# Interfacial reactions of Ti/ and Zr/$Si_{1-x}Ge_x$/Si contacts with rapid thermal annealing

Yukio Yasuda* and Osamu Nakatsuka
*Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University*
*Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

Shigeaki Zaima
*Center for Cooperative Research in Advanced Science and Technology, Nagoya University*
*Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

The interfacial reactions of Ti/ and Zr/$Si_{0.5}Ge_{0.5}$/Si systems by rapid thermal annealing (RTA) have been investigated at temperatures from 580 to 900°C. In Ti/$Si_{0.5}Ge_{0.5}$ systems, C49-$TiSi_2$ is transformed to C54-Ti$(Si_{1-y}Ge_y)_2$ by RTA for 30 sec at about 750°C, whose transformation temperature is lower than that of $TiSi_2$ in Ti/Si systems. The C54-Ti$(Si_{1-y}Ge_y)_2$ has Si-rich chemical compositions and, on the other hand, the formation of Ge piling up is observed. In the case of Zr/$Si_{0.5}Ge_{0.5}$ systems, $Zr_5Ge_4$ and C49-Zr$(Si_{1-y}Ge_y)_2$ is produced at 580°C and 700°C, respectively. The reaction between Zr and $Si_{1-x}Ge_x$ occurs uniformly and the Ge fraction of C49-Zr$(Si_{1-y}Ge_y)_2$ is close to $y$=0.5. It is considered that Ge atoms have an influence on the reduction of formation temperature of C54 and C49 phases in Ti/ and Zr/$Si_{1-x}Ge_x$ systems, respectively. The electrical properties such as Schottky barrier heights in Ti/ and Zr/$Si_{0.5}Ge_{0.5}$ systems can be explained on the basis of interfacial reactions.

*Keywords*: Ti/SiGe system; Zr/SiGe system; Interfacial reaction; Electrical property; Schottky barrier height

## 1. Introduction

The increase in parasitic series resistance such as ohmic contact resistance at metal/Si contacts has become one of the most serious problems with shrinking the dimension in ultra-large scale integrated circuits (ULSI's) [1]. In the generation of 0.1 m rule devices, a contact resistivity lower than $10^{-8}$ cm$^2$ would be necessary to realize ULSI's with the high performance. In order to form the ohmic contact with very low resistivity and high reliability, both an understanding of determining factors of electrical properties at metal/Si interfaces and a development of new contact materials is essential.

We have systematically investigated the solid-phase reactions and electrical properties of transition-metal/Si(100) systems, in which contact resistivities as low as $10^{-8}$ cm $^2$ have been reported for Zr/ and Hf/$n^+$-Si(100) contacts [2-5]. However, there are some limitation factors, such as the bandgap, the electron affinity and the solid solubility of impurity atoms in Si, for achieving much lower contact resistivity.

In particular, it is essentially difficult to reduce the contact resistivities for both $n^+$- and $p^+$-Si simultaneously by using a contact material in complimentary metal-oxide-semiconductor (CMOS) devices. Because the sum of Schottky barrier heights (SBH's) for $n^+$- and $p^+$-Si is equal to the bandgap of Si, $E_g$, a material with a low contact resistivity for one type of Si is disadvantageous for the other type. In addition, the lowering of contact resistivity for $p^+$-Si is limited by the maximum doping concentration of impurities into Si, since the solid solubility of B atoms in Si is lower than those of $n$-type impurities such as As and P atoms. Therefore, it is necessary to introduce new technologies for future ULSI's in order to realize the contact resistivity for $p^+$-Si as low as $10^{-8}$ cm$^2$.

For this purpose, we have introduced an idea of bandgap engineering in ohmic contact systems, in which $Si_{1-x}Ge_x$ and/or Ge films are used as intermediate layers between metal films and heavily diffused regions of Si substrates [6-9]. The application of $Si_{1-x}Ge_x$ in the ohmic contact system has some advantages such as; (1) good compatibility with Si processes, (2) controllability of the bandgap (3) heteroepitaxial growth on Si(100) substrates, and (4) possibility in realizing higher doping concentration of impurities than that in Si. Figure 1 shows a schematic energy band diagram of a metal/$p$-$Si_{1-x}Ge_x$/$p$-Si heterostructure. Since the $E_g$ of $Si_{1-x}Ge_x$ can be changed from 1.12 to 0.66 eV with increasing the Ge fraction, $x$, and the band offset is mainly formed at the valence band edge

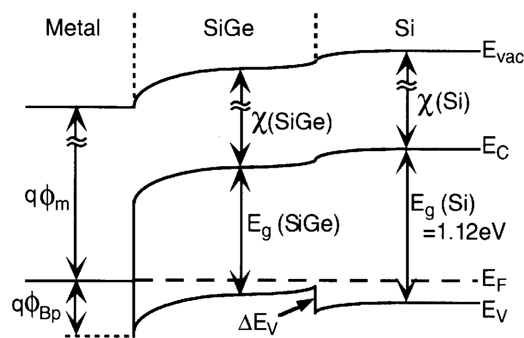


Fig. 1. A schematic energy band diagram of a metal/$p$-$Si_{1-x}Ge_x$/Si systems, where $E_g$ is the bandgap, ë the electron affinity, $Ö_m$ the work function of metal, $Ö_{Bp}$ the Schottky barrier height and $\Delta E_V$ the difference in energy of the valence bang edges.

*e-mail: yasuda@alice.xtal.nagoya-u.ac.jp

of $Si_{1-x}Ge_x$/Si interfaces [10].

In the previous papers [7-9], we have reported the changes in SBH's of both *n*- and *p*-type Ti/$Si_{0.8}Ge_{0.2}$/Si systems with the annealing temperature. However, the solid-phase reaction at metal/$Si_{1-x}Ge_x$ contacts is not completely understood yet. Recently, the process technology using $Ge^+$ ion implantation to reduce contact resistance and the application of SiGe films to gate electrodes have been also proposed [11, 12]. Therefore, the understanding of solid-phase reactions in metal-Si-Ge systems become more and more important. In the present paper, we have investigated the interfacial reactions of Ti/ and Zr/$Si_{0.5}Ge_{0.5}$/Si contacts with a rapid thermal annealing (RTA).

The solid-phase reaction at the Ti/ and Zr/$Si_{0.5}Ge_{0.5}$/Si interfaces was observed by x-ray diffraction (XRD) and Auger electron spectroscopy (AES). The characteristic features related with the solid phase reaction of these systems have been discussed.

## 2. Experiments

Substrates used were n-type Si(100) wafers with a resistivity of 8-12 cm. $Si_{0.5}Ge_{0.5}$ layers with a thickness of 100 nm were epitaxially grown on the substrates at 460°C by molecular beam epitaxy (MBE) in an ultrahigh-vacuum (UHV) chamber, whose base pressure was below $1x10^{-10}$ Torr. $Si_{0.5}Ge_{0.5}$ films were evaporated using electron beam guns (e-guns).After the $Si_{0.5}Ge_{0.5}$ film growth, the substrates were dipped into a diluted HF solution (HF : $H_2O$ = 1 : 50) in order to remove native oxide layers and then rinsed in deionized (DI) water for 2-5 sec to obtain H-passivated surfaces [9]. Ti and Zr films with a thickness of 50 and 25 nm were deposited on the surfaces by e-guns in an UHV chamber with a base pressure below $5x10^{-10}$ Torr, respectively. The samples were taken out to the atmosphere and annealed at 580-900°C for 30 sec using a RTA system. The RTA treatment was carried out in an $N_2$ ambient.

Changes in the crystalline phase by annealing were examined by a thin film XRD apparatus using a CuK source. In-depth profiles of the chemical composition of films were obtained by AES measurements using $Ar^+$-ion sputtering. Sheet resistance of films were measured by a four-point probe method.In order to form Schottky diodes, the *n*- and *p*-$Si_{0.8}Ge_{0.2}$ layers with a thickness of 100 nm were grown on *n*- and *p*-Si substrates, respectively.

The pseudomorphic growth of $Si_{0.8}Ge_{0.2}$ layers on Si(100) substrates were confirmed by XRD. The doping concentration of *n*- and *p*-$Si_{0.8}Ge_{0.2}$ layers were $1x10^{17}$ and $1x10^{16}$ $cm^{-3}$, respectively.

Ohmic contacts with Si substrates were formed on the backside of substrates through heavily-doped diffusion layers using Al electrodes. The Ti and Zr film thickness of the samples used in electrical measurements was 150-200 nm. The value of Schottky barrier heights was determined from the temperature dependence of current-voltage (I-V) characteristics.

## 3. Results and discussion

Figure 2 shows the sum of SBH's for *n*- and *p*-type diodes in Ti/Si [9], Ti/$Si_{0.8}Ge_{0.2}$/Si [9], Zr/Si and Zr/$Si_{0.8}Ge_{0.2}$/Si systems annealed for 30 min in UHV, as a function of temperature. Theoretically the sum of SBH's should be equal to the bandgap of semiconductors. The measured values in Ti/ and Zr/Si systems are almost constant in this annealing temperature range, although these values are slightly smaller than the bandgap of Si. In the case of Zr/$Si_{0.8}Ge_{0.2}$/Si systems, the sum of SBH's is also slightly smaller than the bandgap of pseudomorphic $Si_{0.8}Ge_{0.2}$ films and hardly changes with annealing temperature. One of the reasons on the discrepancy between the measured value and the bandgap is considered to be an influence of defects formed at the interfaces [9].

However, the sum of SBH's in Ti/$Si_{0.8}Ge_{0.2}$/Si systems is about 0.9 eV, which is much smaller than the bandgap expected from the Ge fraction of $Si_{0.8}Ge_{0.2}$ films. It is hard to explain this phenomenon only by defects, because the ideality factors obtained in Zr/ and Ti/$Si_{0.8}Ge_{0.2}$ systems are almost the same values of about 1.2. In addition, the sum of SBH's in Ti/$Si_{0.8}Ge_{0.2}$ systems is gradually decreases with increasing the annealing temperature. Therefore, it can be considered that there are some substantial differences in the solid phase reaction between these systems.Figure 3 shows XRD patterns obtained from (a) a Ti/Si sample at 750°C and (b) Ti/$Si_{0.5}Ge_{0.5}$/Si samples at 580°C-900°C by RTA. At a temperature of 580°C, only peaks related to $Ti_5Si_3$ are observed in Ti/$Si_{0.5}Ge_{0.5}$/Si systems.The energy bandgap of Si and pseudomorphic $Si_{0.8}Ge_{0.2}$ are also indicated.

This result indicates that the formation of silicide at the interface occurs preferentially at low temperatures, although the thermodynamic properties such as heats of formation is similar to each other between Ti-Si and TiGe systems [13], which is also consistent with our previous results examined by X-ray photoelectron spectroscopy (XPS) for very thin Ti films deposited on $Si_{0.8}Ge_{0.2}$ layers below 300°C [7].

After RTA at 700°C, some peaks related to C49-$TiSi_2$ are observed in addition to the peaks of $Ti_5Si_3$. The peak positions of C49-$TiSi_2$ in Ti/$Si_{0.5}Ge_{0.5}$/Si system are found to shift to lower diffraction angles from that of C49-$TiSi_2$ formed in Ti/Si systems. The lattice spacing estimated by the diffraction peak from the (131) plane is larger by about one percent than that in Ti/Si systems. In the case of Ti/Ge systems, C49-$TiGe_2$ is not a stable phase, because the first phase formed by annealing at low temperatures is not C49-$TiGe_2$ but $Ti_6Ge_5$ and that

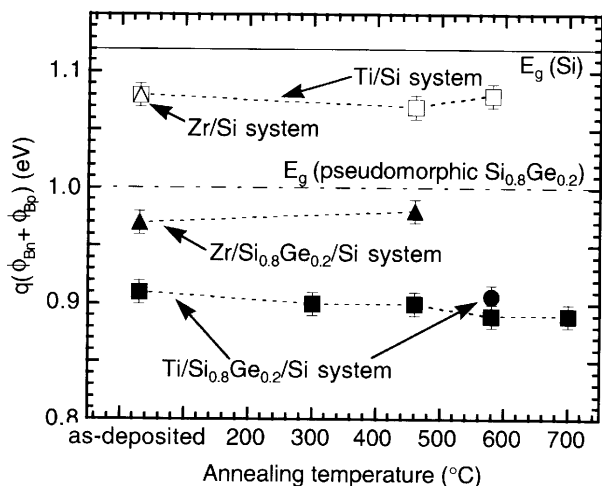


Fig. 2 The sum of Schottky barrier heights of *n*- and *p*-type diodes in Ti/Si [9], $Ti/Si_{0.8}Ge_{0.2}/Si$ [9] systems and Zr/Si and $Zr/Si_{0.8}Ge_{0.2}/Si$ systems, as a function of annealing

$Ti_6Ge_5$ is transformed to $C54\text{-}TiGe_2$ at high temperatures [9, 14, 15]. However, the estimated lattice spacing suggests that Ge atoms are contained in $C49\text{-}TiSi_2$ crystallites in $Ti/Si_{0.5}Ge_{0.5}$ systems.

The XRD patterns show the formation of a new reaction product above 750°C, as seen in Fig. 3(b). The diffraction peaks can be related with $C54\text{-}Ti(Si_{1-y}Ge_y)_2$. It should be emphasized that all peaks are observed between the diffraction peaks expected from $C54\text{-}TiSi_2$ and $C54\text{-}TiGe_2$. Boutarek *et al.* [16] have reported that $C54\text{-}TiSi_2$ and $C54\text{-}TiGe_2$ are totally miscible and that the lattice constant has a linear relationship with Ge concentration. The Ge fractions of $C54\text{-}Ti(Si_{1-y}Ge_y)_2$ are estimated for these samples using the lattice constants of $C54\text{-}TiSi_2$ and $C54\text{-}TiGe_2$ formed on Si(100) and Ge(100) substrates, respectively. The evaluated values are summarized in Table I. It is seen that $C54\text{-}Ti(Si_{1-y}Ge_y)_2$ formed under these annealing conditions has Si-rich chemical compositions compared with $Si_{0.5}Ge_{0.5}$ layers and that the Ge fraction is gradually decreased with increasing the annealing temperature.

These facts suggest that excess Ge atoms are accumulated in the SiGe side at the interface because of the formation of Si-rich $C54\text{-}Ti(Si_{1-y}Ge_y)_2$. The AES depth profiles of $Ti/Si_{0.5}Ge_{0.5}/Si$ samples annealed by RTA at 700°C and 800°C for 30 sec are shown in Fig. 4. At 700°C, it is found that Ge atoms are diffused in the germanosilicide layer to near the surface and pile up near the metal/SiGe interface. The atomic ratio of Ge and Si in the region with a flat Si profile is very close to the value in Table I. After RTA at 800°C, although the depth profiles of Ge atoms is hardly changed, the atomic ratio of Si atoms in the germanosilicide region increases from about 50 % at 700°C to about 55%.

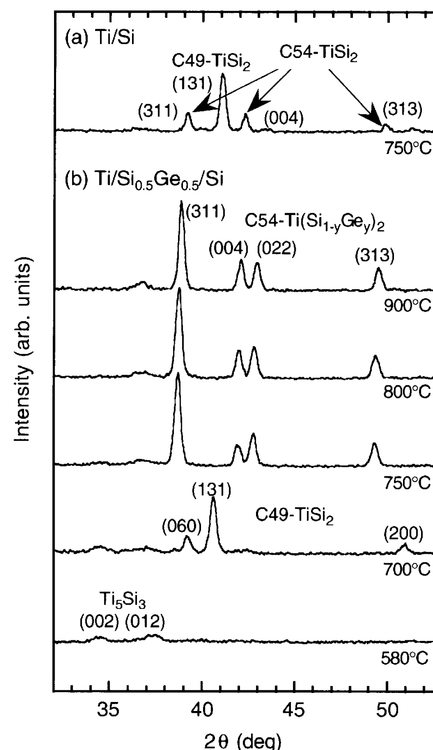


Fig. 3. XRD patterns of (a) Ti/Si samples after RTA at 750°C for 30 sec and (a) $Ti/Si_{0.5}Ge_{0.5}/Si$ samples after RTA at 580-900°C for 30 sec.

This fact is also consistent with the results obtained in Table I and means that the reaction is mainly dominated by the diffusion of Si atoms into germanosilicide layers. Therefore, the piling up of Ge atoms is considered to from by the solid phase reaction between Ti and $Si_{0.5}Ge_{0.5}$ layers, which is not occurred in $Zr/Si_{1-x}Ge_x$ systems as mentioned below. The formation of Si-rich $C54\text{-}Ti(Si_{1-y}Ge_y)_2$ layers and the lowering of the Ge fraction in $C54\text{-}Ti(Si_{1-y}Ge_y)_2$ with increasing the annealing temperature is thought to be related with lower heats of formation of $C54\text{-}TiSi_2$ (-57.0 kJ/mol) than $C54\text{-}TiGe_2$ (-47.5 kJ/mol) [17].

Table I. Ge fractions, *y* of $C54\text{-}Ti(Si_{1-y}Ge_y)_2$ evaluated for different crystallographic planes from Fig. 3(b).

| | Ge fraction, *y* | | |
|---|---|---|---|
| hkl | 750°C | 800°C | 900°C |
| 311 | 0.297 | 0.271 | 0.195 |
| 004 | 0.227 | 0.206 | 0.147 |
| 022 | 0.267 | 0.243 | 0.172 |
| 313 | 0.269 | 0.251 | 0.182 |
| Average | 0.26 | 0.24 | 0.17 |

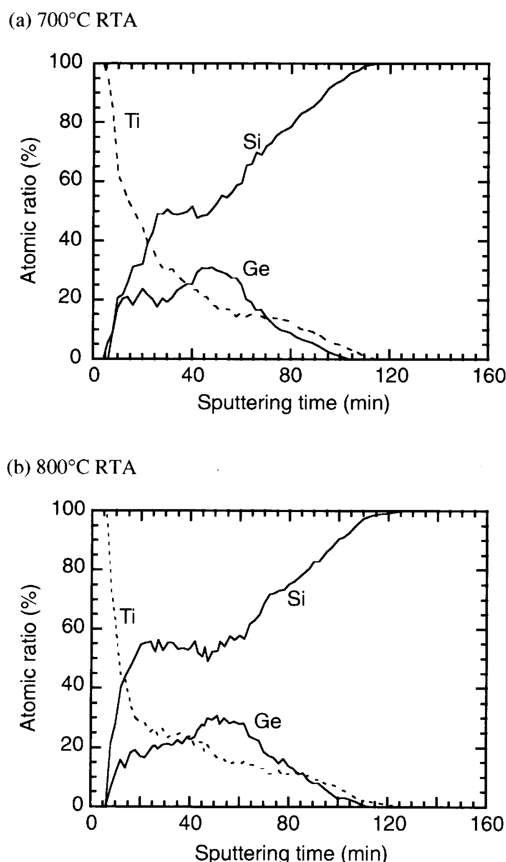


Fig. 4. AES in-depth profiles of $Ti/Si_{0.5}Ge_{0.5}/Si$ sample after RTA at (a) 700°C and (b) 800°C for 30 sec.

This fact also suggests that excess Ge atoms segregates to C54-$Ti(Si_{1-y} Ge_y)_2$ grain boundaries by higher temperature annealing.

It has been also reported that Ge-rich $Si_{1-z}Ge_z$ ($z>x$) is precipitated into $Ti(Si_{1-y}Ge_y)_2$ grain boundaries [17, 18]. Therefore, the segregation of excess Ge atoms into grain boundaries is also expected in our experiment.

Figure 5 shows the temperature dependence of sheet resistance for $Ti/Si_{0.5}Ge_{0.5}/Si$ and Ti/Si samples.The sheet resistance of $Ti/Si_{0.5}Ge_{0.5}/Si$ systems decreases with the transformation from C49 to C54 phases by annealing below 700°C and has a minimum value of 3.4 **Ù**/sq. at 750°C, which is as low as a value of 1.9 **Ù**/sq. for C54-$TiSi_2$ in Ti/Si systems annealed at 800°C. However, the sheet resistance increases again after the annealing above 750°C in the $Ti/Si_{0.5}Ge_{0.5}/Si$ system. These facts suggest that the increase in sheet resistance is related with grain boundary decorations due to the segregation of excess Ge atoms by annealing above 750°C [17].

In the case of Ti/Si systems , both XRD peaks of C49- and C54-$TiSi_2$ can be observed after 750°C RTA, as shown in Fig. 3(a). The comparison between Figs. 3(a) and 3(b) indicates that the transformation temperature to the C54 phase is reduced in $Ti/Si_{0.5}Ge_{0.5}/Si$ systems compared

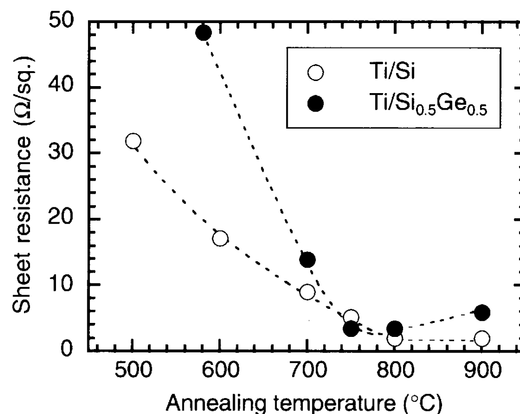


Fig. 5. Temperature dependence of sheet resistance in $Ti/Si_{0.5}Ge_{0.5}/Si$ and Ti/Si samples.

with Ti/Si systems. Therefore, it is considered that Ge or Ge-rich $Si_{1-z}Ge_z$ existing at the boundaries of C49-$(Si_{1-y} Ge_y)_2$grains play an important role in promoting the phase transformation from C49 to C54, such as nucleation sites of C54-$Ti(Si_{1-y}Ge_y)_2$.

The solid phase reaction in $Zr/Si_{0.5}Ge_{0.5}$ systems is very different with that in $Ti/Si_{0.5}Ge_{0.5}$ systems. Figure 6 shows the XRD patterns of $Zr/Si_{0.5}Ge_{0.5}/Si$ samples after RTA at 580°C-900°C. In this system, diffraction peaks from $Zr_5Ge_4$ and Zr crystallites can be observed at 580°C and the formation of C49-$Zr(Si_{1-y}Ge_y)_2$ is confirmed in the annealing temperature range from 700°C to 900°C by XRD. However, no peaks indicating the formation of Zr silicides are observed below 700°C, in contrast to the above-mentioned Ti case. These results clearly indicate that Ge atoms react more actively with Zr atoms than Si atoms in $Zr/Si_{1-x}Ge_x/Si$ systems. On the other hand, since C49-$ZrSi_2$ are formed by RTA above 800°C in Zr/Si systems, the formation temperature of C49 phases in Zr/ $Si_{1-x}Ge_x/Si$ systems is lower than that in Zr/Si systems.

The Ge fraction, $y$ of C49-$Zr(Si_{1-y}Ge_y)_2$ after RTA at 700, 800 and 900°C were evaluated in the same manner as that of C54-$Ti(Si_{1-y}Ge_y)_2$. The results are plotted in the Fig. 7 together with the results obtained for $Ti/Si_{0.5}Ge_{¡0.5}$ systems, as a function of annealing temperature. It should be noted that the Ge fraction of C49-$Zr(Si_{1-y}Ge_y)_2$ is larger than that of C54-$Ti(Si_{1-y}Ge_y)_2$ formed in this temperature range and hardly changes in this temperature range between 700 and 900°C. Wan*g et a*l. [19] have reported that C49-$Zr(Si_{1-y}Ge_y)_2$ with the Ge fraction o*f y*=x is the final phase of the solid phase reaction between Zr and $Si_{1-x}Ge_x$ at 700°C for 20 min for all compositions examined, $x$=0-0.5. In our experiments, the Ge faction, $y$ of C49-$Zr(Si_{1-y}Ge_y)_2$ is smaller than that of $Si_{0.5}Ge_{0.5}$ and, moreover, the XRD peaks related with $Zr_5Ge_4$ can be found slightly even at 900°C.

These facts suggest that the formation of C49-$Zr(Si_{1-y}Ge_y)_2$ is not completed under the RTA time of 30

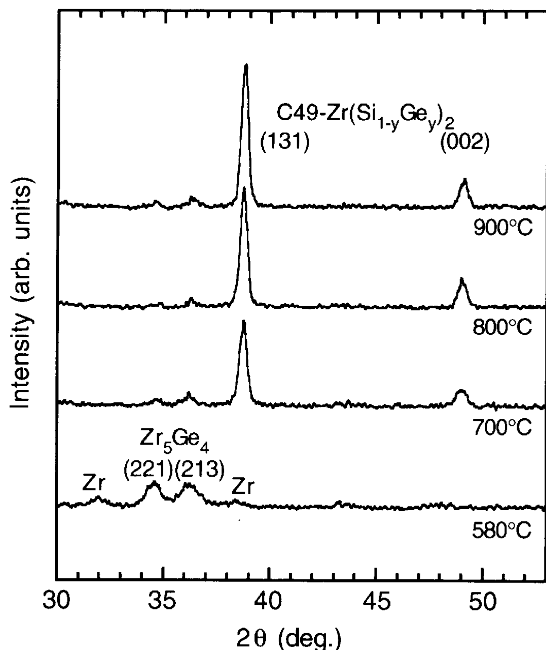


Fig. 6. XRD patterns of Zr/$Si_{0.5}Ge_{0.5}$/Si sample after RTA at 580-900°C for 30 sec.

sec. In any case, it can be concluded that the formation of Si-rich Ti($Si_{1-y}Ge_y$)$_2$ is a characteristic feature in the solid phase reaction between Ti and $Si_{1-y}Ge_y$. From the AES depth profiles of Zr/$Si_{0.5}Ge_{0.5}$/Si samples with $Si_{0.5}Ge_{0.5}$ layers and Ge-rich regions are not formed after RTA at 700°C, it is concluded that Zr uniformly react unlike the Ti/$Si_{0.5}Ge_{0.5}$/Si system.

This fact means that no segregation of Ge atoms occurs in the Zr/Si $_{1-x}Ge_x$ reaction [19]. The behavior of the sum of SBH's as seen in Fig. 2 can be explained by the difference in the solid phase reaction between Ti/ and Zr/$Si_{1-x}Ge_x$ systems. As reported in our previous papers [7, 9], Si atoms preferentially react with Ti atoms at low temperatures and Ge atoms start to react above 400°C in Ti/$Si_{1-x}Ge_x$ systems. The measured SBH's below 400°C has been explained by an increase in the Ge fraction of $Si_{1-x}Ge_x$ at the interface due to this reactivity difference between Si and Ge atoms with Ti.

In the annealing temperature range from 400 to 700°C, an increase in the Ge fraction in SiGe layers has been also observed by annealing for 30 min in UHV [9]. These previously obtained results are also consistent with the results as mentioned above. On the other hand, the Ge piling up near the interface is not ruled out in Zr/$Si_{1-x}Ge_x$ systems. These facts strongly indicate that the electrical properties such as SBH's are thought to be dominated by the differences of solid phase reaction in these systems.

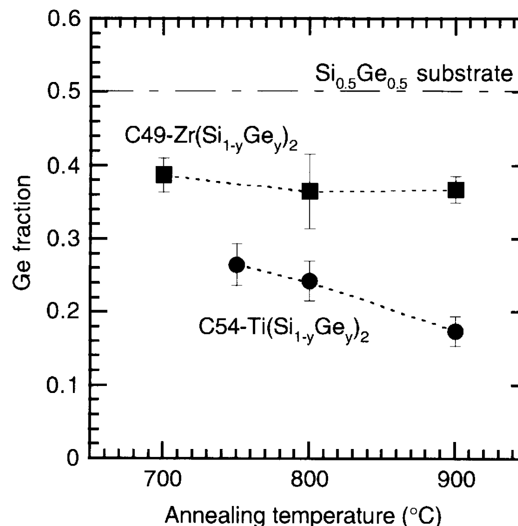


Fig. 7 Annealing temperature dependence of Ge fraction of C54-Ti($Si_{1-y}Ge_y$)$_2$ and C49-Zr($Si_{1-y}Ge_y$)$_2$ formed after RTA of Ti/ and Zr/$Si_{0.5}Ge_{0.5}$ samples, respectively. Dash-dotted line is the Ge fraction of the intermediate $Si_{0.5}Ge_{0.5}$ layer.

## 4. Conclusions

The interfacial reactions of Ti/ and Zr/$Si_{0.5}Ge_{0.5}$/Si systems by RTA have been investigated in the temperature range of 580 to 900°C by XRD and AES. In Ti/$Si_{0.5}Ge_{0.5}$ systems, C49-$TiSi_2$ and $Ti_5Si_3$ is formed below 700°C and C49-$TiSi_2$ is transformed to C54-Ti($Si_{1-y}Ge_y$)$_2$ with the Ge fractions of $y$<0.5 at about 750°C.

The Ge fraction of Si-rich C54-Ti($Si_{1-y}Ge_y$)$_2$ gradually decreases with increasing the annealing temperature. On the other hand, $Zr_5Ge_4$ and C49-Zr($Si_{1-y}Ge_y$)$_2$ are formed by RTA at 580°C and above 700°C, respectively, and C49-Zr($Si_{1-y}Ge_y$)$_2$ has a Ge fraction close to $y$=0.5.

Moreover, the piling up of Ge atoms near the metal/SiGe interface region is observed in Ti/$Si_{0.5}Ge_{0.5}$ systems and not in Zr/$Si_{0.5}Ge_{0.5}$ systems.

These differences in Ti/ and Zr/$Si_{0.5}Ge_{0.5}$ systems is considered to affect on the electrical characteristic at the interfaces. It is also found that the formation temperatures of C54-Ti($Si_{1-y}Ge_y$)$_2$ and C49-Zr($Si_{1-y}Ge_y$)$_2$ is lower than those of C54-$TiSi_2$ and C49-$ZrSi_2$ in metal/Si systems, respectively.


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