Silicide formation and stability of Ti/SiGe and Co/SiGe

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Abstract

The formation and stability of the products of Ti and Co reacting with Si_{1-x}Ge_x substrates were investigated. For the Ti/SiGe system, when a C54 Ti\(_{(Si_{1-x}Ge_x)}_2\) layer forms, the Ge index \(v\) is initially the same as the Ge index of the Si\(_{1-x}Ge_x\) substrate (i.e. \(v = x\)). Thereafter Si\(_{1-x}Ge_x\) from the substrate continues to diffuse into the C54 layer via lattice and grain-boundary diffusion. Some of the Si which diffuses into the C54 lattice replaces Ge in the lattice, and the C54 Ti\(_{(Si_{1-x}Ge_x)}_2\) becomes silicon enriched (i.e. \(y < x\)). For the Co/SiGe system, it was determined that a silicon enriched Co\(_{(Si_{1-x}Ge_x)}_2\) layer was formed at \(-400^\circ C\). As the annealing temperature was increased, the reacted layer became even more Si enriched. For both materials systems, Ge-enriched Si\(_{1-x}Ge_x\) (\(z > x\)) islands were observed. It was found that for Co/Si\(_{1-x}Ge_x\), the reacted layer consisted of CoSi\(_2\) and Si\(_{1-x}Ge_x\) after high-temperature annealing (\(\approx 700^\circ C\)). We propose that these processes are driven by a reduction in the crystal energy of the C54 Ti\(_{(Si_{1-x}Ge_x)}_2\) phase in the Ti/SiGe system and the Co\(_{(Si_{1-x}Ge_x)}_2\) phase in the Co/SiGe system which accompanies the replacement of Ge with Si.

Keywords: Silicides; Titanium; Cobalt; Annealing

1. Introduction

Epitaxial Si_{1-x}Ge_x alloys on Si(100) are of interest because of their potential device applications. Recently, advanced devices have been demonstrated based on Si_{1-x}Ge_x/Si heterojunctions [1-4]. In device applications, it may be necessary to make Schottky or Ohmic contacts with the epitaxial Si_{1-x}Ge_x alloys. Metal silicides are important candidates for such contacts. Knowledge about reactions between thin metal films and epitaxial Si_{1-x}Ge_x is essential for applications with Si_{1-x}Ge_x devices. Recently, significant effort has been made to study the phase formation of metal/Si_{1-x}Ge_x reactions and the properties of reacted materials [5-20]. Currently the C54 phase of titanium disilicide (TiSi\(_2\)) is used in microelectronics for interconnects and source and drain contacts. Also, CoSi\(_2\) is being considered as an alternate to TiSi\(_2\) for these applications because of some advantages of CoSi\(_2\), such as its epitaxial nature with Si and stability in the presence of dopants. The C54 phase of TiSi\(_2\) and CoSi\(_2\) have similar low resistivities (\(\approx 15 \mu \Omega \text{cm}\)) [21]. The importance of TiSi\(_2\) and CoSi\(_2\) in Si-based devices and the increasing use of Si_{1-x}Ge_x motivates the investigation of the metallization of Ti or Co on Si_{1-x}Ge_x alloys [11-20].

The bilayer solid-phase Ti-Si and Ti-Ge reactions usually result in the formation of at least two prominent phases in each reaction. The two phases observed in the Ti-Si reaction are C49 TiSi\(_2\) (base-centered orthorhombic [22]) and C54 TiSi\(_2\) (face-centered orthorhombic [23]). The two phases formed in the Ti-Ge solid phase reaction are Ti\(_5\)Ge\(_5\) and C54 TiGe\(_2\) (isomorphic with C54 TiSi\(_2\)) [23,24]. There is no analogy in the Ti-Si system for Ti\(_5\)Ge\(_5\) and likewise C49 TiGe\(_2\) has not been observed in the Ti-Ge solid-phase reaction. It has been shown previously that C54 Ti\(_{(Si_{1-x}Ge_x)}_2\), isomorphic with C54 TiSi\(_2\), results from the high-temperature solid-phase reaction of Ti and Si_{1-x}Ge_x over the entire alloy composition range (0.0 < x < 1.0) [11,12,25].

The cobalt silicide phases, CoSi\(_2\), CoSi\(_3\), and CoSi\(_2\), form in sequence when a Co/Si bilayer structure is annealed [20,26,27]. The formation temperatures of CoSi\(_2\) and CoSi\(_3\) are \(\approx 400^\circ C\) and \(\approx 550^\circ C\), respectively. Previous studies found that the Co\(_3\)Ge\(_2\) and CoGe\(_2\) phases formed after annealing a Co/Ge bilayer structure at temperatures above 300 \(^\circ C\), with formation of Co\(_3\)Ge\(_2\), at about 300 \(^\circ C\) and CoGe\(_2\) at about 600 \(^\circ C\) [20,28]. According to the bulk ternary phase diagram of the Co-Si-Ge system, a miscible ternary compound Co(Si\(_{1-x}Ge_x\)) (\(x < 0.67\)) exists, which is based on cubic CoSi [29]. The crystal structures of CoSi\(_2\) and CoGe\(_2\) are different. CoSi\(_2\) has a cubic CaF\(_2\) structure while CoGe\(_2\) has an orthorhombic structure [28].

In the present study of bilayer solid-phase reactions of Ti and Co with Si_{1-x}Ge_x (x = 0.32 for Ti and x = 0.20 for Co), we have investigated phase formation and stability of the formed phases at various annealing temperatures. X-ray diffraction (XRD), energy dispersive X-ray spectroscopy...
2. Experiment

In this study, 25 mm diameter, n-type, Si(100) wafers with a resistivity of 0.8–1.2 Ω cm were used as substrates. Strained single-crystal Si_{1-x}Ge_x (x=0.20 and 0.32) alloy thin films, 800 Å to 2500 Å thick, were epitaxially grown on atomically clean Si substrates at 550 °C in a custom-made molecular beam epitaxy (MBE) system (base pressure <2×10^{-10} Torr). The procedure for obtaining an atomically clean Si substrate has been described previously [25]. For Ti metallization, 400 Å of titanium was deposited from an in-situ hot-filament Ti source. Upon completion of the titanium deposition, the samples were annealed in-situ at temperatures of 530 °C, 570 °C, 660 °C, or 700 °C for 10 min. The Si_{1-x}Ge_x thin film samples prepared for Co metallization were transferred from the MBE chamber. Prior to Co metallization, which was carried out in a separate UHV chamber with a base pressure <3×10^{-10} Torr using an electron beam evaporator, the Si_{1-x}Ge_x sample was cleaned by the same procedure for cleaning the Si wafer except that the thermal desorption was performed at 700 °C. For each Co/SiGe sample, a 200 Å polycrystalline Co layer was deposited. The metallized sample was then annealed in-situ at 400 °C, 500 °C, 600 °C, or 700 °C for 20 min.

3. Results

3.1. Ti/Si_{0.68}Ge_{0.32} solid-state reaction

XRD was used to determine the structure of the titanium germanosilicide films that formed from the 10 min annealing of the Ti/Si_{0.68}Ge_{0.32} bilayer structures. The XRD scan of the sample annealed at 530 °C contained peaks corresponding to diffraction from the (150) and (200) planes of C49 Ti(Si_{1-x}Ge_x)_2. The XRD scans of the samples annealed at 570 °C, 660 °C, and 700 °C all contained peaks corresponding to diffraction from the (311), (004), (022), and (313) planes of C54 Ti(Si_{1-x}Ge_x)_2 (see Fig. 1). The diffraction peaks of the C54 phase found in the 570 °C, 660 °C, and 700 °C samples were observed to shift to higher angles with increasing annealing temperature, indicating changes in the spacing of the diffraction planes. The Ge indices of the C54 Ti(Si_{1-x}Ge_x)_2 in these samples were calculated by: (1) calculating the diffraction plane spacings using XRD, (2) calculating the C54 lattice parameters from the plane spacings, (3) calculating the volumes of the C54 unit cells, and (4) comparing the calculated unit cell volumes with the known unit cell volumes of C54 TiSi_2 and C54 TiGe_2. In a study by Boutarek and Madar [30], it was observed that the C54 Ti(Si_{1-x}Ge_x)_2 unit cell volume varies linearly with the Ge index y. In this study, the C54 composition determination was based on the C54 unit-cell volume (using all three lattice parameters instead of just a single lattice parameter) to reduce errors which would occur if the C54 unit cell was distorted by strain. The Ge indices of the C49 Ti(Si_{1-x}Ge_x)_2 formed at 530 °C and the C54 Ti(Si_{1-x}Ge_x)_2 formed at 570 °C, 660 °C and 700 °C are 0.31, 0.32, 0.28, and 0.24, respectively. These results indicate that the Ge indices of Ti(Si_{1-x}Ge_x)_2 in the samples annealed at 530 °C and 570 °C are approximately equal to the Ge index of the deposited Si_{0.68}Ge_{0.32} alloy (i.e. y=0.32). At the higher annealing temperatures of 660 °C and 700 °C, the observed decrease in the Ge index indicates that Ge in the C54 Ti(Si_{1-x}Ge_x)_2 is being replaced by Si (i.e. y<0.32). The XRD scans of these samples included the range where the Si (400), Ge (400), and Si_{1-x}Ge_x (400) diffraction peaks occur, as shown in Fig. 1. At 530 °C and 570 °C, the only XRD peaks observed in this range corresponded to the Si substrate and the remaining unreacted Si_{0.68}Ge_{0.32} alloy layer. At 660 °C and 700 °C, in addition to the peak of the unreacted Si_{0.68}Ge_{0.32}, a peak corresponding to Si_{0.41}Ge_{0.59} (z=0.59±0.04) was observed.

Scanning electron micrographs of the surface morphologies of the samples annealed at 660 °C and 700 °C are shown in Fig. 2. After annealing at 660 °C, the formation of decorations along the C54 grain boundaries was observed (Fig. 2(a)). An increase in the average size and areal density of the decorations was observed for the sample annealed at 700 °C (Fig. 2(b)). Grain boundary decorations were not observed in the samples annealed at 530 °C or 570 °C. The morphology, structure, and composition of the C54 grains and the grain boundary decorations of the 700 °C sample were more closely examined using XTEM, EDXS, and micro-diffraction. It was found that the decorations are Ge-rich Si_{1-x}Ge_x alloy (z>x), where x is the Ge index of the Si_{0.68}Ge_{0.32} alloy layer. It was also observed that the Si_{1-x}Ge_x decorations extend from the sample surface to the underlying Si_{0.68}Ge_{0.32} alloy layer, effectively separating the neighboring C54 Ti(Si_{1-x}Ge_x)_2 grains [31].
3.2. CoSi$_{10}$Ge$_{0.20}$ solid-state reaction

XRD scans of the samples annealed at 400 °C and 700 °C are shown in Fig. 3. For the 500 °C and 600 °C annealed samples, the diffraction patterns are similar to those of the 400 °C annealed sample. The two peaks shown in Fig. 3 for the 400 °C annealed sample can be associated with two diffracting planes of the cubic CoSi structure. This suggests that the reacted layers at these temperatures contain materials with the CoSi structure. However, the peak positions of peaks were located at angles lower than those of CoSi. This shift can be associated with an expansion of inter-plane spacing of the corresponding diffraction planes. Because homogenous solid solutions between CoSi and CoGe exist, the phase formed at these temperatures should be Co(Si$_1$ - Ge$_1$), which has a larger lattice constant than CoSi, causing the observed peak shifts. By assuming that the lattice constant of Co(Si$_1$ - Ge$_1$) is a linear interpolation of CoSi and CoGe, we calculated the Ge indices y of Co(Si$_1$ - Ge$_1$). The calculated Ge indices are 0.12, 0.09 and 0.05 for the samples annealed at 400 °C, 500 °C, and 600 °C, respectively. These y values are considerably less than the Ge index in the underlying Si$_{10}$Ge$_{0.20}$ layer, and decrease with increasing annealing temperature. For the 700 °C annealed sample, peaks associated with CoSi$_2$ and a weak peak associated with the (210) diffraction of CoSi were observed in the X-ray diffraction scan. No Co–Ge phase was observed. These results indicate that at this temperature Ge had nearly completely segregated out from the Co(Si$_1$ - Ge$_1$) phase. A broad peak associated with the (400) plane of Si$_{10}$Ge$_{0.20}$ was also identified in this sample.

A scanning electron micrograph of the surface morphology of the sample annealed at 500 °C is shown in Fig. 4. "Flower-shaped" features were observed. The sample annealed at 400 °C had the same surface morphology but the contrast between the flower-shaped features and the surrounding smooth area is less pronounced than that of the 500 °C annealed sample. Scanning micro-probe AES was used to determine the element compositions on the surface of these flower-shaped features and the surrounding smooth area. It was found that these flower-shaped features were Ge-enriched clusters, and the Ge composition increased with increasing annealing temperature. Whether these Ge-rich clusters are Si$_{1}$Ge$_{z}$ (z > x) is not clear at present because Co Auger signals were also detected when probing the cluster area. But these Co signals may originate from the open area (i.e. the area not covered by the cluster) nearby or under the cluster. It was also found that the Ge composition is uniform over the smooth surface area. AFM was used to examine the surface roughness of
These results indicate that the Ge index in the Co(Si$_{1-y}$Ge$_y$) layer obtained by XRD can only be considered to be an average Ge composition in the entire reacted layer. The fact that the decrease of the Ge index in the Co(Si$_{1-y}$Ge$_y$) layer was accompanied by an increase of Ge content in the flower-shape clusters when the annealing temperature was increased implies that Ge inside the Co(Si$_{1-y}$Ge$_y$) lattice was replaced by Si, and excess Ge diffused to the grain boundaries and the surface to form the Ge-enriched clusters. AFM was also used to examine the surface roughness of these samples. It was found that the Ge-rich clusters extended above the surrounding smooth surface.

### 4. Discussion

It was observed that the Ti(Si$_{1-y}$Ge$_y$)$_2$ and Co(Si$_{1-y}$Ge$_y$) phases were not stable when in contact with the Si$_{1-y}$Ge$_x$ alloy. The results indicated that germanium segregated out of these germanosilicide phases (replaced by silicon available from the substrate) effectively changing the composition of the germanosilicide. In the Ti-Si$_{1-y}$Ge$_x$ system, the measured compositions indicate that the Ti + Si$_{1-y}$Ge$_x$ → C54 Ti(Si$_{1-y}$Ge$_y$)$_2$ + Si$_{1-y}$Ge$_y$ ($y < x < z$) reaction can be separated into a two-step process: (1) C54 formation and (2) germanium segregation (Eqs. (1) and (2), respectively).

\[
\text{Ti} + \text{Si}_{1-y}\text{Ge}_x \rightarrow \text{C54 Ti(Si}_{1-y}\text{Ge}_y)_2
\]

\[
\text{C54 Ti(Si}_{1-y}\text{Ge}_y)_2 + \text{Si}_{1-y}\text{Ge}_y \rightarrow \text{C54 Ti(Si}_{1-y}\text{Ge}_y)_2 + \text{Si}_{1-y}\text{Ge}_y (y < x < z)
\]

Our results indicate that at the C54 formation temperature the C54 Ti(Si$_{1-y}$Ge$_y$)$_2$ forms with the same Ge index as the deposited Si$_{1-y}$Ge$_y$ layer (i.e. y = x). As the annealing temperature is increased, Ge on the C54 lattice is replaced by Si and the Ge index of the C54 Ti(Si$_{1-y}$Ge$_y$)$_2$ decreases ($y < x$). The decrease in the Ge index of the C54 titanium germanosilicide occurs concurrently with the observed formation of Ge-rich Si$_{1-y}$Ge$_x$ alloy grain boundary decorations ($z > x$). Excess Ge which diffuses to the C54 grain boundaries combines with Si and Ge from the substrate and nucleates as Ge-rich Si$_{1-y}$Ge$_x$ ($z > x$). The nucleation of Si$_{1-y}$Ge$_x$ at the C54 grain boundaries establishes a sink for excess Ge and enables the replacement of Ge with Si on the C54 lattice to continue.

With the Co/Si$_{1-y}$Ge$_x$ system, an intermediate ternary phase, i.e. Co(Si$_{1-y}$Ge$_x$), was formed at annealing temperatures from 400 °C up to 600 °C. The Ge index in this ternary phase was lower than that of the underlying Si$_{1-y}$Ge$_x$ layer and decreased with increasing annealing temperature. The distribution of Ge was not uniform in the reacted layer with the top part of the reacted layer being relatively rich in Ge. The temperature dependence of the Ge composition suggests that Ge inside the Co(Si$_{1-y}$Ge$_y$) lattice was replaced by Si during the annealing. The Ge atoms segregated out from the ternary compound and diffused to the sample surface.
and formed Ge-enriched clusters through grain boundary and surface diffusion.

A possible driving force for the segregation of Ge from the C54 Ti(Si$_{1-x}$Ge$_x$)$_2$ and Co(Si$_{1-x}$Ge$_x$)$_2$ lattices can be found in the relative crystal energies between the C54 TiSi$_2$ and C54 TiGe$_2$ structures and between the CoSi and CoGe structures. As a first-order approximation, the heat of formation of these materials can be used as an approximation of the relative crystal energies of these materials. We further assume that the heat of formation (i.e. crystal energy) of a ternary compound is a linear interpolation between the heat of formation values of its two end-point binary compounds (another first-order approximation). Under these approximations, the crystal energies of Ti(Si$_{1-x}$Ge$_x$)$_2$ and Co(Si$_{1-x}$Ge$_x$)$_2$ alloys will be lowered if Ge atoms are replaced by Si atoms in both structures because the heats of formation (TiSi$_2$ and CoSi) are lower than the germanides (TiGe$_2$ and CoGe). From thermodynamic data, the heats of formation are $-57.0$, $-47.5$, $-100.4$, and $-34.2$ kJ mol$^{-1}$ for TiSi$_2$, TiGe$_2$, CoSi, and CoGe, respectively [30]. This suggests that the crystal energy will drop if the Ge atoms are replaced by Si atoms in both structures. Using these data, the amount of crystal energy reduction, $\Delta G$, by replacing Ge with Si in these two structures can be calculated using the following equation:

$$\Delta G = -(9.5\text{ kJ mol}^{-1}) \delta y \text{ for Ti(Si}_{1-x}\text{Ge}_x\text{)}_2$$
$$\Delta G = -(66.2\text{ kJ mol}^{-1}) \delta y \text{ for Co(Si}_{1-x}\text{Ge}_x\text{)}_2$$

where $\delta y$ is the change in Ge index in the C54 Ti(Si$_{1-x}$Ge$_x$)$_2$ or Co(Si$_{1-x}$Ge$_x$)$_2$ structure. Eq. (3) was obtained using an approximation which states that the heat of formation (i.e. crystal energy) of a ternary compound is a linear interpolation between the heat of formation values of its two end-point binary compounds. From this analysis, it can be expected that the Ge segregation in the Co(Si$_{1-x}$Ge$_x$)$_2$/Si$_{1-x}$Si$_x$ system would be more severe than in the Ti(Si$_{1-x}$Ge$_x$)$_2$/Si$_{1-x}$Si$_x$ system. Our results support this supposition. We suggest that the diffusivities of silicon and germanium in these structures, which are not available at present, will effect the speed of the segregation, but will not alter the general tendency of the segregation. The above discussion may be extended to other metal/SiGe systems to estimate the stability of the metal-SiGe compounds in those systems formed by solid-state reaction.

It is interesting to compare the formation temperature of CoSi$_2$ in the Co/Si binary system with that in the Co/Si$_{1-x}$Ge$_x$ system. The formation temperature of CoSi$_2$ is around 550 °C in the Co/Si system. But in the Co/Si$_{1-x}$Ge$_x$ system, CoSi$_2$, together with some residual CoSi, was only observed at higher temperatures (700 °C) as shown in Fig. 3. At this temperature, Ge was totally separated from the formed Co–Si phases, and no Co–Ge phase was observed. These observations suggest that CoSi$_2$ nucleated after all Ge atoms were segregated out from the Co(Si$_{1-x}$Ge$_x$)$_2$. It is worth pointing out that the heat of formation of CoSi$_2$ ($-102.9$ kJ mol$^{-1}$) is significantly lower than that of CoGe$_2$ ($17.4$ kJ mol$^{-1}$). This may explain why CoGe$_2$ was not observed in the 700 °C annealed sample.

5. Conclusion

The formation and stability of C54 Ti(Si$_{1-x}$Ge$_x$)$_2$ and Co(Si$_{1-x}$Ge$_x$,SiGe) produced from the solid-phase reaction of Ti and Co with Si$_{1-x}$Ge$_x$ have been investigated. For the Ti/SiGe system, the reaction can be separated into two stages: $\text{Ti + Si}_{1-x}\text{Ge}_x \rightarrow \text{C54 Ti(Si}_{1-x}\text{Ge}_x\text{)}_2$ and

$$\text{C54 Ti(Si}_{1-x}\text{Ge}_x\text{)}_2 + \text{Si}_{1-x}\text{Ge}_x \rightarrow \text{C54 Ti(Si}_{1-x}\text{Ge}_x\text{)}_2 + \text{Si}_{1-x}\text{Ge}_x$$

where $y < x < z$. For the Co/SiGe system, a Co(Si$_{1-x}$Ge$_x$)$_2$ layer with $y = 0.12$ was initially formed. It was found that the Ge indices in the C54 Ti(Si$_{1-x}$Ge$_x$)$_2$ and Co(Si$_{1-x}$Ge$_x$)$_2$ decreased with increasing annealing temperature. A thermodynamic driving force is used to explain these results. The replacement of Ge with Si in titanium and cobalt germanosilicide causes a reduction of the crystal energy. In the Ti/Si$_{1-x}$Ge$_x$ system, excess Ge combines with the Si and Ge diffusing into the C54 grain boundaries from the substrate and nucleates as Si$_{1-x}$Ge$_x$ ($z > x$) along the grain boundaries. In the Co/Si$_{1-x}$Ge$_x$ system, excess Ge diffuses to the sample surface through grain boundary and surface diffusion to form Ge-enriched clusters. Once Ge is segregated out from Co(Si$_{1-x}$Ge$_x$)$_2$, CoSi$_2$ begins to nucleate from the CoSi.

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References


