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Thermal reaction of nickel and $\text{Si}_{0.75}\text{Ge}_{0.25}$ alloy

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The interfacial reactions and chemical phase formation between nickel and ultrahigh vacuum chemical vapor deposited $\text{Si}_{0.75}\text{Ge}_{0.25}$ alloy have been studied within the temperature range of 300–900 °C for forming low resistive and uniform silicide films for future application in SiGe based metal–oxide–semiconductor field effect transistor devices. The silicided films were characterized by the x-ray diffraction, Auger electron spectroscopy, scanning electron microscopy, transmission electron microscopy, and micro-Raman microscopy techniques. Smooth and uniform nickel monogermanosilicide $\text{NiSi}_{0.75}\text{Ge}_{0.25}$ films have been observed for samples annealed at around 400–500 °C. For annealing temperatures of 500 °C and above, Ge-rich $\text{Si}_{1-z}\text{Ge}_z$ grains where $z > 0.25$ were found among Ge deficient $\text{Ni}_y(\text{Si}_w\text{Ge}_{1-w})_{1-y}$ grains where $w < 0.25$ and the $\text{Ni}_y(\text{Si}_{1-w}\text{Ge}_w)_{1-y}$ phase is thermally stable up to an annealing temperature of 800 °C. We found that the Ni/SiGe reaction is mainly diffusion controlled with Ge and Ni as the dominant diffusing species compared to Si during the annealing process. In addition, Ge has been found to promote agglomeration especially above 700 °C, leading to an abrupt increase in the sheet resistance. © 2002 American Vacuum Society. [DOI: 10.1116/1.1507339]

I. INTRODUCTION

The growth technology for a good quality epitaxial $\text{Si}_{1-x}\text{Ge}_x$ film has matured and $\text{Si}_{1-x}\text{Ge}_x$ based devices are finding their potential applications in the area of high-speed electronic and optoelectronic devices.^{1,2} In addition, these materials are promising for the future very large scale integrated circuits such as complementary metal–oxide–semiconductor (CMOS) technology due to their compatibility with the conventional Si processing technology. One of the common requirements for the device structures is to form a good metal/ $\text{Si}_{1-x}\text{Ge}_x$ ohmic contact that will not degrade the device performance. Interfacial reactions of metals such as Ni,³ Pt,^{4,5} Pd,^{5,6} Ti,^{7–10} and Co^{11,12} with $\text{Si}_{1-x}\text{Ge}_x$ films have been studied for low-resistant ohmic contacts and also as contacts for Schottky barrier infrared detectors.^{13,14} In these reactions, the formation of a ternary phase is generally accompanied by some Ge segregation at the interface, par-

ticularly for furnace annealing. On the other hand, rapid thermal annealing (RTA) that is currently commonly used in the wafer fabrication, with its ultrashort annealing time, is expected to improve the Ge segregation effect at the interface.¹⁵

In MOS technologies, silicide materials used as the contact of source/drain and poly-Si regions must have metal-like conductivity.^{16–20} Moreover, silicides should preferably have high thermal stability during the subsequent thermal treatments in the down-stream processing steps. TiSi_2 was the most commonly used self-aligned silicide (salicide) technology for Si technologies greater than 0.35 μm due to its low resistivity and relatively high temperature stability.²¹ However, the formation of TiSi_2 is dependent on linewidth²² and its sheet resistance increases dramatically with decreasing linewidth, especially for linewidth less than 0.35 μm .²³ In order to overcome these disadvantages, CoSi_2 has been used as the silicide materials for subquarter micron devices.²⁴ The resistivity and thermal stability of CoSi_2 are similar to that of TiSi_2 . Even though the sheet resistance of CoSi_2 is almost

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FIG. 1. Sheet resistance of Ni-silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ samples annealed at various temperatures.

independent of linewidth, it has a higher Si consumption compared to Ti, leading to higher leakage current across shallow junctions. As a result, the precise control of Si consumption in CoSi_2 technology is critical. Recently, there are lot of interests in using nickel-monosilicide (NiSi) for silicide applications.^{25–28} NiSi is a potentially suitable candidate for the silicide process due to its low resistivity, less Si consumption, one step thermal annealing at lower temperature, and ability to maintain low resistivity even for linewidth down to $0.1\ \mu\text{m}$.²⁹ One of the major challenges of NiSi in Si device application is its relatively poor thermal stability beyond 700°C that leads to the formation of high resistivity NiSi₂ film.

In the strained-Si SiGe based CMOS device processing, the thermal budget should be as low as possible to maintain the strain in its ultrathin Si epitaxial layer.³⁰ Similar to the standard Si CMOS process, Ni is a potential candidate in this

FIG. 2. X-ray diffraction pattern of Ni-silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ samples annealed at different temperatures. The x-ray peaks from $\text{Si}_{0.75}\text{Ge}_{0.25}$ are included for comparison.

FIG. 3. Raman spectra of Ni-silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ samples annealed at different temperatures. The peaks from $\text{Si}_{0.75}\text{Ge}_{0.25}$ are included for comparison.

respect as NiSiGe can be formed at relatively low temperature around $400\text{--}500^\circ\text{C}$. In this article, we have studied the chemical phase formation and interfacial thermal reaction along with the distribution of the reacting species viz., Ni, Si, and Ge in the $\text{Ni}/\text{Si}_{0.75}\text{Ge}_{0.25}$ material system annealed at different temperatures. Particular attention is paid to the low temperature regime to establish a process window for the

(a)

(b)

FIG. 4. SEM micrographs of Ni-silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ samples after annealing at (a) 700°C , and (b) 900°C .

FIG. 5. Cross-section TEM images of Ni-silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ films annealed at (a) 500 and (b) 800 °C. At 800 °C, the film is discontinuous.

formation of uniform NiSiGe film for its application to the future strained-Si SiGe CMOS devices.

II. EXPERIMENT

$\text{Si}_{1-x}\text{Ge}_x$ wafers were grown in an ultrahigh vacuum chemical vapor deposition reactor. The starting substrate was a *p*-type Si. A Si buffer layer, a relaxed graded $\text{Si}_{1-y}\text{Ge}_y$ ($y:0 \rightarrow 0.25$) layer of thickness 3.0 μm , and a uniformly relaxed $\text{Si}_{1-x}\text{Ge}_x$ layer ($x=0.25$) of thickness 3.0 μm were subsequently grown over the substrate. The samples were subjected to standard SC-I and SC-II cleaning processes followed by a dip in 20% HF for oxide removal. After the native oxide removal, the wafers were loaded in a sputtering chamber. A layer of Ni of about 250 Å was deposited over the $\text{Si}_{0.75}\text{Ge}_{0.25}$ samples at a deposition pressure of $\sim 10^{-6}$ Torr. The Ni-deposited samples were annealed in a N_2 ambient to form germanosilicide layers by RTA at different temperatures *viz.*, 300, 400, 500, 600, 700, 800, and 900 °C for 60 s. The germanosilicide films were characterized by four-point probe technique, x-ray diffraction (XRD) and micro-Raman technique. Scanning electron microscopy (SEM), cross-sectional transmission electron microscopy (XTEM), and Auger electron spectroscopy (AES) were employed to study the surface micrograph, interfacial structure of the germanosilicide/SiGe films, elemental distribution, and depth profiles of the reacting species, respectively. The XTEM images were obtained using a Philips CM200FEG transmission electron microscope operating at 200 kV. A TEM beam spot size of 1.9 nm was used to collect elemental information from the cross-sectional samples using the electron dispersive x-ray spectroscopy (EDS) technique.

FIG. 6. AES elemental mapping of Ni-silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ samples annealed at 500 °C. (a) Ge, (b) Ni, and (c) Si. The elements are almost uniformly distributed over the surface.

III. RESULTS AND DISCUSSION

Figure 1 shows the sheet resistance of Ni-silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ samples annealed at different temperatures. The sheet resistance exhibits a minimum at the annealing temperature of about 500 °C and gradually increases from 3.9 to 13.2 $\Omega/\square$ in the temperature range of 500 to 800 °C. Beyond 800 °C, the sheet resistance of the Ni-silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ sample increases abruptly. As the sheet resistance of the silicided film depends on the chemical phases formed and their film morphology, scanning electron microscopy analysis on

(a)

(b)

(c)

FIG. 7. AES elemental mapping of Ni-silicided Si_{0.75}Ge_{0.25} samples annealed at 600 °C. (a) Ge, (b) Ni, and (c) overlapping of Ni and Ge. The surface contains mostly a germanosilicide film with small amount of Ge. Si was found to be present uniformly over the entire surface.

those samples annealed beyond 800 °C shows that this is due to strong agglomeration and island formation of the Ni-silicided films.

Figure 2 shows the x-ray diffraction results of the Ni-silicided Si_{0.75}Ge_{0.25} samples annealed at different temperatures. Generally, the compounds formed in Ni/Si_{1-x}Ge_x systems are of a silicide- or germanide-like or a mixture of both. Comparing the data available in standard powder diffraction file,³¹ the peaks in XRD spectra of the Ni-silicided Si_{0.75}Ge_{0.25} system in the present study are found to be shifted compared to those of pure Ni/Si or Ni/Ge. Most of the phases are identified as nickel-germanosilicides

(a)

(b)

(c)

FIG. 8. AES elemental mapping of Ni-silicided Si_{0.75}Ge_{0.25} sample annealed at 700 °C. (a) Ge, (b) Ni, and (c) overlapping of Ni and Ge. Again the surface consists of mostly germanosilicide with an increasing amount of surface areas having higher concentration of Ge as compared to that of the 600 °C annealed surface. Si was found to be present uniformly over the entire surface.

Ni_y(Si_{1-x}Ge_x)_{1-y},³² which was confirmed by energy diffraction spectroscopy experiments and other groups.³³ It is clear from the XRD spectra that for samples annealed at 300 °C and above, the basic phase formation is largely unchanged. Germanosilicide, Ni_y(Si_{1-x}Ge_x)_{1-y}, phases are predominately detected in the samples annealed within the range of 400–800 °C. The reaction is predominantly diffusion controlled and in addition to Ni, Ge was found to be another dominant diffusing species in the Ni/Si_{0.75}Ge_{0.25} sys-

(a)

(b)

(c)

FIG. 9. AES elemental mapping of Ni-silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ sample annealed at 800 °C. (a) Ge, (b) Ni, and (c) Si. The amount of areas of high counts of Ge and Ni is almost the same with a uniform distribution of Si over the entire surface.

tem. This will be clearer later from the Auger elemental mapping. As Ge atoms are the minority in the underlying $\text{Si}_{0.75}\text{Ge}_{0.25}$ substrate, the dominant diffusion of Ge during the phase formation of $\text{Ni}_y(\text{Si}_{1-x}\text{Ge}_x)_{1-y}$ could lead to the formation of a Ge deficient $\text{Ni}_y(\text{Si}_w\text{Ge}_{1-w})_{1-y}$ phase where $w < 0.25$ at higher temperatures. It will be shown later that at 500 °C and above, a Ge-rich $\text{Si}_{1-z}\text{Ge}_z$ ternary phase where $z > 0.25$ was also formed. In the present Ni/ $\text{Si}_{0.75}\text{Ge}_{0.25}$ system, no NiSi_2 -like phase was detected even at 800 and 900 °C. However, in Ni/Si system, the low resistivity NiSi phase transforms to higher resistivity NiSi_2 phase at anneal-

(a)

(b)

(c)

FIG. 10. AES elemental mapping of Ni-silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ sample annealed at 900 °C. (a) Ge, (b) Ni, and (c) Si. The amount of areas of high count of Ge is larger than that of Ni.

ing temperatures exceeding 700 °C.^{34,35} Thus, we deduce that the presence of Ge in $\text{Si}_{1-x}\text{Ge}_x$ alloy could have suppressed the formation of disilicide phases. Moreover, based on the x-ray diffraction results, the $\text{Ni}_y(\text{Si}_{1-x}\text{Ge}_x)_{1-y}$ phase degrades if the annealing temperature is above 800 °C.

Figure 3 shows the results of micro-Raman experiment at room temperature for samples annealed between 500 and 900 °C. The Raman peaks from the bare $\text{Si}_{0.75}\text{Ge}_{0.25}$ substrate has also been included for comparison. The Raman peak corresponding to NiSi generally appears at around the wave number range of 213–217 cm^{-1} .³⁶ We see from Fig. 3 that this peak from Ni/ $\text{Si}_{0.75}\text{Ge}_{0.25}$ system is appearing at the

FIG. 11. AES depth profiles of Ni, Si, and Ge in Ni-silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ samples annealed at (a) 500, (b) 600, (c) 700, and (d) 800 °C.

wave number of around 213 cm^{-1} . Thus, it confirms the presence of monosilicide phases. These phases remain unchanged up to an annealing temperature of 800 °C. For annealing temperatures above 800 °C, the monosilicide peak at 213 cm^{-1} becomes broader indicating the degradation of monogermanosilicide phases that has also been observed in the x-ray diffraction results shown in Fig. 2. In Fig. 3, a peak was observed at around 467 cm^{-1} wave number for the annealing temperature of 600 °C and above. This peak becomes sharper and has shifted towards the higher wave numbers with increasing annealing temperature. We believe that this peak is from the $\text{Si}_{1-x}\text{Ge}_x$ of the Ni-germanosilicide grains. As discussed, these grains have a lower Ge concentration with increasing annealing temperature as compared to the $\text{Si}_{0.75}\text{Ge}_{0.25}$ substrate, thus leading to the shift in the Raman peak correspondingly.³⁷ The formation of the Ge-deficient $\text{Ni}_y(\text{Si}_{1-w}\text{Ge}_w)_{1-y}$ grains was further confirmed by TEM analysis.

Figures 4(a) and 4(b) show the SEM micrographs of the Ni-silicided samples annealed at 700 and 900 °C, respectively. For the annealing temperature range of 300–600 °C, results similar to Fig. 4(a) have been observed. In all these results, the silicided film's surface was still relatively smooth but the formation of small grains (i.e., islands) had started at 700 °C. The size of the grains gradually increased with increasing annealing temperature. It has been observed that at the annealing temperatures above 700 °C, agglomeration

started to take place. At 900 °C, very huge grains appearing as discontinued islands due to strong agglomeration were observed, leading to very abrupt increase in the sheet resistance as seen in Fig. 1. Similar results have been well documented for $\text{Ti/Si}_{1-x}\text{Ge}_x$ and $\text{Co/Si}_{1-x}\text{Ge}_x$ systems.^{36–39}

The formation of grains generally starts by grain boundary grooving in the silicide films during annealing. Both thermodynamic and kinetic factors influence the thermal grooving.¹⁹ From thermodynamics, the grooving process takes place to maintain local energy equilibrium at the intersection of grain boundary and the film surface or interface, and atoms will diffuse away from the highly curved boundaries. This agrees well with our observation in which grooving was found both at the surface and at the silicide/substrate interface in TEM images. Diffusion kinetics also plays a significant role in grooving or agglomeration as the physical transport of atoms will force to change interface and surface contact angles. Due to the strong temperature dependence of the physical transport of atoms, the effect of agglomeration and island formation is prominent at higher annealing temperatures.^{40,41} In addition, the depth of the groove is also found to be proportional to the diffusion coefficient of the moving atoms. Comparing to the Ni/Si system that agglomeration normally occurs at 750 °C,³⁵ the presence of Ge in the $\text{Si}_{0.75}\text{Ge}_{0.25}$ alloy and in the formed $\text{Ni}_y(\text{Si}_w\text{Ge}_{1-w})_{1-y}$ film that also acts a dominant diffuser during the RTA anneal seems to enhance the thermal grooving in the $\text{Ni/Si}_{0.75}\text{Ge}_{0.25}$

system. This is partially attributed to the higher heat of formation for metal–Si than for metal–Ge.⁴²

Figures 5(a) and 5(b) show the XTEM images of the Ni–silicide/ $\text{Si}_{1-x}\text{Ge}_x$ interface annealed at 500 and 800 °C, respectively. The elemental composition was determined by an energy dispersive x-ray system. At 500 °C, a layer of relatively uniform $\text{NiSi}_{0.75}\text{Ge}_{0.25}$ with a thickness of about 74 ± 15 nm was found. However, a very small amount of Ge-rich $\text{Si}_{1-z}\text{Ge}_z$ grains sandwiched in between the $\text{NiSi}_{0.75}\text{Ge}_{0.25}$ grains was detected. Similar results were also obtained for a lower temperature at 400 °C except that the $\text{NiSi}_{0.75}\text{Ge}_{0.25}$ was relatively uniform without the presence of any Ge-rich $\text{Si}_{1-z}\text{Ge}_z$ grains. The distribution of such SiGe grains increases with annealing temperature. At 800 °C, the silicide grains were much thicker of about 174 ± 18 nm but it was very discontinuous and surrounded by Ge-rich $\text{Si}_{1-z}\text{Ge}_z$ grains as shown in Fig. 5(b). Due to thermal agglomeration, germanosilicide grains are losing their columnar structure at the surface and at the interface of silicide/substrate. However, it is clear from the TEM images that the silicide/ $\text{Si}_{1-x}\text{Ge}_x$ interface remains smooth within the annealing temperature range analyzed. The TEM EDS analyses had also confirmed that the Ni–silicided films are basically Ni–germanosilicides with variable Ge compositions at different annealing temperatures.

Figures 6–10 show the AES elemental mapping of the Ni–silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ samples annealed at temperatures of 500, 600, 700, 800, and 900 °C, respectively. The mapping of 500 °C annealed sample shows that Ni, Si, and Ge are uniformly distributed over the surface, indicating the formation of a uniform $\text{NiSi}_{0.75}\text{Ge}_{0.25}$ film. For the sample annealed at 600 °C, most parts of the surface consisted of Ni and the remaining parts consisted of higher concentration of Ge. Both Ni and Ge were not uniformly distributed near the surface. On the other hand, Si was found to be uniformly distributed over the entire surface, showing that the surface film was mostly germanosilicide with some Ge-rich $\text{Si}_{1-z}\text{Ge}_z$ regions. For the sample annealed at 700 °C, again Si was found to be distributed uniformly over the entire surface but the amount of surface areas with higher concentration of Ge detected in the film had increased compared to that of the 500 and 600 °C annealed surfaces. This shows that more Ge-rich grains had formed near the surface at the expense of shrinking Ni–germanosilicide grains. From this we can assume that Ni has diffused into the substrate. The elemental maps of the samples annealed at 800 and 900 °C show that more regions of having higher concentration of Ge were detected. Qualitatively, at 800 °C, relatively high counts of Ge and Ni were detected from almost equal areas. But at 900 °C, high counts of Ge was observed from more areas than that of Ni. Interestingly, Si maintained its relative uniform distributed over the entire surface at these two temperatures. This indicates that the germanosilicide films suffered agglomeration starting from 700 °C. Thus, by systematically mapping of the surface of the Ni–silicided $\text{Si}_{0.75}\text{Ge}_{0.25}$ films, it is clear that the thermal reaction is predominantly diffusion controlled. During the thermal reaction,

Ni is diffusing into the substrate forming thicker Ni–germanosilicide while more Ge is diffusing out from the $\text{NiSi}_{0.75}\text{Ge}_{0.25}$ substrate and laterally from the Ni–germanosilicide grains. This leads to the formation of Ge-rich $\text{Si}_{1-z}\text{Ge}_z$ grains where $z > 0.25$ among Ge deficient $\text{Ni}_y(\text{Si}_w\text{Ge}_{1-w})_{1-y}$ grains near the surface with increasing annealing temperature.

The reaction kinetics is related to the thermodynamic driving forces. In the present case, with higher mobility of the atoms at higher temperatures, two kinds of driving forces coexist: (1) the chemical reactions between the NiSi, NiGe, and Si–Ge alloy, and (2) the reduction of mismatch energy at the phase boundary. The growth of silicide usually follows a linear-parabolic law.⁴³ The linear part is due to a control by chemical reaction and is usually observed for short annealing time. The parabolic growth is obtained when the limiting step is diffusion through the compound being formed. In this case, flux of diffusing species is expressed by the Nerst Einstein equation and can be assumed to be proportional to the heat of reaction.⁴³ The heat of formation of NiSi and NiGe is -45 and -32 kJ/mol, respectively,⁴⁴ which suggests that thermodynamically Ni will prefer to react with Si compared to Ge in the $\text{Si}_{1-x}\text{Ge}_x$ alloy. Ni and Ge are the dominant diffusing species in the Ni/ $\text{Si}_{1-x}\text{Ge}_x$ system.

In addition, our results indicate that Ge may have segregated from the $\text{Ni}_y(\text{Si}_{1-x}\text{Ge}_x)_{1-y}$ grains and diffused into the grain boundaries to react with the $\text{Si}_{1-x}\text{Ge}_x$ grains, leading to the formation of Ge-rich $\text{Si}_{1-z}\text{Ge}_z$ grains. This is supported by the fact that at lower annealing temperatures the driving force for the formation of nickel–germanosilicide is higher than that of Ge segregation out from the silicides. The values for heats of formation suggest that for NiGe, the crystal energy could be reduced if Si atoms could replace the Ge atoms. Due to this replacement, the reduction of crystal energy is -13 kJ/mol.⁴⁴ After the formation of Ni–germanosilicide film on $\text{Si}_{0.75}\text{Ge}_{0.25}$ substrate, Si and Ge are still continuously available from the underlying $\text{Si}_{0.75}\text{Ge}_{0.25}$ layer to participate in the thermal reaction with the already present germanosilicide film. During the thermal reaction, Ni diffuses into the substrate while more Ge compared to Si diffuses out towards the surface with increasing annealing temperature leading to reduction of Ge composition in the ternary phase. This finding is confirmed by the AES depth profiling as shown in Fig. 11. At 500 °C, Ni, Si, and Ge have come into reaction. The phase is germanosilicide with small amount of Ge present. As the annealing temperature increases, the interdiffusion of the elements increases and at 600 °C, there is no significant change except that more Ge diffuses out and more Ni diffuses in compared to values at 500 °C. At 700 and 800 °C, the interdiffusion increases significantly and the amount of Ni in the Ni–germanosilicide phase had been decreased compared to that of the 600 °C annealed samples. In addition, the amount of Ge has increased. Thus, the depth profiling results are qualitatively in good agreement with the AES mapping results. It should also be noted that from the AES depth profiling, no Ge has been

found to segregate at the silicide/Si_{0.75}Ge_{0.25} interface during silicidation.

IV. CONCLUSION

We have studied the chemical phase formation during the thermal reaction between nickel and Si_{0.75}Ge_{0.25} alloy. The phases formed are mainly germanosilicides Ni_y(Si_{1-x}Ge_x)_{1-y}. This has been confirmed by x-ray diffraction spectra, Raman spectroscopy, cross-section TEM/EDS, and AES elemental mapping and depth profiling. In the thermal reaction, Ge and Ni are the dominant diffusing species compared to Si. Agglomeration took place at a lower annealing temperature compared to that of the Ni/Si system due to the presence of Ge. As a result, the sheet resistance of the silicided films increased abruptly for annealing temperatures above 800 °C. Ni-germanosilicide Ni_y(Si_{1-w}Ge_w)_{1-y} phase where $w \leq 0.25$ was thermally stable up to an annealing temperature of 800 °C. The germanosilicide/Si_{0.75}Ge_{0.25} interface remained smooth at all annealing temperatures. We have found that the suitable process window for forming relatively uniform Ni germanosilicide in the Ni/Si_{0.75}Ge_{0.25} system is within 400–500 °C.

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