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# Interfacial reactions of the Co/$Si_{1-x}Ge_x$ system

Jian-Shing Luo [a], Wen-Tai Lin [a,*], C.Y. Chang [b], W.C. Tsai [b], S.J. Wang [c]

[a] *Department of Materials Science and Engineering, National Cheng Kung University, Tainan 70101, Taiwan, ROC*
[b] *Department of Electrical Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, ROC*
[c] *Department of Electrical Engineering, National Cheng Kung University, Tainan 70101, Taiwan, ROC*

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## Abstract

Thermal reactions of Co(200 Å)/$Si_{0.76}Ge_{0.24}$(1500 Å)/Si and Co(200 Å)/$Si_{0.54}Ge_{0.46}$(1000 Å)/Si systems in a vacuum of 1–$2\times10^{-6}$ Torr were studied. At temperatures above 200°C Ge segregation appeared even though no silicides and/or germanosilicides were formed. At a temperature of 225–550°C Co($Si_{1-y}Ge_y$) was formed, in which the Ge concentration was deficient. The formation temperatures of $CoSi_2$ in the Co/$Si_{1-x}Ge_x$ systems, where $x=0.24$ and 0.46, were above 575°C, being relatively higher than that in the Co/Si system. At temperatures above 500°C the island structure, Ge segregation to the surface of the exposed $Si_{1-x}Ge_x$ films, and the penetration of reacted layer into the Si substrate occurred. At temperatures above 700°C a SiC layer was grown on the film surface. For the $Si_{0.54}Ge_{0.46}$ films the penetration of the reacted layer into the Si substrate occurred even at 350°C owing to the wave structure of the as-grown $Si_{0.54}Ge_{0.46}$ films. A Si layer interposed between Co and $Si_{0.76}Ge_{0.24}$ films is an effective scheme to grow a continuous $CoSi_2$ contact at 550–600°C without inducing Ge segregation and hence the strain relaxation in the $Si_{0.76}Ge_{0.24}$ films.

*Keywords:* Interfacial reactions; Co/$Si_{1-x}Ge_x$ systems

## 1. Introduction

There has been considerable interest in the $Si_{1-x}Ge_x$ alloy system because of its potential applications in high-speed and high-performance electronic devices [1,2]. The formation of metal–$Si_{1-x}Ge_x$ ohmic contacts is required for the device applications. Recently, the thermal reactions of metals such as Ni, Pd, Pt, Ti, Co, W, and Cr with $Si_{1-x}Ge_x$ films have been studied [3–12]. Ternary phases and Ge segregation were generally found in the thermal reactions of metal/$Si_{1-x}Ge_x$. In a salicide formation technique $CoSi_2$ has received much attention since it can significantly reduce the contact resistance of Si devices and act as a solid diffusion source to form shallow junctions. The impetus for studying the Co/Si system is easily transferred to the Co/$Si_{1-x}Ge_x$ system. Thermal reactions of Co/$Si_{1-x}Ge_x$ system have been studied by various methods [8–10]. In this paper, the effect of Ge concentration on retarding the phase formation and the microstructure of the reacted layer, the variation of chemical compositions in the reacted layer and $Si_{1-x}Ge_x$ films, and the strain relaxation in the $Si_{1-x}Ge_x$ films are studied. Meanwhile, a scheme for growing the stable $CoSi_2$ contact on $Si_{0.76}Ge_{0.24}$ films is demonstrated.

## 2. Experimental procedures

Epitaxial $Si_{0.76}Ge_{0.24}$ and $Si_{0.54}Ge_{0.46}$ layers about 1500 Å thick were grown on n-type Si(100) at 550°C by ultra-high vacuum chemical vapor deposition. Prior to Co deposition the $Si_{1-x}Ge_x$ layers were first cleaned by RCA method and then treated for oxide removal by immersion in buffered HF for 1 min followed by a rinse in deionized water. The specimens were then dried with a flow of $N_2$ and immediately loaded into the chamber. An overlayer of Co 200 Å thick was deposited onto the $Si_{1-x}Ge_x$ layers at room temperature by electron gun evaporation at a rate of 1 Å $s^{-1}$. The base pressure was about $1\times10^{-6}$ Torr. The as-deposited samples were annealed at a temperature of 200–750°C in a vacuum of 1–$2\times10^{-6}$ Torr. Phase identification was carried out by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The microstructure was observed by plan-view TEM and cross-sectional TEM (XTEM). The chemical composition of the films was analyzed by energy-dispersive spectrometry (EDS) in a transmission electron microscope equipped with a field emission gun using an electron probe of 50 Å.

## 3. Results and discussion

For the Co/$Si_{1-x}Ge_x$ ($x=0.24$ and 0.46) films annealed at 200°C no cobalt silicides and/or cobalt germanosilicides

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[*] Corresponding author.

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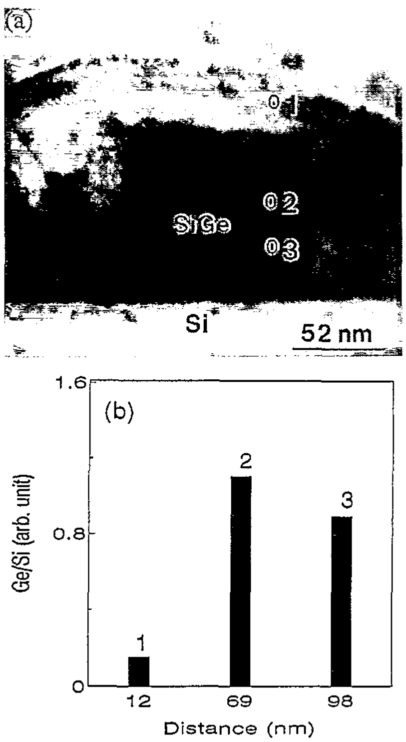

Fig. 1. (a) XTEM micrograph and (b) the depth profile of the Ge/Si concentration ratio for the Co/$Si_{0.54}Ge_{0.46}$ sample annealed at 200°C for 0.5 h.

were formed. However, from XTEM/EDS analysis an intermixing layer of Co, Si, and Ge, about 350 Å thick, was formed. One example is shown in Fig. 1 in which the concentration ratio of Ge/Si in the mixing layer changed from 0.05 at the surface to 1.10 at the interface near the side of SiGe layer, while the Co concentration decreased as a function of distance from the film surface. It is evident that at 200°C even though no cobalt compounds were formed segregation of Ge atoms from the mixing layer to the $Si_{1-x}Ge_x$ layer underneath was in progress.

In the present study CoSi and $CoSi_2$ structures appeared at 225 and above 575°C, respectively. However, $Co_5Ge_7$ and $CoGe_2$ phases were not observed. This result is consistent with previous reports [8–10,13]. It is interesting to note that for the Co/Ge system CoGe, $Co_5Ge_7$, and $CoGe_2$ form sequentially at temperatures above 220, 280, and 600°C [14]. From XTEM/EDS analysis the cubic CoSi structure was of $Co(Si_{1-y}Ge_y)$ and most of the $CoSi_2$ structure were nearly Ge-free as shown in Figs. 2 and 3, respectively. $Co(Si_{1-y}Ge_y)$ is of a solid solution of CoSi and CoGe [15]. Generally, the $Co(Si_{1-y}Ge_y)$ compound is deficient in Ge and its chemical compositions are inhomogeneous presumably because of the incomplete reactions between Co and $Si_{1-x}Ge_x$ layers. In the $Co(Si_{1-y}Ge_y)$ layer the Co concentration gradually approached the stoichiometric value as the temperature was increased, while the Ge/Si concentration ratio remained in the range 0.02–0.18 for the Co/$Si_{0.76}Ge_{0.24}$ samples and 0.13–0.30 for the Co/$Si_{0.54}Ge_{0.46}$ samples, respectively, without significantly changing as a function of

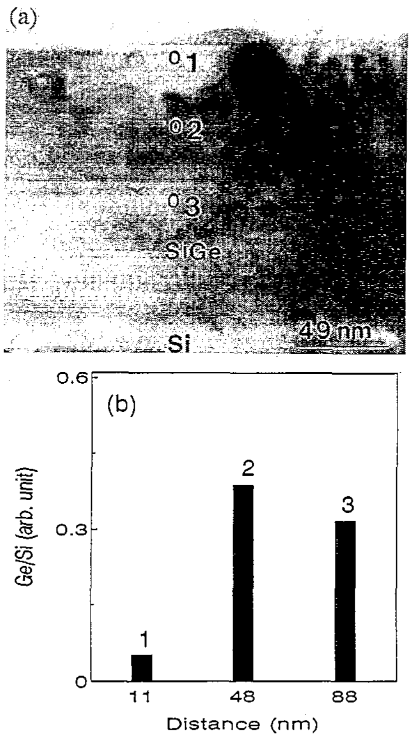

Fig. 2. (a) XTEM micrograph and (b) the depth of the Ge/Si concentration ratio for the Co/$Si_{0.76}Ge_{0.24}$ sample annealed at 350°C for 0.5 h. The $Co(Si_{1-y}Ge_y)$ grain is labelled 1 and the regions labelled 2 and 3 are of the $Si_{0.76}Ge_{0.24}$ film.

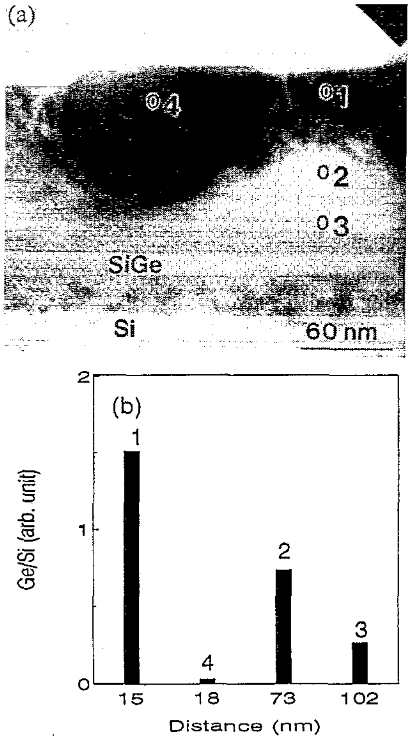

Fig. 3. (a) XTEM micrograph and (b) the depth profile of the Ge/Si concentration ratio for the Co/$Si_{0.76}Ge_{0.24}$ sample annealed at 600°C for 0.5 h. The regions labelled 1, 2, and 3 are of the $Si_{0.76}Ge_{0.24}$ film and the $CoSi_2$ grain is labelled 4.

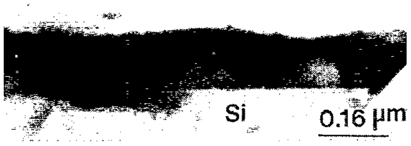

Fig. 4. XTEM micrograph of the Co/$Si_{0.76}Ge_{0.24}$ sample annealed at 600°C shows that part of the reacted layer penetrates into the Si substrate.

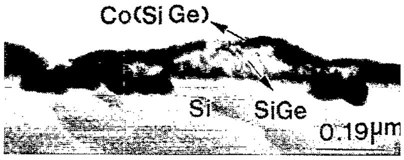

Fig. 5. XTEM micrograph of the Co/$Si_{0.54}Ge_{0.46}$ sample annealed at 350°C shows the penetration of the reacted layer into the Si substrate.

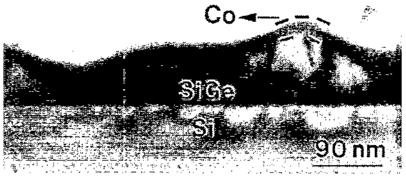

Fig. 6. XTEM micrograph shows the wave structure of the as-grown $Si_{0.54}Ge_{0.46}$ film.

temperature. It has been reported that a single phase of $Co(Si_{1-y}Ge_y)$ with the Ge/Si ratios ranging from 0.11 to 1.00 can be formed at 760°C [15]. The ejected Ge atoms were pushed to the interface between the $Co(Si_{1-y}Ge_y)$ layer and the unreacted $Si_{1-x}Ge_x$ layer, forming a Ge-rich $Si_{1-x}Ge_x$ layer as shown in Fig. 2. At temperatures above 500°C an island structure began to form and part of the $Si_{1-x}Ge_x$ layer emerged as shown in Fig. 3, in which Ge segregated to the surface of the exposed $Si_{1-x}Ge_x$ film. Meanwhile, the penetration of the reacted layer into the Si substrate was observed as shown in Fig. 4. For the Co/$Si_{0.54}Ge_{0.46}$ system the reacted layer protruded to the Si substrate even at 350°C as shown in Fig. 5. This result is due to the wave structure of the as-grown $Si_{0.54}Ge_{0.46}$ film shown in Fig. 6, in which the thinner part of the $Si_{0.54}Ge_{0.46}$ film is not thick enough to completely consume the Co layer during thermal reaction, and thus the remaining Co tends to diffuse into the Si substrate to form Co(Si, Ge) compound. It has been reported that for epitaxial $Si_{1-x}Ge_x$ layer grown on Si at high misfit, strain relaxation may result in island formation or roughening of the surface of the $Si_{1-x}Ge_x$ films [16].

In the Co/$Si_{0.74}Ge_{0.26}$ and Co/$Si_{0.54}Ge_{0.46}$ systems $CoSi_2$ appeared at temperatures above 575 and 650°C, respectively, while in the Co/Si system the reacted layer was completely transformed to $CoSi_2$ at 550°C. Examples for Co/Si, Co/$Si_{0.74}Ge_{0.26}$, and Co/$Si_{0.54}Ge_{0.46}$ systems annealed at 550°C are shown in Figs. 7–9, respectively. It is interesting to note that a significant amount of Co remained in the Co/$Si_{0.54}Ge_{0.46}$ system and no island structures were present in the Co/Si system. The ejection of Ge from the reacted $Si_{1-x}Ge_x$ layer and the sluggish interfacial reactions in the Co/$Si_{1-x}Ge_x$ system compared with those in the Co/Si system could be explained in terms of the difference between the heats of formation for Co–Si and Co–Ge [17]. The heat of formation for Co–Si is much higher than that for Co–Ge, and hence the reaction between Co and the $Si_{1-x}Ge_x$ layer is considered to be dominated by the reaction of Co and Si.

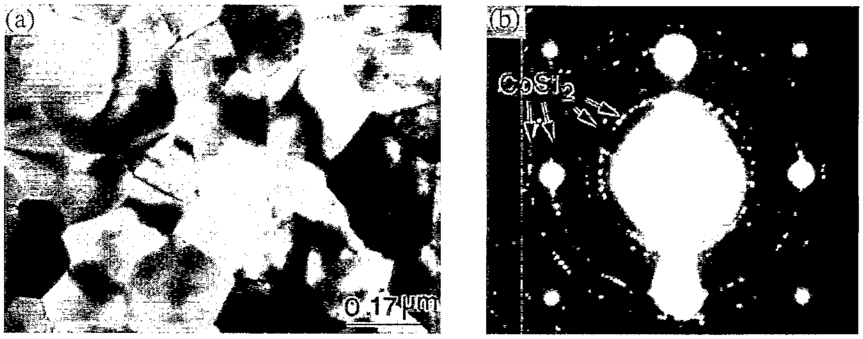

Fig. 7. (a) Plan-view TEM micrograph of the Co/Si sample annealed at 550°C, and (b) the electron diffraction pattern (DP) of (a).

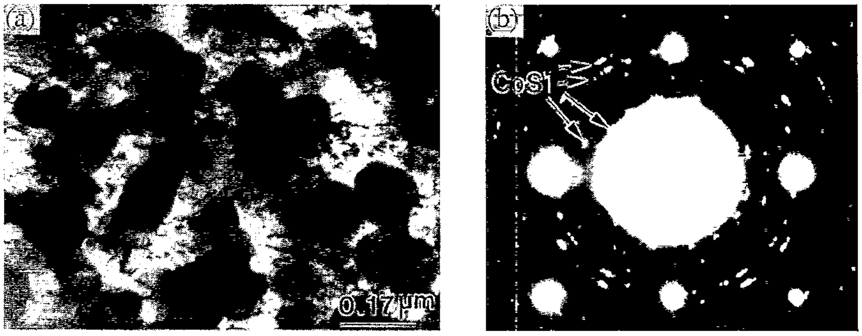

Fig. 8. (a) Plan-view TEM micrograph of the Co/$Si_{0.76}Ge_{0.24}$ sample annealed at 550°C, and (b) DP of (a).

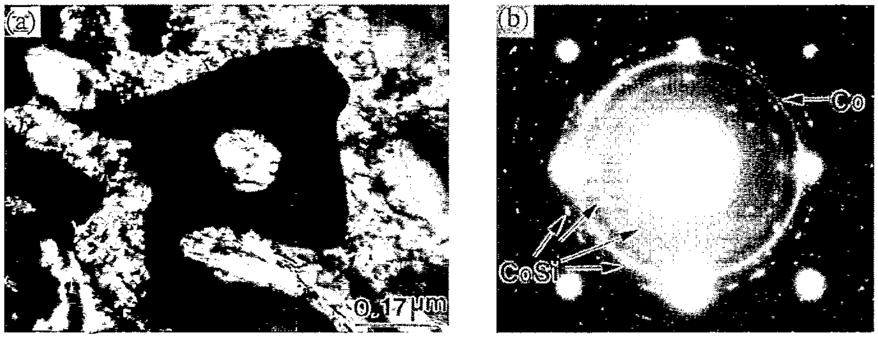

Fig. 9. (a) Plan-view TEM micrograph of the Co/$Si_{0.54}Ge_{0.46}$ sample annealed at 550°C, and (b) DP of (a).

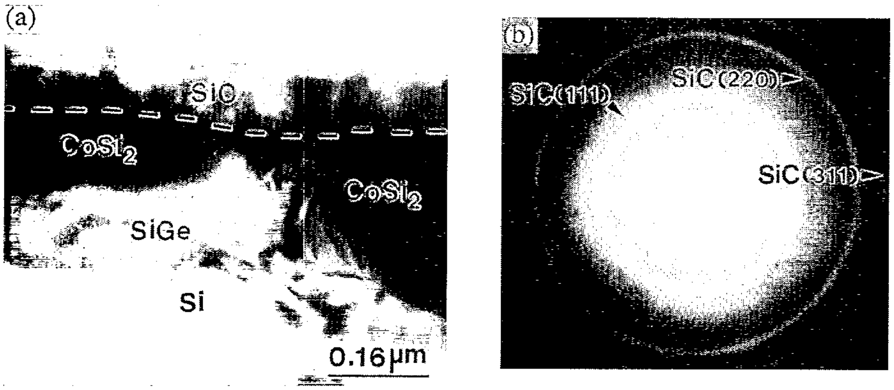

Fig. 10. (a) XTEM micrograph of the Co/$Si_{0.76}Ge_{0.24}$ sample annealed at 750°C shows the growth of SiC layer on the film surface. (b) DP of the SiC layer.

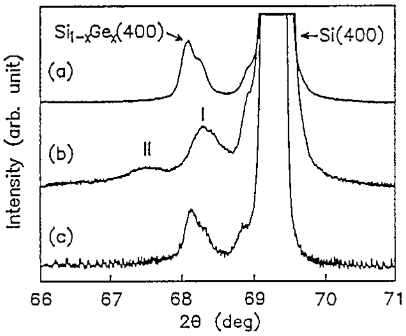

Fig. 11. XRD patterns of (a) the as-grown $Si_{0.76}Ge_{0.24}$ film, (b) the Co/$Si_{0.76}Ge_{0.24}$ sample annealed at 600°C, and (c) the Co/Si/$Si_{0.76}Ge_{0.24}$ sample annealed at 600°C. Angular regions marked by I and II in (b) correspond to the (004) reflections from the Ge-deficient and the Ge-rich $Si_{1-x}Ge_x$ layers, respectively.

In the present study, all the annealings were carried out in a vacuum of $1\text{–}2\times10^{-6}$ Torr. On annealing the Co/$Si_{1-x}Ge_x$/Si systems at temperatures above 700°C a cubic SiC layer appeared on the film surface as shown in Fig. 10, in which the island structure of $CoSi_2$ and the segregation of Ge were also observed. However, even for the films annealed in an $N_2$ furnace at 750°C no SiC layer was formed. Similar results were also observed in the Si substrates annealed under the same conditions [18]. For the Si substrates annealed at 800°C in a vacuum of $1\text{–}2\times10^{-6}$ Torr a limited thickness around 1600 Å of a SiC layer could be achieved after 1.5 h annealing, implying that in the present study the main carbon source was the carbon-containing residue present at the chamber walls, which included hydrocarbon, CO, and $CO_2$ [19]. Below the formation temperature of SiC, 700°C, the carbon-containing residue seems to have no significant effect on the thermal reactions of the Co/$Si_{1-x}Ge_x$/Si systems.

In Fig. 11 the decrease and increase of the lattice constant of the $Si_{0.76}Ge_{0.24}$ film annealed at 600°C indicate that the strain relaxation and enhancement appear concurrently in the film. Similar results have been observed by Buxbaum et al. in the Pd/$Si_{1-x}Ge_x$ system [20]. They attributed this phenomenon to the creation of defects. It is worth noting that at temperatures above 500°C significant segregation of Ge occurred in the $Si_{1-x}Ge_x$ films as shown in Fig. 3. For the Co(100 Å)/Si(325 Å)/$Si_{0.76}Ge_{0.24}$(1500 Å)/Si system annealed at 550–600°C a continuous $CoSi_2$ layer was formed on the surface of the $Si_{0.76}Ge_{0.24}$ film. One example is shown in Fig. 12, in which the thickness, the Ge concentration and the lattice constant of the $Si_{0.76}Ge_{0.24}$ film remained nearly unchanged from EDS/XTEM and XRD analysis. The corresponding XRD pattern of this film is shown in Fig. 11. As a consequence, one of the causes for the strain variation in the annealed $Si_{1-x}Ge_x$ film may be the segregation of Ge in the film during annealing. Nevertheless, it is evident that an Si layer interposed between the Co and $Si_{0.76}Ge_{0.24}$ films is an effective scheme to grow a continuous $CoSi_2$ contact at 550–600°C without inducing segregation of Ge and hence the strain relaxation in the $Si_{0.76}Ge_{0.24}$ films. This result is consistent with the report that, in the absence of ternary phases at the semiconductor-rich side of the phase diagram,

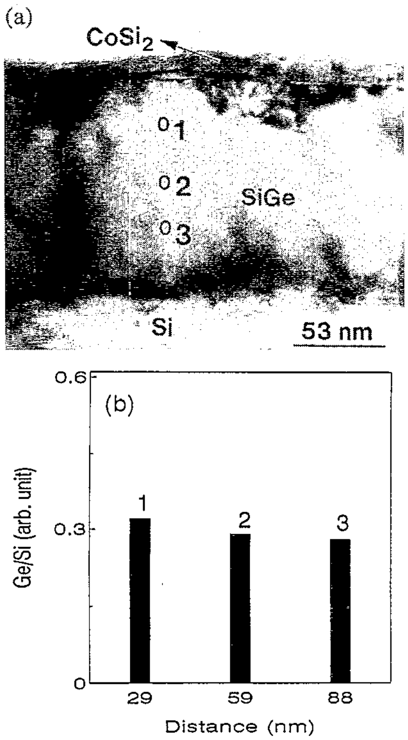

Fig. 12. (a) XTEM micrograph and (b) the depth profile of the Ge/Si concentration ratio in the $Si_{0.76}Ge_{0.24}$ film for the $Co/Si/Si_{0.76}Ge_{0.24}$ sample annealed at 600°C. A continuous $CoSi_2$ layer was formed on the surface of the $Si_{0.76}Ge_{0.24}$ film and no apparent segregation of Ge occurred in the $Si_{0.76}Ge_{0.24}$ film.

the silicide could be chosen as a stable contact to the $Si_{1-x}Ge_x$ films [21].

In the present study, in order to grow a stoichiometric $CoSi_2$ layer on the $Si_{0.76}Ge_{0.24}$ film the thicknesses of the deposited Co and Si layers were determined to be 100 and 325 Å, respectively, from the theoretical calculation. If the Co layer is not fully consumed by the Si layer the remaining Co tends to react with the underlying $Si_{0.76}Ge_{0.24}$ film to form the $CoSi_2$ islands and simultaneously enrich the Ge concentration of the surface of $Si_{0.76}Ge_{0.24}$ film owing to Ge segregation. Interfacial roughness may result in a high contact resistivity [22]. If the Si layer is not fully consumed by Co the remaining Si may form an Si layer or a SiGe layer with less Ge concentration at the interface. A change in the Ge concentration of the SiGe layer may alter the contact resistivity since the band gap of the SiGe layer is a function of Ge concentration. More details remain to be further studied.

## 4. Summary and conclusions

Thermal reactions of the $Co/Si_{0.76}Ge_{0.24}$ and $Si_{0.54}Ge_{0.46}$ systems were studied. Ge was ejected from the reacted $Si_{1-x}Ge_x$ layer at temperatures above 200°C even if no silicides or germanosilicides were formed. At a temperature of 225–550°C $Co(Si_{1-y}Ge_y)$ was formed, in which the Ge concentration was deficient. The Ge concentration played a role in retarding the formation of $CoSi_2$ in the $Co/Si_{1-x}Ge_x$ films during annealing. At temperatures above 500°C an island structure, Ge segregation to the surface of the exposed $Si_{1-x}Ge_x$ layer, and the reacted layer penetrating into the Si substrate appeared. At temperatures above 700°C an SiC layer was formed on the film surface because of the residual carbon-containing gases present at the chamber walls. For the $Si_{0.54}Ge_{0.46}$ films the reacted layer penetrated into the Si substrate even at 350°C owing to the wave structure of the asfigwn $Si_{0.54}Ge_{0.46}$ films. Strain variation in the annealed $Si_{1-x}Ge_x$ films may result from the Ge segregation. An Si layer interposed between Co and $Si_{0.76}Ge_{0.24}$ films is an effective scheme to form a continuous $CoSi_2$ contact at 550–600°C without inducing Ge segregation and hence the strain relaxation in the $Si_{0.76}Ge_{0.24}$ films.

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