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

L. J. Jin
Singapore-Massachusetts Institute of Technology (MIT) Alliance, 4 Engineering Drive 3, Singapore 117576

K. L. Pey
Singapore-Massachusetts Institute of Technology (MIT) Alliance, 4 Engineering Drive 3, Singapore 117576 and Microelectronic Center, School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798

W. K. Choi
Singapore-Massachusetts Institute of Technology (MIT) Alliance, 4 Engineering Drive 3, Singapore 117576 and Microelectronics Laboratory, Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576

E. A. Fitzgerald, D. A. Antoniadis, A. J. Pitera, and M. L. Lee
Singapore-Massachusetts Institute of Technology (MIT) Alliance, 4 Engineering Drive 3, Singapore 117576 and Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139-66307

D. Z. Chi
Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602

Md. A. Rahman and T. Osipowicz
Physics Department, National University of Singapore, Centre for Ion Beam Applications (CIBA), Block S12, 2 Science Drive 3, Singapore 117542

C. H. Tung
Institute of Microelectronics, 11 Science Park Road, Science Park 2, Singapore 117685

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The effect of Pt alloy in Ni(Pt ~ 5 and 10 at. %) on the agglomeration and Ge out diffusion in nickel germanosilicide formed on Si_0.75Ge_0.25(100) has been studied. A remarkable improvement in the agglomeration behavior with increasing Pt atomic percentage is observed by sheet resistance measurements while still maintaining Ni(Pt) monogermanosilicide phase between 400 and 800 °C. Ge out diffusion from the monogermanosilicide grains has been suppressed up to a temperature of 700 °C with the addition of Pt, evident by x-ray diffraction and micro-Raman spectroscopy. In addition, that improvement of surface morphology and suppression of Ge out diffusion with increasing Pt atomic percent is also confirmed by Rutherford backscattering and cross-sectional transmission electron microscopy. The improved morphology and agglomeration are explained by a grain-boundary model which includes kinetic effects. The suppression of Ge out diffusion from the germanosilicide grains is attributed to reduced atomic diffusion and the presence of stronger Pt–Si and Pt–Ge bonds due to the addition of Pt. © 2005 American Institute of Physics.

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I. INTRODUCTION

NiSi is one of the potential candidates for future complementary metal-oxide-semiconductor (CMOS) fabrication due to its low-temperature formation and less Si consumption. However, NiSi can be easily transformed into the NiSi_2 phase at higher temperatures. In addition, it is reported that NiSi will agglomerate at temperature as low as 600 °C, but using 5 at. % Pt alloy in the Ni can improve the thermal stability and surface morphology of NiSi on Si substrate. In recent years, Si_{1-x}Ge_x substrates have drawn great interest due to its higher performance such as higher hole mobility in p-metal-oxide-semiconductor field-effect-transistor (MOSFET) and prevention of the formation of the NiSi_2 phase by the presence of Ge. As a result, the germanosilicidation between metal and SiGe becomes important. Previous studies have shown that a uniform NiSiGe ternary compound forms on SiGe at 400 °C and Ge-rich SiGe grains form at 500 °C. So for the Ni–SiGe system, the morphological stability is still an issue.

In this paper, we study the formation of Ni(Pt) germanosilicide with different Pt atomic percentages at different annealing temperatures. A remarkable improvement in the agglomeration behavior and reduction in Ge out diffusion with increasing Pt atomic percentage in Ni is shown.

II. EXPERIMENT

The growth condition of the relaxed Si_{0.75}Ge_{0.25} substrate used can be found elsewhere. The Si_{0.75}Ge_{0.25}(100) substrate was cleaned by Piranha, followed by a HF dip. About 10-nm Ni, Ni(Pt ~ 5 at. %), and Ni(Pt ~ 10 at. %)
films were sputter deposited on the Si$_{0.75}$Ge$_{0.25}$ substrate, respectively. The base pressure was below $5 \times 10^{-7}$ Torr. These samples were rapid thermal annealed (RTA) at 400–800 °C for 60 s in a N$_2$ ambient. The four-point probe technique was used to measure the sheet resistance of the annealed films as they were. Two-dimensional area detector x-ray diffraction (XRD) with Cu K$_\alpha$ radiation was carried out to identify the phases and crystal orientation of the annealed films. Micro-Raman spectroscopy technique was used to study the phase formation and Ge out diffusion from the germanosilicide films. The film morphology and composition were also studied by cross-sectional transmission electron microscopy (TEM) and energy dispersive x-ray (EDX). In addition, the layer structure of the germanosilicide film was investigated using the Rutherford backscattering spectroscopy (RBS) technique.

III. RESULTS AND DISCUSSION

A. Sheet resistance results

The effect of the Pt alloy on the sheet resistance of the germanosilicide formed on Si$_{0.75}$Ge$_{0.25}$ substrate is shown in Fig. 1. For the pure Ni/Si$_{0.75}$Ge$_{0.25}$ samples, a dramatic increase in the sheet resistance from 19.6 to $\sim 3.3 \times 10^4$ Ω/sq (i.e., the sheet resistance of the substrate) took place after annealing at 650 °C. Severe agglomeration of the NiSi$_x$Ge$_y$ films has been confirmed by scanning electron microscopy (SEM) analysis (not shown). For the Ni(Pt ~5 at. %) and Ni(Pt ~10 at. %)/Si$_{0.75}$Ge$_{0.25}$ samples, a dramatic increase in the sheet resistance only began after annealing at 800 °C. For annealing temperature at 600–800 °C, the sheet resistance values are lower than that of the pure Ni/Si$_{0.75}$Ge$_{0.25}$ sample. The sheet resistance remains almost unchanged for Ni(Pt ~10 at. %) and Ni on Si$_{0.75}$Ge$_{0.25}$ after annealing from 400 to 700 °C and 400 to 600 °C, respectively. For the Ni(Pt ~5 at. %)/Si$_{0.75}$Ge$_{0.25}$ samples, most of the sheet resistance values are higher than the samples using 10 at. % Pt for temperature greater than 600 °C but lower than that of the samples using pure Ni.

For comparison, we observed that a 10 at. % Pt in the Ni(Pt) alloy on Si substrate plays an important role in keeping a lower sheet resistance (<20 Ω/sq) when annealed between 400 and 750 °C. On the other hand, for the pure Ni/Si sample, a low sheet resistance can only be observed from samples annealed at 400–600 °C. The effect of Pt appears similar to the results on Si$_{0.75}$Ge$_{0.25}$ substrates. But the film agglomeration is more severe in the case of the Si$_{0.75}$Ge$_{0.25}$ substrate than that of the Si substrate at the same annealing temperature. For the pure Ni on Si$_{0.75}$Ge$_{0.25}$ or Si substrates annealed at 650 °C, the sheet resistance of NiSi$_x$Ge$_y$ (~$3.3 \times 10^4$ Ω/sq) is much higher than that of NiSi (~64 Ω/sq), indicating that the presence of Ge in the substrate degrades the surface morphology of the silicide film greatly. It has recently been reported that the germanosilicide film contains Ge-rich SiGe grains at 550–600 °C. As a result, the degradation of the sheet resistance is possibly due to the occurrence of a Ge-rich phase.
B. Phase formation and Ge out diffusion

According to Vegard'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,$^{12}$ and PtGe (Ref. 4) have the same crystallographic structure, i.e., orthorhombic and Pnma space group. From the XRD spectra, shown in Fig. 2, Ni(Si$_{1-x}$Ge$_x$) or Ni(Pt)(Si$_{1-x}$Ge$_x$) is the only dominant phase detected from samples annealed at 400–800 °C. At 400 and 500 °C, the Ni(Si$_{1-x}$Ge$_x$) or Ni(Pt)(Si$_{1-x}$Ge$_x$) peaks are constant. However, these peaks shift to larger $2\theta$ values with increasing temperature. According to Bragg's law, an increasing $2\theta$ value corresponds to a decreasing plane spacing. As a result, the corresponding lattice constant decreases, indicating a smaller $x$ in the germanosilicide film than that in the substrate. Comparing the peak shift among the Ni(Si$_{1-x}$Ge$_x$) substrates formed at various RTA temperatures, it can be clearly seen that for Ni/Si$_{0.75}$Ge$_{0.25}$, there is a broad peak at about 200 cm$^{-1}$, corresponding to the Ni(Si$_{0.75}$Ge$_{0.25}$) phase at 400 and 500 °C. Whereas two sharp peaks at $\approx 193$ and 213 cm$^{-1}$ were found at 600 °C and above, which are similar to the reported results of NiSi peaks.$^{13}$ 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. The difference in the Ge concentration in the Ni(Si$_{1-x}$Ge$_x$) 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$_{1-x}$Ge$_x$) with $x \approx 0.25$ (0.25 is the Ge concentration of the substrate). These results are in agreement with the Auger mapping and TEM results reported by Pey et al.$^{14}$ In addition, the decrease in the Ge concentration in the Ni(Si$_{1-x}$Ge$_x$) phase was further supported by the shift of the Ni–Si(Ge) peak towards higher wave numbers with increasing temperature.

For the Ni(Pt$\approx 10$ at. %)/Si$_{0.75}$Ge$_{0.25}$ system, as shown in Fig. 3(c), one broad Ni(Pt)(Si$_{0.75}$Ge$_{0.25}$) peak can still be seen at 600 °C, and only one distinct shape peak was found above 700 °C. For the Ni(Pt$\approx 5$ at. %)/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 previously described mechanism where the Ge out diffusion depletes the Ge concentration in the Ni(Pt)(Si$_{1-x}$Ge$_x$) 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 retained in the Ni(Pt)(Si$_{1-x}$Ge$_x$) grains with more Pt into the Ni(Pt) alloy.

Figure 3(d) shows the evolution of the peak position of the strongest Raman peak of Ni and Ni(Pt$\approx 5$ and 10 at. %) on the Si$_{0.75}$Ge$_{0.25}$ substrates at various RTA temperatures. It
TABLE I. Layer structure and element atomic ratio of RBS results (x varies from 0 to 0.25 and y varies from 0.25 to 1 depending on that annealing temperature).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Total film layers</th>
<th>Composition of film layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Si0.75Ge0.25(400 °C)</td>
<td>1</td>
<td>First layer: Ni(Si0.75Ge0.25)</td>
</tr>
<tr>
<td>Ni/Si0.75Ge0.25(500 °C)</td>
<td>1</td>
<td>First layer: Ni(Si0.75Ge0.25)</td>
</tr>
<tr>
<td>Ni/Si0.75Ge0.25(600 °C)</td>
<td>3</td>
<td>First layer: Ge-rich Si1−Ge2, y=0.25</td>
</tr>
<tr>
<td>Ni/Si0.75Ge0.25(700 °C)</td>
<td>3</td>
<td>Second layer: Ni(1−x,Ge0.25), y=0.25</td>
</tr>
<tr>
<td>Ni(Pt ~ 10 at. %)/Si0.75Ge0.25(400 °C)</td>
<td>2</td>
<td>Third layer: Ni(1−x,Ge0.25), y=0.25</td>
</tr>
<tr>
<td>Ni(Pt ~ 10 at. %)/Si0.75Ge0.25(600 °C)</td>
<td>2</td>
<td>First layer: Ni0.96Pt0.04(Si0.75Ge0.25)</td>
</tr>
<tr>
<td>Ni(Pt ~ 10 at. %)/Si0.75Ge0.25(700 °C)</td>
<td>3</td>
<td>Second layer: Ni0.96Pt0.04(Si0.75Ge0.25)</td>
</tr>
<tr>
<td>Ni(Pt ~ 10 at. %)/Si0.75Ge0.25(800 °C)</td>
<td>3</td>
<td>Third layer: Ni0.92Pt0.08(Si0.75Ge0.25), y=0.25</td>
</tr>
</tbody>
</table>

is very clear that there is no change in the wave number of Ni(Pt ~ 5 and 10 at. %)(Si1−Ge)x from 400 to 500 °C. However, there is a slight change in the wave number from Ni(Si1−Ge)x in the same temperature range. When the annealing temperature is increased to 600 °C, a dominant wave-number shift occurs for the Ni–Si(Ge) peak, which is attributed to the Ge out diffusion from the germanosilicide phase. However, with an increase in the Pt atomic percentage, the wave-number shift from 500 to 600 °C is greatly reduced, which means that more Ge is still present in the germanosilicide grain. When the annealing temperature is increased to 700 °C, the wave-number shift only dominantly occurs in Ni(Pt ~ 10 at. %)–Si(Ge). We conclude that more Ge remains in the germanosilicide grain with the addition of Pt when the annealing temperature is below 700 °C. By comparison, there is no apparent shift for the Ni(Pt ~ 0 and 5 at. %)–Si(Ge) peak from 600 to 700 °C, which implies that x < 0.25 at 600 °C, and as a result, the Raman peak remains at almost the same location.

The RBS analysis shown in Table I confirms that the uniform NiSiGe film occurs at 400 and 500 °C for the pure Ni/SiGe system. However, when the annealing temperature increases to 600 °C and above, Ge-rich SiGe grains form. For the Ni(Pt ~ 10 at. %)/SiGe system, the uniform Ni(Pt)(Si0.75Ge0.25) film is stable up to 600 °C, and Ge-rich SiGe grains only appear at 700 °C and above.

Figure 4 show the TEM images of the Ni and Ni(Pt ~ 10 at. %)(Si1−Ge)x film on Si0.75Ge0.25 substrate annealed at 600 and 700 °C. Agglomeration and Ge out diffusion of the germanosilicide film occur in the pure Ni system above 600 °C [see Figs. 4(a) and 4(b)]. In contrast, the Ni0.9Pt0.1(Si1−Ge,y)x film is quite uniform and continuous with the Ge concentration similar to its Si0.75Ge0.25 substrate at 600 °C [Fig. 4(c)] and Ge out diffusion starts at 700 °C [Fig. 4(d)]. According to an EDX analysis, the Ge concentration in the germanosilicide is reduced but increased in the Ge-rich SiGe grain with increasing annealing temperature.

C. Mechanism of agglomeration

A model based on thermal grooving at the grain boundaries via diffusion is used for illustrating the mechanism of agglomeration in the germanosilicide film.\textsuperscript{15,16} For a polycrystalline film on a single-crystal substrate, two local equilibrium relationships need to be considered. One is the bal-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4}
\caption{Cross-sectional TEM micrographs of 10-nm Ni on Si0.75Ge0.25 annealed at (a) 600 °C and (b) 700 °C and 10-nm Ni(Pt ~ 10 at. %) on Si0.75Ge0.25 annealed at (c) 600 °C and (d) 700 °C, respectively. Here x < y < z < 0.25 and w > v > u > 0.25.
}
\end{figure}
ance of the surface and grain-boundary energies, the other is the interface and grain-boundary energies, as shown in Eqs. (1) and (2), respectively.15,16

\[ \gamma_{gb} = 2 \gamma_c \cos \theta, \]  

(1)

\[ \gamma_{gb} = 2 \gamma_i \cos \theta, \]  

(2)

where \( \gamma_{gb} \) is the grain-boundary energy, \( \gamma_c \) is the surface energy, \( \gamma_i \) is the interface energy, and \( \theta \) and \( \theta_i \) are the groove angles at the surface and interface, respectively.17 By lowering \( \gamma_{gb} \), or either increasing \( \gamma_c \) or \( \gamma_i \), it is possible to reduce aggregation. \( \gamma_{gb} \) can be reduced upon alloying,18 and Pt has been added for this purpose. The addition of high-melting-point metals such as Pt also has the effect of increasing \( \gamma_c \) and \( \gamma_i \).19–21 There exists a certain critical value for grain size, \( L_c \), below which agglomeration will not occur.22 This critical value has an inverse relationship with \( \gamma_{gb} \) and is proportional to both \( \gamma_c \) and \( \gamma_i \). The addition of Pt will result in the favorable energy changes mentioned above, thus increasing \( L_c \) such that agglomeration becomes more difficult. The model also proposed that a reduction in the grain size will be able to withhold agglomeration. The XRD spectra of the Ni(Pt~0, 5, and 10 at. %)SiGe revealed that the inclusion of Pt also causes a reduction in the grain size of the germanosilicide. From Fig. 2, the full width at half maximum (FWHM) of the XRD peaks for the samples alloyed with Pt were shown to increase. As the Scherrer equation states that grain size is inversely related to FWHM,23 thus it can be concluded that the grain size has reduced due to the inclusion of Pt. This was verified by the TEM images in Fig. 4.

In addition, the kinetics of the process to get to the equilibrium in Eqs. (1) and (2) will be important. Grain-boundary, interface, and surface diffusions play important roles in this process.

The melting temperatures of NiSi and NiGe are 980 and 860 °C, respectively. Thus NiSiGe compounds are expected to have lower melting points than pure NiSi and consequently higher diffusivities. This should result in a worse surface morphology for NiSiGe films as compared to pure NiSi films as higher diffusivities will make agglomeration easier. This detrimental effect can be compensated by the addition of Pt into NiSiGe as the melting temperature of Ni(Pt)SiGe solution is possibly higher than NiSiGe due to the fact that the melting point of PtSiGe is expected to be between PtSi (1230 °C) and PtGe (1075 °C).4 This implies that atomic diffusion will be slower in the solid solution as a higher melting point is indicative of a stronger bonding between atoms, thus making surface, interface, and grain-boundary diffusions more difficult.18 Consequently, improved surface morphology and decreased agglomeration behavior with increasing Pt atomic percentage are expected by the addition of Pt into the Ni film. In addition, it is believed that the breakdown of chemical bonds in the triple junction of grain boundaries is the main controlling step for groove development. Pt–Si (501.2 kJ/mol) and Pt–Ge (between 400 and 500 kJ/mol) have stronger bonding than Ni–Si (318 kJ/mol) and Ni–Ge (290 kJ/mol), as a result, reduced breakdown rates of chemical bonds due to the addition of Pt could also be responsible for the improved morphological stability of NiSiGe.

D. Mechanism of Ge out diffusion

Out diffusion of Ge from NiSiGe occurs due to the fact that the heat of formation of NiSi (–45 kJ/mol) is lower than that of NiGe (–32 kJ/mol).24 In inspecting the case for Pt and SiGe, it is more favorable for Pt to react with Si rather than Ge. Using the formula given by Zhang,4 one mole of atoms of Ni(Si0.75Ge0.25) or Pt(Si0.75Ge0.25) and one mole of atoms of Si0.75Ge0.25 in the initial state will reach equilibrium with around one mole of atoms of Ni(Si0.97Ge0.03) or Pt(Si0.97Ge0.03) and Si0.64Ge0.36 at 600 °C. From this perspective, it can be seen that the addition of Pt will not affect the preferential formation of silicides. Furthermore, the melting temperature of Ni(Pt)SiGe is anticipated to be higher than that of NiSiGe due to the addition of high-melting-temperature Pt. As a result, all types of diffusion should be reduced in the solid solution as discussed previously, thus preventing thermodynamic equilibrium from being achieved unless the temperature is further increased, leading to possible suppression of Ge out diffusion. In addition, during the formation of Ge-rich SiGe grain, the presence of stronger Pt–Si and Pt–Ge bonds, compared with the bonding of Ni–Si and Ni–Ge, will reduce the dissociation of germanosilicide, thus preventing Ge out diffusion.

IV. CONCLUSIONS

Maintaining a low sheet resistance in NiSiGe at high temperatures is accomplished by adding suitable amounts of Pt. The addition of 5 and 10 at. %Pt was shown to have drastic effects on the germanosilicide stability resulting in improved surface morphology and suppression of Ge out diffusion. The overall stability of the germanosilicide is increased with increasing Pt concentration up to 10 at. % of Pt.

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