are often called tie lines are not properly tie lines but actually the boundaries of three-phase domains; they may be called tie lines only through an unfortunate stretching of the words. Illustrations of true tie lines in silicide ternary systems, for example, in the system TiSi_2 , CrSi_2 , and WSi_2 , can be found in Refs. 11 and 12.

In general, tie lines in ternary diagrams have to be determined experimentally. This is a tedious procedure, which explains the absence of such lines in many published equilibrium diagrams. One interesting aspect of the system that is of concern here is that it is possible to make first approximation calculations of the tie lines on the basis of classical thermodynamics. In order to accomplish this, it will be assumed that the solid solution Si-Ge behaves as an ideal solid solution, where the free energy is determined only by the entropy of mixing. A second assumption is that in the compound solid solution the enthalpy varies linearly with the composition, and the entropy again is only the entropy of mixing. In both solid solution phases it is assumed, therefore, that there exist no privileged Si-Ge interactions. In order to simplify the matter we shall consider the equilibrium between one mole of compound (N atoms, Avogadro's number, of Ti, Si plus Ge), and one mole of solid solution alloy (N atoms of Si plus Ge), with equal total amounts of Si and Ge. This would be represented by a point exactly in the center of the two-phase field. In order to write the free energy of the system, pure Si and pure Ge will be assumed to be at the reference state with free energy 0. Pure TiSi_2 will also be assumed to have a free energy of zero. Then the free energy of TiGe_2 is $+m$, where m is the difference between the heats (enthalpies) of formation of the two compounds. Here m is taken as equal to 8.0 kJ/mole according to the estimation in Ref. 5. There exist experimental values for the heat of formation of TiSi_2 , however, no such values could be found for TiGe_2 . For consistency, theoretical values were used for the heats of formation of TiSi_2 and TiGe_2 .⁵ The equilibrium compound shall have a concentration of Ge that varies from 0.5 by z (Ge concentration $y=0.5-z$), while the conservation of matter dictates that the solid solution shall assume a concentration of Ge given by $x=0.5+(2/3)z$. One can now write the free energies of both the compound ΔG_1 and alloy ΔG_2 . The calculation is simplified by the choice of one mole of each phase. For the compound,

$$\Delta G_1 = m(0.5 - z) + \frac{2}{3}RT[(0.5 - z)\ln(0.5 - z) + (0.5 + z)\ln(0.5 + z)], \quad (1)$$

where the $\frac{2}{3}$ factor in front of the entropy of mixing term reflects the fact that only the Si and Ge atoms mix, and R is the gas constant. Similarly for the second phase (alloy) one obtains

$$\Delta G_2 = RT[(0.5 - \frac{2}{3}z)\ln(0.5 - \frac{2}{3}z) + (0.5 + \frac{2}{3}z)\ln(0.5 + \frac{2}{3}z)]. \quad (2)$$

Calculating z is now simply a matter of finding the minimum for the free energy of the system ($\Delta G = \Delta G_1 + \Delta G_2$) given by the sum of the two equations above. With Si and Ge as reference states, TiSi₂ would not also be at the reference state. However, taking the true value of the free energies of the compounds into consideration would affect the value of ΔG_1 by a constant that does not affect the position of the composition that has the minimum ΔG (i.e., the constant term drops when taking the derivative of ΔG).

For the starting Ge/Si ratio of 50/50 one finds that at 700 °C z is equal to 0.21. Thus a compound with a Ge concentration [Ge/(Ge+Si)] of $y=0.29$ at 700 °C shall be in equilibrium with an alloy with a concentration of Ge of $x=0.64$. This defines one tie line. Note that as with the equilibrium between two phases in binary systems, the equilibrium concentrations do not correspond to the minimum free energies of either phase.¹⁰ Similar calculations for different overall concentrations (i.e., other Ge/Si ratios) define other tie lines. The results are displayed in Fig. 2(b). In order to give an idea of how the tie lines vary as a function of temperature a hypothetical set of tie lines at absolute zero (assuming the continued stability of the solid solutions down to 0 K) are shown in Fig. 2(a). Of course, with increasing temperature, the dominant effect of entropy will cause the tie lines to become increasingly parallel to lines issuing from the Ti apex of the diagram as shown in Fig. 2(c).

Having now determined a sufficiently accurate equilibrium diagram the features observed in Fig. 1 can be explained. In the development of the equilibrium diagram it was assumed that the atomic mobilities were such that the ternary system could reach the lowest-energy configuration directly. In reality the mobilities of the silicon and germanium atoms affect the path by which the total energy of the system is minimized. If the mobilities of silicon and germanium in the substrate were equivalent to those in the C54 compound, equilibrium conditions would prevail during the course of the reaction, and the C54 compound would form with the equilibrium concentrations of Si-Ge [for a thin C54 compound equilibrated with a Si_{0.67}Ge_{0.33} substrate at 700 °C this would be Ti(Si_{0.90}Ge_{0.10})₂]. If this were the case then there would be no need for further equilibration. However, the mobilities of the silicon and germanium atoms in the Si-Ge alloy and in the C54 TiM₂ compound are very different and cause the formation of the third phase during the reaction.

For practical purposes the mobilities of silicon and germanium in the substrate are negligibly small with respect to those in the titanium germanosilicide. It is evident that following the formation of the C54 Ti(Si_{0.67}Ge_{0.33})₂, the compound will become more rich in silicon through the con-

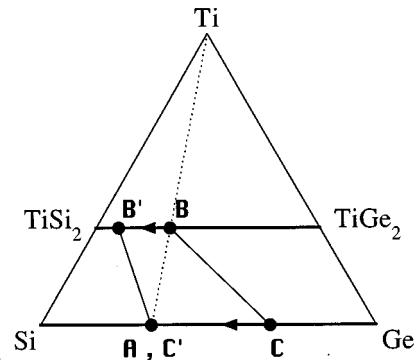


FIG. 3. The effects of germanium segregation on the compositions of the C54 TiM₂ compound and Si-Ge alloy phases during the Ti(Si_{0.67}Ge_{0.33})₂-Si_{0.67}Ge_{0.33} reaction, plotted on the Ti-Si-Ge ternary phase diagram. The compositions of the Si_{0.67}Ge_{0.33} substrate and the initial C54 Ti(Si_{0.67}Ge_{0.33})₂ are indicated by points A and B, respectively. The composition of the initial Si-Ge precipitate is indicated by point C. As Ge segregates out of the C54 compound the composition of the compound progresses from point B to point B', and the interface composition of the precipitate progresses from point C to point C'. Stability is obtained when the composition of the C54 compound reaches point B' and the surface composition of the precipitate reaches point C'.

sumption of the substrate (for the present purpose the Si-Ge alloy shall be assumed to be infinitely thick). Given the constant number of Si+Ge atoms in the compound the “silicon enrichment” of the compound will be accompanied by the precipitation of a germanium-rich Si-Ge alloy. Figure 1 shows clearly that the alloy precipitates form at the grain boundaries of the compound. The selection of these precipitation sites could be the object of some more detailed considerations. For the present purpose, suffice it to observe that precipitation at grain boundaries is due to a minimization of surface energy.

We note that the nucleation barrier of the precipitation process would lead to a region of metastability in which the compound and substrate compositions could deviate from the tie line stability compounds. However, once nucleation occurs the system should evolve towards the equilibrium state.

The dynamics of the germanium segregation process can be examined in terms of the calculated C54 Ti(Si_{1-y}Ge_y)₂-Si_{1-x}Ge_x tie lines. Since the diffusion of silicon and germanium is fast in the compound and negligible in the substrate, the reaction proceeds as atoms pass from the C54 TiM₂-substrate interface through the compound (where the exchange of silicon and germanium occurs) and to the C54 TiM₂-precipitate interface.³ Simultaneously, n number of Si+Ge atoms (in a 0.67:0.33 ratio) are removed from the substrate, and there is precipitation of n Si+Ge atoms at the C54 TiM₂ grain boundary. The initial concentrations of the silicon and germanium atoms in the precipitate will correspond to the alloy composition that is in equilibrium with the initial Ti(Si_{0.67}Ge_{0.33})₂ compound (namely, Si_{0.30}Ge_{0.70} at 700 °C). The composition of the Si_{0.67}Ge_{0.33} substrate is indicated in Fig. 3 by point A and the composition of the C54 Ti(Si_{0.67}Ge_{0.33})₂, which initially forms is indicated by point B. The initial precipitate composition is indicated by point C (as determined by the calculated tie lines).

After a finite amount of atom exchange has occurred, the C54 compound is slightly richer in silicon, and its composition on the equilibrium diagram has moved to the left of the initial $\text{Ti}(\text{Si}_{0.67}\text{Ge}_{0.33})_2$ composition (to the left of point *B*). The atom exchange process will continue, but now the Si-Ge alloy accumulating at the surface of the precipitate shall be slightly richer in silicon. As the segregation continues, the composition of the C54 changes, and thus the composition of the Si-Ge alloy accumulating at the precipitates changes (i.e., the composition of the precipitate at the C54 TiM_2 -precipitate interface is different from the average composition of the precipitate). Throughout this process the composition of the interface of the Si-Ge precipitate will be determined by the tie line in equilibrium with the appropriate C54 compound, and the composition at the surface of the precipitate shifts to the left of point *C* in Fig. 3. The atom exchange process shall proceed until the compositions at the interfaces are in equilibrium.

It is evident that the atom exchange process will continue until the $\text{Si}_{1-x}\text{Ge}_x$ substrate, the C54 $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2$ layer, and the $\text{Si}_{1-z}\text{Ge}_z$ precipitates reach equilibrium. This implies that the process continues until the surface composition of the precipitate is the same as the substrate (i.e., point *C'* equals point *A*). At this stage of the reaction both the C54 TiM_2 -precipitate interface (tie line *C'-B'*) and the C54 TiM_2 -substrate interface (tie line *A-B'*) are stable.

The progression of the atom exchange process can be observed by measuring composition changes that occur as the annealing duration is increased. To explore this effect, two C54 $\text{Ti}(\text{Si}_{0.40}\text{Ge}_{0.60})_2$ samples were prepared following the same procedures described in Refs. 3 and 4. The samples were annealed for a duration of 10 and 100 min, respectively. The compound compositions were determined from x-ray diffraction, and the results were $\text{Ti}(\text{Si}_{0.60}\text{Ge}_{0.40})_2$ and $\text{Ti}(\text{Si}_{0.74}\text{Ge}_{0.26})_2$ for the 10- and 100-min anneals, respectively. The equilibrium model used to calculate the tie lines

displayed in Fig. 2 indicates that at 700 °C an alloy of composition $\text{Si}_{0.40}\text{Ge}_{0.60}$ would be in equilibrium with a compound composition of $\text{Ti}(\text{Si}_{0.74}\text{Ge}_{0.26})_2$. We note that the composition of the 100-min anneal is equal to that predicted from the calculation, while the composition after the 10-min anneal had progressed to more than half the final composition. These results lend quantitative support to the calculations that guide the dynamic description of the interface reactions.

In this study, we have examined both the energetics and the dynamics of the Ti-Si-Ge ternary reaction, more specifically, the formation and stability of C54 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$ in contact with $\text{Si}_{1-x}\text{Ge}_x$. In the ternary phase diagram it is possible to model the two-phase domain [$\text{C54 Ti}(\text{Si}_{1-y}\text{Ge}_y)_2$ and $\text{Si}_{1-x}\text{Ge}_x$] and calculate tie lines using simple thermodynamic arguments for the crystal energies of the two materials. The simple energy balance described above indicates that these two materials can coexist, however, $x \neq y$. This indicates that following the formation of C54 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$ from the reaction of Ti with $\text{Si}_{1-x}\text{Ge}_x$, the composition of the C54 compound and/or the Si-Ge alloy must change for the system to reach equilibrium.

The results presented here demonstrate that what seemed to be unexplained phenomena of the segregation of Ti-Si-Ge compounds annealed at high temperature can be explained by a proper understanding of the ternary equilibrium diagram and of the role played by actual tie lines. The dynamics by which the C54 $\text{Ti}(\text{Si}_{1-y}\text{Ge}_y)_2/\text{Si}_{1-x}\text{Ge}_x$ system progresses from the as-formed state ($y=x$) to the equilibrium state ($y < x$) can be related to the calculated tie lines and the diffusion properties of Si and Ge in the alloy (negligible) and in the C54 compound (rapid).

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