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Interfacial reactions of Ni on $\text{Si}_{1-x}\text{Ge}_x$ ($x=0.2, 0.3$) at low temperature by rapid thermal annealing

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The interfacial reaction of Ni with relaxed $\text{Si}_{1-x}\text{Ge}_x$ ($x=0.2, 0.3$) films in the low temperature range, viz., 300–500 °C, has been investigated and compared with that of Ni with Si (i.e., $x=0$). $\text{Ni}_2(\text{Si}_{1-x}\text{Ge}_x)$ and $\text{Ni}_3(\text{Si}_{1-x}\text{Ge}_x)_2$ were observed at 300 °C whereas a uniform film of $\text{Ni}(\text{Si}_{1-x}\text{Ge}_x)$ was formed at 400 °C for both $\text{Si}_{0.8}\text{Ge}_{0.2}$ and $\text{Si}_{0.7}\text{Ge}_{0.3}$ substrates. At 500 °C, a mixed layer consisting of $\text{Ni}(\text{Si}_{1-y}\text{Ge}_y)$ and $\text{Si}_{1-z}\text{Ge}_z$ was formed with a relation of $z > x > y$. Sheet resistance measurement results show that the silicided film attains its lowest value at an annealing temperature of 400 °C. The approximate values of the resistivity of the corresponding uniform $\text{Ni}(\text{Si}_{1-x}\text{Ge}_x)$ ($x=0.2, 0.3$) derived from the transmission electron microscope and sheet resistance results are 19 and 23 $\mu\Omega\text{ cm}$, respectively. © 2002 American Institute of Physics. [DOI: 10.1063/1.1482423]

1. INTRODUCTION

SiGe alloys offer significant potential applications in the fabrication of high-speed electronic and optoelectronic devices.^{1–3} For SiGe device applications, a metallic-like/ $\text{Si}_{1-x}\text{Ge}_x$ contact fabricated using a technology similar to the salicide (self-aligned-silicide) process plays a key role for the proper operation of the circuits.⁴ Recently, the interfacial reactions of metal/ $\text{Si}_{1-x}\text{Ge}_x$ have been studied for many metal films. This includes Ti, Co, Pt, Pd, and Ni.^{5–9} A ternary compound (i.e., metal–germanosilicide) is generally formed. Ge segregation has been observed at annealing temperatures above 300 °C for Ni reacting with $\text{Si}_{0.76}\text{Ge}_{0.24}$ by vacuum annealing for 30 min.¹⁰ As Ge segregation will degrade the contact performance significantly, low temperature annealing silicidation processes using rapid thermal annealing (RTA) to reduce Ge segregation are preferred for future SiGe based devices.

For future SiGe based device application, the silicide technology must be thermally stable and form a uniform low sheet resistivity silicide film for a wide range of Ge concentrations. Among metal silicides, nickel monosilicide (NiSi) is currently one of the most promising candidates for the next generation of deep submicron Si based integrated circuits.¹¹ NiSi possesses low resistivity, low silicon consumption, low processing temperature, and is relatively insensitive to the linewidth of the Si substrate.^{10,12,13} To leverage the advent of Ni silicide process in the Si technology for SiGe based microelectronic applications, the interfacial reactions of Ni with relaxed $\text{Si}_{1-x}\text{Ge}_x$ ($x=0.2, 0.3$) films in the temperature range of 300–500 °C was studied.

II. EXPERIMENT

The relaxed $\text{Si}_{1-x}\text{Ge}_x$ films were grown with the ultra-high vacuum chemical vapor deposition (UHVCVD) technique. A SiGe buffer layer was grown on *p*-type (100) silicon wafers to the desired concentrations at a grading rate of 10% Ge μm^{-1} , at 900 °C and 25 mT, prior to the deposition of a

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FIG. 1. XRD spectra of Ni-silicided $\text{Si}_{1-x}\text{Ge}_x$ ($x=0.2, 0.3$) films annealed at different temperatures for 60 s. XRD spectrum of the Ni-silicided Si film annealed at 400 °C for 60 s is also included for comparison.

2.5 μm relaxed SiGe film. Details of the growth conditions and the characterizations of the relaxed SiGe films can be found elsewhere.^{14–16} Prior to Ni deposition, the relaxed SiGe films were cleaned by the standard RCA method and then immediately loaded into an evaporation chamber. Atomic force microscopy (AFM) analysis showed that the relaxed SiGe films maintained the characteristic cross-hatch pattern after the clean. Ni films of about 280 Å thick were deposited onto the relaxed SiGe at room temperature by electron gun evaporation at a rate of 0.5 Å/s. The base pressure was below 1.0×10^{-6} Torr. RTA was carried out within a temperature of 300–500 °C for 60 s in an N_2 ambient. The silicide films were analyzed by x-ray diffraction with a $\text{Cu K}\alpha$ radiation at a fixed incident angle of 0.5° (Philips X-pert X-ray Diffractometer), and cross-section transmission electron microscopy with energy dispersive spectroscopy (EDS) analysis (Philips CM200 TEM/EDS system). The accuracy of the EDS measurements is about 1 at. % with an electron probe size of 1 nm used in our experiments. The four-point probe method was used to measure the sheet resistance.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of Ni-silicided $\text{Si}_{1-x}\text{Ge}_x$ films annealed in the temperature range of 300–500 °C for 60 s. In addition, the x-ray diffraction result of a Ni-silicided Si film annealed at 400 °C for 60 s is included for comparison. The XRD spectra of the Ni-silicided $\text{Si}_{0.8}\text{Ge}_{0.2}$ films are similar to that of the Ni-silicided $\text{Si}_{0.7}\text{Ge}_{0.3}$ films. The formation of Ni germanosilicides (ternary phase) viz., $\text{Ni}_2(\text{Si}_{1-x}\text{Ge}_x)$ at 300 °C and $\text{Ni}(\text{Si}_{1-x}\text{Ge}_x)$ within the annealing temperature range of 400–500 °C is observed. It can be clearly seen that there is a shift of the characteristic peaks of $\text{Ni}(\text{Si}_{1-x}\text{Ge}_x)$ towards a higher 2θ value at the annealing temperature of 500 °C for the Ni-silicided $\text{Si}_{1-x}\text{Ge}_x$ films using the dotted lines (i) and (ii) shown in Fig. 1. Additionally, a (111) peak of $\text{Si}_{1-x}\text{Ge}_x$ has appeared at 500 °C, which is more easily seen in the $x=0.3$ sample.^{17,18} This is attributed to the segregation of Ge at grain boundaries of nickel germanosilicides during the in-

FIG. 2. Plots of sheet resistance of the Ni-silicided $\text{Si}_{1-x}\text{Ge}_x$ ($x=0.2, 0.3$) and Si samples annealed at different temperatures for 60 s. The as-deposited Ni thickness is ~ 350 and ~ 280 Å on Si and SiGe, respectively.

terfacial reactions of Ni with SiGe films and the subsequent formation of Ge-rich $\text{Si}_{1-x}\text{Ge}_x$. The latter was confirmed by TEM/EDS analysis that will be discussed later in this article. As Ge concentration decreases in the $\text{Ni}(\text{Si}_{1-x}\text{Ge}_x)$ grains, its lattice constant becomes smaller leading to a shift in the peaks towards higher 2θ value. The characteristic peaks of $\text{Ni}(\text{Si}_{1-x}\text{Ge}_x)$ annealed at 500 °C are similar to that of NiSi (Ref. 19) formed during the silicidation of Ni with Si at 400 °C. This similarity is attributed to the lesser Ge concentration in the $\text{Ni}(\text{Si}_{1-x}\text{Ge}_x)$ grains.

The sheet resistance of the Ni-silicided films on relaxed $\text{Si}_{1-x}\text{Ge}_x$ ($x=0.2, 0.3$) and Si at different annealing temperatures is shown in Fig. 2. It is seen from Fig. 2 that all of the silicided films have attained their minimum sheet resistance value at 400 °C. The minimum value of the sheet resistance of the Ni-silicided film on $\text{Si}_{1-x}\text{Ge}_x$ is ~ 3.9 Ω/sq for $x=0.3$ and ~ 3.5 Ω/sq for $x=0.2$, while that on Si is ~ 2.3 Ω/sq. After taking into account the effect of the as-deposited Ni thickness, the sheet resistance of the Ni-silicided film on $\text{Si}_{1-x}\text{Ge}_x$ remains higher than that of Si. It is worth noting that the sheet resistance of the Ni-silicided films on $\text{Si}_{1-x}\text{Ge}_x$ films annealed at 300 and 500 °C is much higher than that at 400 °C. On the other hand, the sheet resistance remains almost unchanged for the Ni-silicided film on Si in the temperature range of interest. This is attributed to the larger resistivity of $\text{Ni}_2(\text{Si}_{1-x}\text{Ge}_x)$ than that of the $\text{Ni}(\text{Si}_{1-x}\text{Ge}_x)$ and the presence of Ge-rich SiGe grains inside the Ni-silicided films on $\text{Si}_{1-x}\text{Ge}_x$ substrates. The difference in the increased gradient of the sheet resistance between the Ni-silicided $\text{Si}_{0.8}\text{Ge}_{0.2}$ film and the Ni-silicided $\text{Si}_{0.7}\text{Ge}_{0.3}$ film was found to be due to the different amount of SiGe grains present in the silicided films.

The cross-section TEM micrographs of the typical Ni-silicided $\text{Si}_{1-x}\text{Ge}_x$ films annealed in the temperature range of 300–500 °C for 60 s are shown in Fig. 3. As shown in Fig. 3(a), the Ni-silicided $\text{Si}_{0.8}\text{Ge}_{0.2}$ film annealed at 300 °C has a rather rough interface with the relaxed SiGe substrate. Its EDS results show that the silicided film is mainly composed of $\text{Ni}_2(\text{Si}_{1-y}\text{Ge}_y)$ with a variable y ($0.15 \leq y \leq 0.2$), while a few $\text{Ni}_3(\text{Si}_{1-z}\text{Ge}_z)_2$ grains with a variable z around 0.3 co-

FIG. 3. Cross-section TEM micrographs of the Ni-silicided $\text{Si}_{1-x}\text{Ge}_x$ films annealed at (a) 300 °C ($x=0.2$), (b) 400 °C ($x=0.2$), (c) 400 °C ($x=0.3$), and (d) 500 °C ($x=0.2$).

exist in it. At 400 °C, the EDS results of the uniform Ni-silicided film show that it is a layer of $\text{Ni}(\text{Si}_{1-x}\text{Ge}_x)$ with a Ge concentration which is the same value as that of SiGe substrates for both $x=0.2$ and $x=0.3$. The Ni-silicided $\text{Si}_{1-x}\text{Ge}_x$ films annealed at 500 °C consist mainly of a mixture of Ge-deficient $\text{Ni}(\text{Si}_{1-y}\text{Ge}_y)$ ($y < x$) grains and Ge-rich $\text{Si}_{1-z}\text{Ge}_z$ ($x < z$) grains, where x is the Ge concentration of SiGe substrates. For example, y is ~ 0.1 and z is ~ 0.65 for the $x=0.2$ sample shown in Fig. 3(d). In Figs. 3(b) and 3(c), the thickness of the Ni-silicided $\text{Si}_{1-x}\text{Ge}_x$ film annealed at 400 °C is about 60 and 55 nm for $x=0.3$ and $x=0.2$, respectively. Thus the resistivity of $\text{Ni}(\text{Si}_{1-x}\text{Ge}_x)$ film is estimated to be about 19 and 23 $\mu\Omega\text{ cm}$, for $x=0.2$ and 0.3, respectively.

We were surprised to observe the $\text{Ni}_3(\text{Si}_{1-z}\text{Ge}_z)_2$ phase in our experiments since Ni_3Si_2 is generally not observed in the thin film reaction of Ni with crystalline silicon due to the complicated structure of Ni_3Si_2 that is orthogonal,^{20–22} while it could be formed easily in the reactions of bulk couple or powder of Ni with Si.^{23,24} Since both Ni_2Si and NiSi have a similar crystal structure and belong to the same space group, this leads to a high activation energy required for the Ni_3Si_2 formation. Gas *et al.*²⁵ suggested that the absence of Ni_3Si_2 in the sequence of phases formed from the thin film reaction of Ni with Si is due to the requirement of relatively high nucleation temperature that is larger than the initial temperature of the formation of NiSi . In the interaction of Ni particles with amorphous Si film, however, the formation of a Ni_3Si_2 phase was observed.²⁶ The fast rate of nickel diffu-

sion in amorphous silicon or higher rates of reaction front propagation were proposed to be the possible reasons of the formation of Ni_3Si_2 . On the other hand, we postulate that in the presence of Ge, as a Ge atom is larger than that of Si, the Si in the Si–Ge system has a higher mobility than Ge leading to a reduction of the activation energy for the formation of Ni_3Si_2 grains as well as making the reaction kinetics favorable. In addition, the degree of symmetry of $\text{Ni}_3(\text{Si}_{1-z}\text{Ge}_z)_2$ is possibly lower than that of Ni_3Si_2 due to the large size of Ge atoms and therefore $\text{Ni}_3(\text{Si}_{1-z}\text{Ge}_z)_2$ can be formed more easily. Both of the above reasons could lead to the formation of $\text{Ni}_3(\text{SiGe})_2$ in relaxed SiGe. However, to understand the exact mechanisms for the formation of the $\text{Ni}_3(\text{SiGe})_2$ phase in the thin film reaction of Ni with relaxed SiGe film, additional studies are needed.

IV. CONCLUSION

In summary, uniform and low sheet resistivity NiSiGe films can be formed on relaxed $\text{Si}_{1-x}\text{Ge}_x$ ($x=0.2, 0.3$) at 400 °C annealing temperature. $\text{Ni}_2(\text{Si}_{1-x}\text{Ge}_x)$ and $\text{Ni}_3(\text{Si}_{1-x}\text{Ge}_x)_2$ were detected for samples annealed at a lower temperature of 300 °C. A mixed layer consisting of $\text{Ni}(\text{Si}_{1-y}\text{Ge}_y)$ and $\text{Si}_{1-z}\text{Ge}_z$ was formed with a relation of $z > x > y$ for a higher anneal temperature of 500 °C. The variations in the measured sheet resistance values of the Ni-silicided $\text{Si}_{1-x}\text{Ge}_x$ films annealed at different temperatures are attributed to the differences in the resistivity and composition of different chemical phases of the Ni-silicided films.

400 °C was found to be a suitable temperature for forming uniform Ni-silicide films on $\text{Si}_{1-x}\text{Ge}_x$ alloy in the range of interest.

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