Effect of Pt on agglomeration and Ge out-diffusion in Ni(Pt) germanosilicide

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Abstract— **The effect of Ni and Ni(Pt) alloy with ~5 and 10 at. % Pt on the agglomeration and Ge out-diffusion in Nickel germanosilicide formed on $Si_{0.75}Ge_{0.25}$(100) has been studied. A remarkable improvement in the agglomeration behavior with increasing Pt atomic percentage is observed by sheet resistance measurements and scanning electron microscopy (SEM). In addition, x-ray diffraction (XRD) shows that only NiSiGe or Ni(Pt)SiGe phase exists from 400 to 800°C. However, Ge out-diffusion from the monogermanosilicide grains is obvious at 600°C and 700°C for Ni/SiGe and Ni(Pt)(Pt at.%~10%)/SiGe, respectively, evident by XRD and micro-Raman spectroscopy. The improved melting temperature of Ni(Pt)SiGe solution compared to that of NiSiGe is the likely reason of seeing better surface morphology and suppressing Ge out-diffusion of the germanosilicide grains observed.**

Index Terms—Agglomeration, Ge out-diffusion

I. INTRODUCTION

Nickel monosilicide is one of the potential candidates for future CMOS fabrication due to its low temperature formation and less Si consumption. However, NiSi is not the final phase like $CoSi_2$ and $TiSi_2$, so it is easy to transform into $NiSi_2$ phase at higher temperatures. In addition, it is reported that NiSi will agglomerate at temperature as low as 600°C,[1] but using Ni alloy with 5% Pt can improve the thermal stability and surface morphology of NiSi on Si substrate.[2] In recent years, $Si_{1-x}Ge_x$ substrate has drawn great interest due to its higher performance such as higher hole mobility in p-MOSFET and prevention of the formation of $NiSi_2$ phase by adding Ge.[3] As a result, the germanosilicidation between metal and SiGe becomes important. Previous studies have shown that uniform NiSiGe ternary compound

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forms on SiGe at 400°C and Ge-rich SiGe grains form at 500°C.[4] So for Ni-SiGe system, the morphology stability is still an issue.

In this paper, we study the formation of Ni(Pt) germaosilicide with different Pt atomic percentages at different annealing temperatures. A remarkable improvement in the agglomeration behavior and Ge out-diffusion with an increase in the Pt atomic percentage is shown. In addition, we also included Si substrate for comparison.

II. EXPERIMENTAL

The growth condition of relaxed SiGe can be found elsewhere.[5-7] The (100) $Si_{0.75}Ge_{0.25}$ substrate was cleaned by Piranha, followed by a HF dip. About 100Å Ni, Ni(Pt)(Pt at.%~ 5%) and Ni(Pt)(Pt at.%~ 10%) films were sputter deposited on the $Si_{0.75}Ge_{0.25}$ substrate, respectively. The base pressure was below $5x10^{-7}$ Torr. These samples were rapid thermal annealed at 400-800°C for 60s in an N_2 ambient. The four point probe technique was used to measure the sheet resistance of the as-deposited and annealed films. XRD with Cu Kα in the Bragg-Brentano geometry was carried out to identify the phases and crystal orientation of the annealed films. The surface morphologies were investigated by SEM. Micro-Raman spectroscopy technique was used to study the phase transformation and Ge out-diffusion from the germanosilicide films.

III. RESULTS AND DISCUSSION

The effect of the Pt alloy on NiSi and Ni($Si_{0.75}Ge_{0.25}$) phase formed on Si and $Si_{0.75}Ge_{0.25}$ substrate is shown in Fig. 1. Fig. 1(a) shows sheet resistance values of using Ni(Pt) alloy with different Pt atomic percentage on Si substrate at different annealing temperatures. It is observed
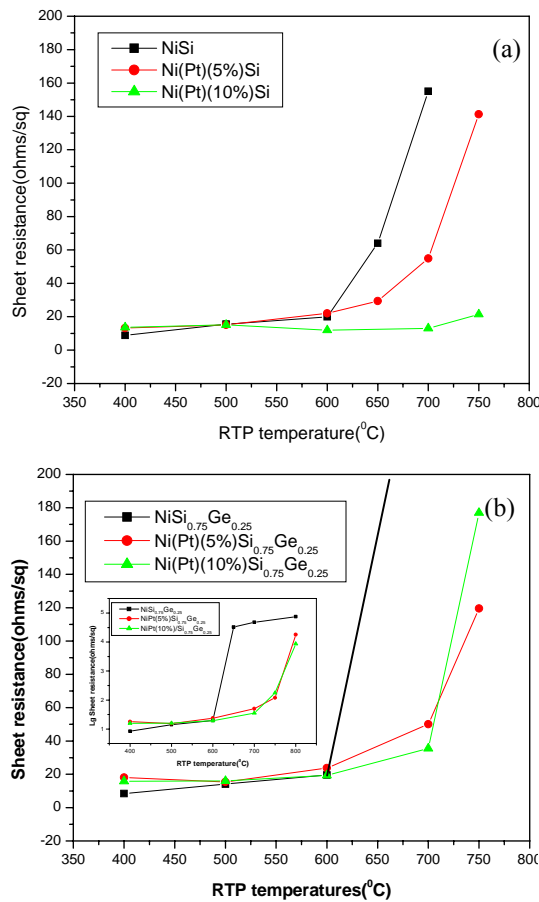
Fig. 1. Sheet resistance of 10nm Ni, NiPt(Pt at.%~5%), and NiPt(Pt at.%~10%) on (a) Si and (b) $Si_{0.75}Ge_{0.25}$ after various RTA. The inset shown in (b) provides all the Rs values using logarithm scale.

that 10% Pt plays an important role in keeping a lower sheet resistance between 400 and 750°C. On the other hand, for the pure Ni, the lower sheet resistance can only be kept from 400 to 600°C. Whereas the sheet resistance values of the samples using 5% Pt are between them. Hence the temperature range for forming lower sheet resistance NiSi has apparently enlarged with increasing atomic percentage of Pt. In addition, there is no $NiSi_2$ formation during the reaction of Ni with Si in the range of 400 to 800ºC.[2] This means that the degraded sheet resistance values are not due to phase transformation, so Pt delays the agglomeration temperature of formed silicide. Fig. 1(b) shows the sheet resistance values of 10nm Ni(Pt) with different Pt atomic percentage on $Si_{0.75}Ge_{0.25}$ after rapid thermal annealed between 400 and 800°C. For the pure $Ni/Si_{0.75}Ge_{0.25}$ samples, a dramatic increase in the sheet resistance from 19.6 to ~3.3×10^4 Ω/sq (i.e. the sheet resistance of the substrate) took place after annealing at 650°C. The reason is attributed to a severe agglomeration of the NiSiGe films as confirmed by SEM analysis that will be discussed in detail in a later section rather than the phase transformation. The agglomeration behavior is more
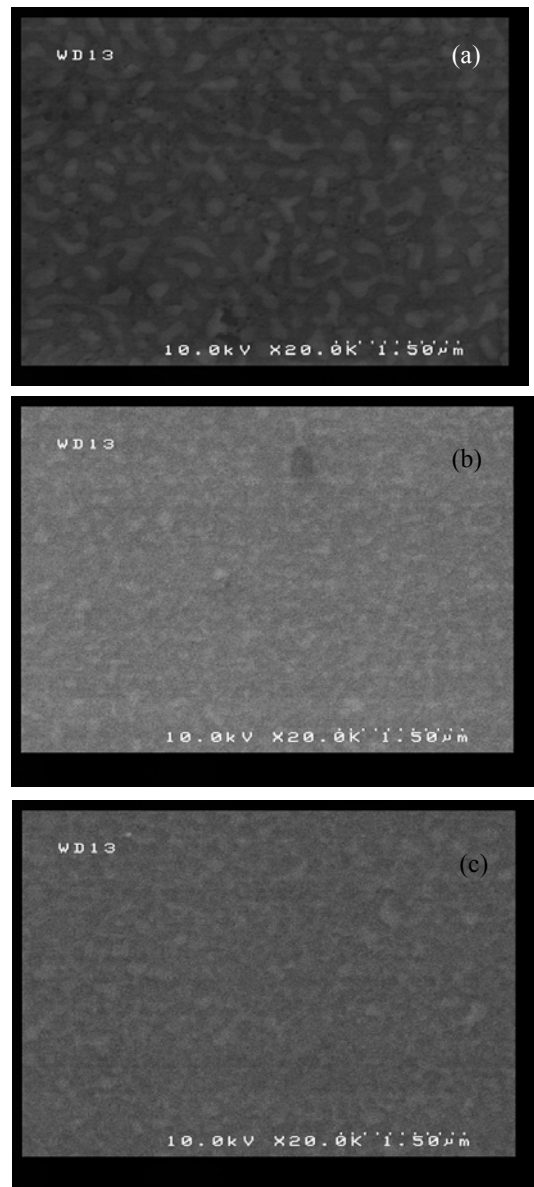

Fig. 2. SEM micrographs of 10nm (a) Ni (b) NiPt(Pt at.%~5%) and (c) NiPt(Pt at.%~10%) on $Si_{0.75}Ge_{0.25}$ RTA at 700ºC.

severe than using the Si substrate. For the pure Ni annealed at 650°C, it is obvious that the sheet resistance of NiSiGe is much higher than that of NiSi, indicating that the presence of Ge in the substrate degrades the surface morphology of the silicide film greatly. It is recently reported that the germanosilicide film contains Ge-rich SiGe grains at 550-600°C.[3] As a result, besides agglomeration, the degraded sheet resistance is possibly due to the occurrence of Ge-rich phase. For the Ni(Pt)(Pt at.%~10%) and Ni(Pt)(Pt at.%~5%)/$Si_{0.75}Ge_{0.25}$ samples, the dramatic increase in the sheet resistance only begun after annealing at 800°C. For the temperature below 800°C, the sheet resistance values are lower than that of the pure Ni/$Si_{0.75}Ge_{0.25}$ sample at the same temperature. The sheet resistance remained almost
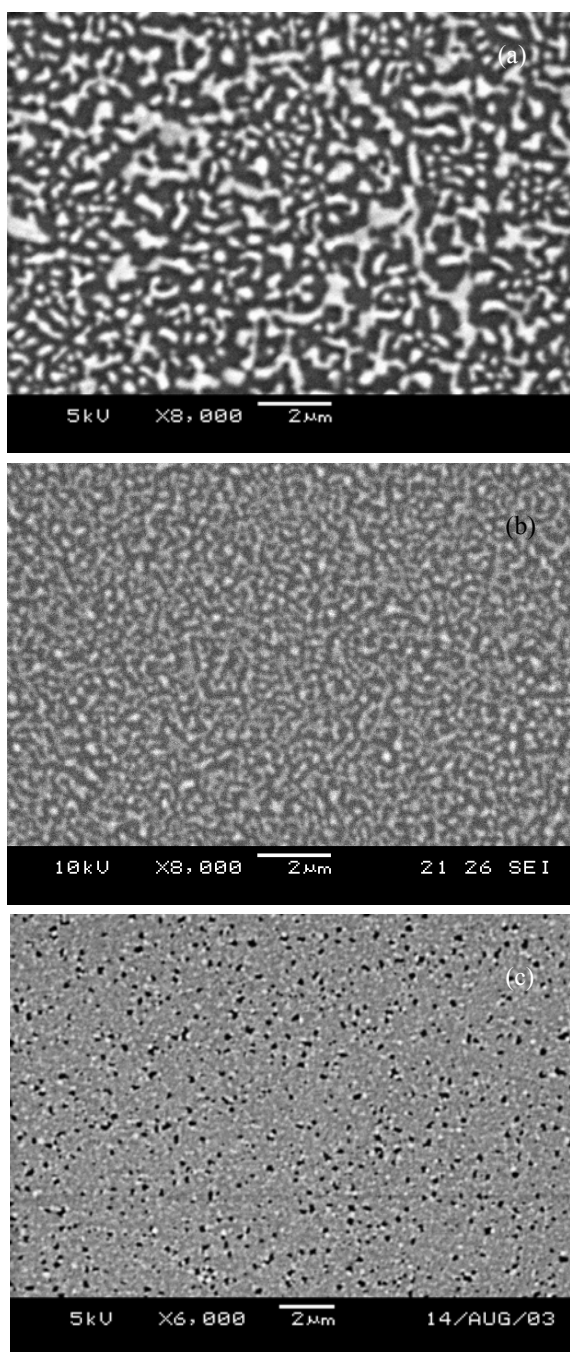
Fig. 3 SEM micrographs of 10nm (a) Ni (b) NiPt(Pt at.%~5%) and (c) NiPt(Pt at.%~10%) on Si RTA at 700°C.

unchanged for Ni(Pt)(Pt at.%~10%) and Ni on $Si_{0.75}Ge_{0.25}$ after annealing from 400 to 700°C and 400 to 600°C, respectively. For the NiPt(Pt at.%~5%)/$Si_{0.75}Ge_{0.25}$ samples, most of the sheet resistance values are higher than the samples using Pt at.% ~10%, but lower than that of the samples using pure Ni.

Figures 2(a), (b) and (c) show the SEM micrographs of 10nm Ni, NiPt(Pt at.%~5%) and NiPt(Pt at.%~10%) on $Si_{0.75}Ge_{0.25}$ annealed at 700°C, respectively. For

$Ni/Si_{0.75}Ge_{0.25}$, severe agglomeration occurs. However, For NiPt(~5%) and NiPt(~10%)/$Si_{0.75}Ge_{0.25}$, the surface remains very smooth. Figures 3(a), (b) and (c) show the SEM micrographs of 10nm Ni, NiPt(Pt at.%~5%) and NiPt(Pt at.%~10%) on Si annealed at 700°C, respectively. Severe degradation occurs at this temperature and a network consisting of many isolated islands appears on the surface of Ni-silicided Si. However, for NiPt(Pt at.%~10%)/Si, only pinholes begin to occur and the surface morphology is still well maintained.

The melting temperature of NiSi is 980°C, however the melting temperature of PtSi is about 1230°C. The melting temperature of Ni(Pt)Si is anticipated to be higher than that of NiSi. As a result, atomic diffusion should be slower in the ternary solution. Improved surface morphology and enhanced agglomeration behavior with increasing Pt atomic percentage are expected by adding Pt into Ni alloy. However, for NiSiGe compounds, the melting temperature of NiGe is lower than that of NiSi, so the morphology will hence be degraded as compared to pure NiSi. But with the addition of Pt into NiSiGe, the melting temperature should be higher than that of NiSiGe since the melting point of PtGe is 1075°C.[3] The addition of Pt should improve the surface morphology of NiSiGe. It is expected that the better surface morphology can be obtained with higher Pt percent.

According to Vergard's law, $Ni(Si_{1-x}Ge_x)$ or $Ni(Pt)(Si_{1-x}Ge_x)$(x is possibly different from that of the substrate) can be formed because NiSi, NiGe, PtSi,[8] and PtGe[3] have the same crystallographic structure orthorhombic and Pnma space group. From the XRD spectra, shown in Figs. 4(a), (b) and (c), NiSiGe or Ni(Pt)SiGe is the only dominant phase detected from 400°C to 800°C. For the NiSiGe or Ni(Pt)SiGe peaks, they are constant at 400 and 500°C. However, these peaks shift to larger 2θ values with increasing temperature. According to the XRD diffraction law, the increased 2θ values correspond to a decreasing plane spacing. As a result, the corresponding lattice constant decreases, indicating a smaller x than that in the substrate. Comparing the peak shift among the Ni, NiPt(5%) and NiPt(10%) germanosilicide, the shift is relatively obvious at 600°C, showing that Ni more Ge has been out-diffused. However, with the presence of Pt, the shift at 600°C becomes smaller with increasing Pt concentration. The effect of Pt suppressing Ge out-diffusion is also confirmed by micro-Raman spectroscopy, as shown in Figs. 5(a), (b) and (c). It can be clearly seen that for $Ni/Si_{0.75}Ge_{0.25}$, there is a broad peak at about $200cm^{-1}$, corresponding to the NiSiGe phase at 400 and 500°C. Whereas two sharp peaks at ~193 and $213cm^{-1}$ were found at 600°C and above, which are similar to the reported results of NiSi peaks.[9] It is believed that the broad peak seen at lower annealing temperatures and the two distinct peaks detected at higher annealing temperatures have the same origin. And the difference in the Ge concentration in
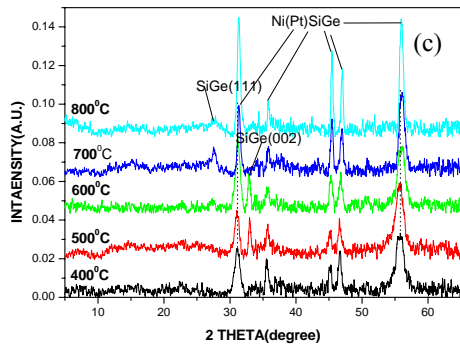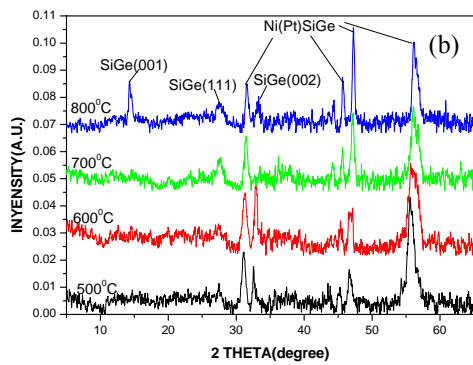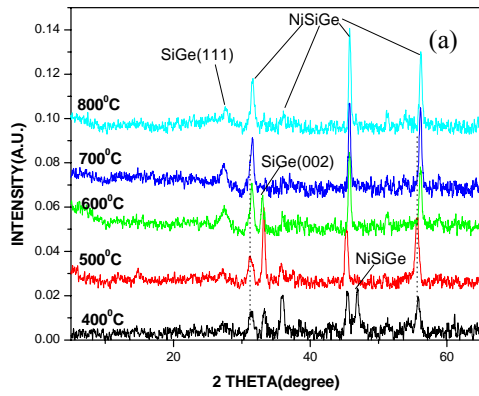
Fig. 4. XRD of 10nm (a) Ni (b) Ni(Pt)(Pt at.%~5%) and (c) Ni(Pt)(Pt at. %~10%) with $Si_{0.75}Ge_{0.25}$ annealed at different RTP temperatures.

Fig. 5. Raman spectra of 10nm (a) Ni (b) NiPt(Pt at.%~5%) and (c) NiPt(Pt. at%~10%) on $Si_{0.75}Ge_{.25}$ annealed at different temperatures.

the NiSiGe grains formed at various temperatures could be the mechanism responsible for the evolution of the broad peak into two distinct Raman peaks corresponding to $Ni(Si_{1-y}Ge_y)$ with $y << x$ where $x=0.25$ of the Ge concentration of the SiGe substrate. These results are in agreement with the Auger mapping and TEM results reported by Pey et al.[4] In addition, the decrease in Ge concentration in the NiSiGe phase were further supported by the intensity of the Ni-Si(Ge) peak towards higher wavenumbers with increasing temperature. On the other hand, refer to the Raman peaks of Ge-Ge, Si-Ge, and localized Si-Si(Ge) at about 300, 400, 430cm^{-1} at 600°C
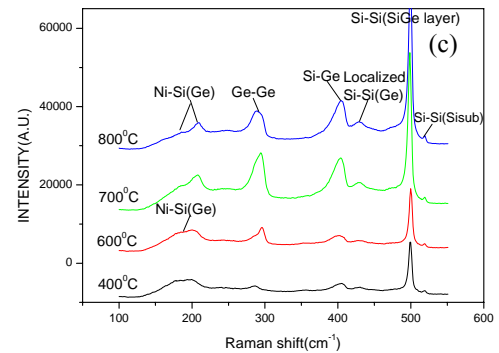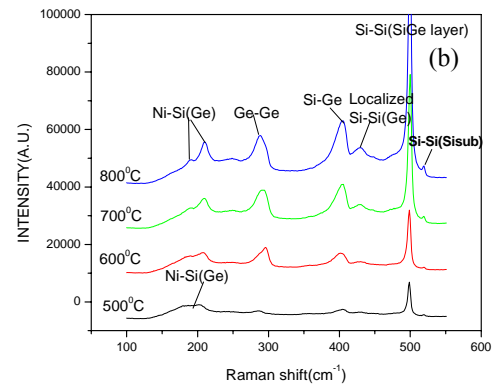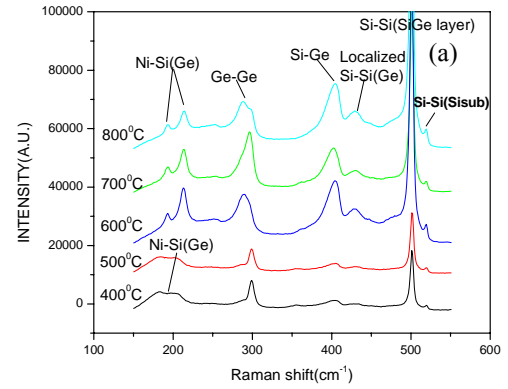
increased greatly compared with the samples annealed at 400 and 500°C. This means that the Ge concentration in SiGe grain was increased.[10] This further proves that Ge was out-diffused at 600°C and above, while Ge-rich SiGe grains formed at the same time. For the NiPt(10%)/$Si_{0.75}Ge_{0.25}$ system, one broad Ni(Pt)SiGe peak was still seen at 600°C, and one distinct shape peak was found above 700°C. For the NiPt(5%)/$Si_{0.75}Ge_{0.25}$ system, the results were similar to that of the Ni/$Si_{0.75}Ge_{0.25}$ system but with less Ge out-diffusion at higher temperature. In the Ni(Pt) system, the evolution of the broad peak into distinct peak(s) with increasing temperature agrees with the

mechanism described previously where the depletion of the Ge concentration in the Ni(Pt)SiGe grains at higher annealing temperatures. Hence, Pt plays a critical role in suppressing Ge out-diffusion from the monogermanosilicide grains since more Ge atoms are remained in the Ni(Pt)SiGe grains with more addition of Pt into the Ni(Pt) alloy.

The mechanism of agglomeration is based on thermal grooving at grain boundaries via diffusion.[11,12] For a polycrystalline film on single crystal substrate, two equilibrium relationships need to be considered. One is the surface and grain boundary energy, the other is the interface and grain boundary energy, as shown in Equation (1), respectively.

$$\gamma_{gb}=2\gamma_s\sin\theta_s;\ \gamma_b=2\gamma_i\sin\theta_i \qquad - \qquad (1)$$

In order to prevent agglomeration, one can lower the grain boundary energy or increase the surface energy or increase the interfacial energy. Comparing the NiSiGe phase to the Ni(Pt)SiGe phase, the interface energy does not change much according to the peaks in the XRD spectra. However, it is known that materials with higher melting temperature have higher surface energy,[13] so the surface energy of Ni(Pt)SiGe is higher due to the improved melting temperature compared to that of NiSiGe. As a result, the surface diffusion reduces, thus agglomeration behavior is minimized. In addition, the addition of impurities will inhibit grain growth and smaller grains are desirable for better surface morphology. The SEM graphs shown in Figs. 2(c) and 3(c) apparently show the reduced grain size due to the addition of Pt.

Out-diffusion of Ge from NiSiGe is due to the fact that the heat of formation of NiSi(-45 kJ/mol) is more favorable than that of NiGe(-32 kJ/mol).[14] So for reaction of Pt with SiGe, Pt is also more favorable to react with Si rather than Ge. Thus the addition of Pt in Ni as an alloy will not improve out-diffusion of Ge from the thermodynamic point of view. On the other hand, from the kinetic point, improved melting temperature will reduce diffusivity, leading to possible suggestion of suppressing Ge out-diffusion. Hence, uniform NiSiGe film due to the addition of Pt minimizes the Ge out-diffusion.

IV. CONCLUSIONS

The annealing temperature window of low sheet resistance NiPtSiGe could be greatly enlarged with increasing Pt atomic percentage. The improvement of the surface morphology and enhanced agglomeration behavior by adding at.~10% Pt were demonstrated. Ge out-diffusion behavior can be firmed by the peaks shift in the XRD spectra and the evolution of a broad germanosilicide peaks and wavenumber shifts in micro-Raman spectra. A better suppression of Ge out-diffusion can be achieved with increasing Pt concentration. The improved agglomeration behavior and suppression of Ge out-diffusion are possibly due to the higher melting temperature of the compounds after adding Pt in Ni.

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