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Textured Ni(Pt) Germanosilicide Formation on a Condensed Si$_{1-x}$Ge$_x$/Si Substrate

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Abstract

A study of Ni and Ni(Pt) germanosilicidation on a condensed Si$_{1-x}$Ge$_x$/Si substrate was performed. The partial relaxation of the condensed SiGe layer resulted in an improvement in the morphological stability of the germanosilicide through the alleviation of compressive stress. Pt alloying to the Ni film resulted in highly textured Ni(Pt) germanosilicide grains, particularly in the (002) orientation, due to the reduction in the interfacial energy caused by the presence of Pt alloy. Pt atoms diffuse slowly and result in a variation in lattice parameters in the Ni(Pt)SiGe grain as a function of depth. Nevertheless, Pt alloying has increased the morphological stability of the NiPtSiGe film.

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$\text{Si}_{1-x}\text{Ge}_x$ is increasingly being utilized in advanced complementary metal oxide semiconductor (CMOS) devices either as a channel stressor, a virtual substrate, or a channel material. The fact that Ge has higher carrier mobility compared to Si makes it attractive for use to further improve the transistor performance. However, unlike Si, Ge is scarce and brittle, which makes the fabrication of a large pure-Ge wafer not economically feasible and not easily handled. Therefore, in CMOS fabrication, the Ge incorporation usually takes the Si$_{1-x}$Ge$_x$ layer on Si, Si$_{1-x}$Ge$_x$ on insulator, or even pure Ge on insulator. However, growing a Si$_{1-x}$Ge$_x$ layer directly on top of a Si wafer remains a challenging task.

The presence of built-in stress due to a lattice mismatch between Si$_{1-x}$Ge$_x$ and Si might lead to the formation of misfit dislocations whenever there is a stress relaxation taking place. This dislocation formation has to be avoided because the presence of dislocations especially at the channel region significantly degrades the device performance. The stress relaxation can be avoided by limiting the thickness of the Si$_{1-x}$Ge$_x$ layer directly grown on Si substrate to be below a certain critical thickness. Because the critical thickness of the Si$_{1-x}$Ge$_x$ layer depends on the Ge content in the layer, such approach seriously limits the thickness of the usable Si$_{1-x}$Ge$_x$ layer, especially for the high Ge content Si$_{1-x}$Ge$_x$ layer directly grown on Si substrate. There are several methods that can be utilized to fabricate these substrates. The use of a very thick graded Si$_{1-x}$Ge$_x$ buffer layer (x varies from 0 to the final intended Ge content) beneath the final Si$_{1-x}$Ge$_x$ layer has only been performed on a relatively low Ge concentration. Germanosilicidation studies on high Ge content Si$_{1-x}$Ge$_x$ substrate can be done on a polycrystalline Si$_{1-x}$Ge$_x$ sample or relaxed SiGe grown on a thick buffer layer. The fabrication of a Si$_{1-x}$Ge$_x$ substrate through condensation method enables the formation of a high Ge concentration strained Si$_{1-x}$Ge$_x$ substrate while keeping the defect density low. This work focuses on the phase formation, morphological stability, and microstructural evolution of Ni(Pt) germanosilicide on a strained Si$_{1-x}$Ge$_x$ substrate formed through condensation method with a final Ge content of $\approx$40 atom %.

**Experimental**

Before a deposition of 20 nm Ni or Ni$_{1-x}$(Pt)$_x$ ($x = 0.1$ or 0.2) film, the surface of the condensed Si$_{1-x}$Ge$_x$ substrate was cleaned using piranha solution (H$_2$SO$_4$:H$_2$O$_2$ = 4:1) for 10 min followed by a 1 min dip in dilute HF (1:50) to ensure the removal of the native oxide. The Ni or Ni$_{1-x}$(Pt)$_x$ film was deposited using a dc magnetron sputtering system with a base pressure better than 2 $\times$ 10$^{-6}$ Torr. Rapid thermal annealing (RTA) was used to perform an isotropic annealing of the samples at 400–800°C for 60 s in a N$_2$ purged ambient. The Raman spectroscopy was employed to analyze the mechanical strain inside the Si$_{1-x}$Ge$_x$ layer. Auger electron spectroscopy (AES) depth profiling analysis was performed on the substrate to evaluate the distribution of the Ge atoms inside the Si$_{1-x}$Ge$_x$. The identification of the phase and crystallographic orientation of the germanosilicide film was carried out using X-ray diffraction (XRD) with Cu K$_\alpha$ radiation [average wavelength ($\lambda$): 1.5418 Å]. Cross-sectional transmission electron microscopy (XTEM) analyses using a JEM 2100 transmission electron microscope were employed to evaluate the microstructure of the Ni germanosilicide formed. The surface morphology of the sample was studied using secondary electron microscopy (SEM) imaging. Four-point probe measurements were performed on the annealed samples to monitor the changes in the electrical sheet resistance.

**Results and Discussion**

*Substrate characterizations.—* The AES depth profiling of the Ge concentration in the as-grown and as-condensed Si$_{1-x}$Ge$_x$ substrates is shown in Fig. 1. The maximum Ge concentration on the surface of the as-condensed sample was $\approx$40 atom %. In the surface region (region I), the Ge content slowly decreased as a function of the thickness to around a depth of 50 nm where the Ge concentration was $\approx$30 atom %. Beyond this point, which can be referred to as region II, the slope became three times steeper than that of region I. It can also be observed that the Ge concentration diminished to less than 5 atom % at a depth of around 85 nm before it completely disappeared at a depth of about 115 nm.
As observed in the XTEM micrograph of the as-condensed Si$_{1-y}$Ge$_y$/Si sample shown in the inset of Fig. 1, the Si$_{1-y}$Ge$_y$ substrate exhibits relatively low density threading dislocations. Most dislocations present in the as-condensed substrate were accumulated at a depth of 86.8 ± 4.4 nm, with a smaller number of them appearing at a depth of 59.4 ± 2.0 nm. The depth at which most dislocations appear corresponds to the area near the Si$_{1-y}$Ge$_y$/Si interface determined from the AES depth profiling analysis in Fig. 1. This is caused by a transition from Si to Si$_1$Ge$_y$ at the Si$_{1-y}$Ge$_y$/Si interface, which results in a built-in stress caused by a lattice mismatch between Si and Si$_1$Ge$_y$. This stress was then released through the formation of point defects or misfit dislocations, which are confined at the Si$_1$Ge$_y$/Si interface. Based on the shift in the Si-Si peak in the Raman analysis of the Si$_{1-y}$Ge$_y$ (not shown), the Si$_1$Ge$_y$ layer is in a partially compressive stress with $\varepsilon = -0.8\%$ [the calculated strain value for the fully strained Si$_1$Ge$_y$ ($x = 0.4$) sample is $\varepsilon_{calc} = -1.54\%$].\(^{26}\) The analyzed sample thickness using a 488 nm laser Raman analysis is on the order of several tens of nanometers, and hence the Raman signal obtained is an average from the probed volume from the surface, which has a varying Ge concentration and a varying strain. This, together with the partial relaxation in the Si$_1$Ge$_y$ layer explained previously, resulted in the discrepancy between the measured and calculated strain values.

**Ni and Ni$_{1-z}$(Pt)$_z$ germanosilicidation on a condensed Si$_{1-y}$Ge$_y$ substrate.**—As shown in the XRD spectra in Fig. 2a, the Ni(Si$_{1-y}$Ge$_y$) formation can be detected in the sample after 400°C annealing and above. After annealing at 400°C, peaks from (102) and (201) planes were the most dominant peaks observed in the spectra. The appearance of additional peaks from (002), (202), and (013) peaks could be detected in the XRD spectra after annealing at higher temperatures, which indicates that the Ni(Si$_{1-y}$Ge$_y$) film has become less textured. XRD analyses of the same sample using a Seeman–Bohlin configuration (not shown) has revealed that the Ni(Si$_{1-y}$Ge$_y$) peaks shift toward a larger diffraction angle (i.e., a reduction in interplanar spacing) as the annealing temperature is increased from 400 to 500°C. This phenomenon is caused by Ge out-diffusion from the Ni(Si$_{1-y}$Ge$_y$) crystal, which is thermodynamically driven by a difference in the heat of formation of NiSi and NiGe.\(^{17}\)

Ni film with 10 atom % Pt alloying was used to study the effect of Pt addition during Ni germanosilicide formation. As observed in the XRD spectra depicted in Fig. 2b, the formation of Ni$_{1-z}$(Pt)$_z$(Si$_{1-y}$Ge$_y$) [where $z \leq 0.1$ and $y \leq 0.4$, it will be written as Ni(Pt)(Si$_{1-y}$Ge$_y$) for simplicity] was fully completed after 400°C annealing and above. Different from the pure-Ni sample, the sample with Pt alloying exhibits a clear texturing in the Ni(Pt)(Si$_{1-y}$Ge$_y$) film. Initially, two diffraction peaks that originated from the (002) and (102) planes of the Ni(Pt)(Si$_{1-y}$Ge$_y$) phase were observed in the XRD spectra. Annealing at higher temperature resulted in a more distinct texturing of the Ni(Pt)(Si$_{1-y}$Ge$_y$) film at the (002) peak. Eventually the (102) peak disappeared, and only the diffraction peak from the (002) plane could be observed in the Ni(Pt)(Si$_{1-y}$Ge$_y$) film. The mechanism of the texturing is explained in the following paragraph.
The growth of a thin film is affected by both interfacial (thickness independent) and strain energies (thickness dependent). To achieve a higher thermodynamic stability, the system always tends to proceed in a certain way to minimize the sum of these two energies. The absence of texturing in the pure-Ni sample might be caused by the interfacial energy of the Ni(Si$_{1-y}$Ge$_y$) film being similar in different planes. This results in the formation of a polycrystalline film with many different orientations, as observed in Fig. 2b. The addition of 10 atom % Pt into the film has resulted in the reduction in interfacial energy between the Ni(Pt)(Si$_{1-y}$Ge$_y$) film and the substrate. It is believed that reduction in interfacial energy was more pronounced in the (002) and (102) planes; thus the nuclei were predominantly growing in these two planes. Increasing the annealing temperature caused a grain growth in the Ni(Pt)(Si$_{1-y}$Ge$_y$) film as well as in its thickness. This changes the governing mechanism during the growth of the film in which the strain energy alters the preferential growth of the sample. This phenomenon is apparent in the Ni(Pt)(Si$_{1-y}$Ge$_y$) sample in which the (002) peak is the only peak observed in the sample after annealing at higher temperatures. Because the SiGe substrate used in this work is epitaxially grown in (001), the (002) planes in the Ni(Pt)(Si$_{1-y}$Ge$_y$) film must be in parallel position with the substrate.

As expected, the peak positions of Ni(Pt)(Si$_{1-y}$Ge$_y$) at 400°C were shifted toward a lower diffraction angle as compared to that in the Ni(Si$_{1-y}$Ge$_y$) sample. The Pt alloying caused the further dilation of the lattice constant of the Ni(Si$_{1-y}$Ge$_y$) and its corresponding d-spacing. All Ni(Pt)(Si$_{1-y}$Ge$_y$) diffraction peaks did not shift to a higher diffraction angle after annealing at higher temperatures up to 600°C, which is different from that of the NiSi$_{1-z}$Ge$_z$ samples. The absence of any peak shift in the annealed Ni$_{1-z}$(Pt)$_z$/Si$_{1-x}$Ge$_x$ samples indicates that with Pt addition, the Ge out-diffusion phenomenon is significantly reduced.

A high resolution transmission electron microscopy (HRTEM) micrograph of the Ni(Pt)(Si$_{1-y}$Ge$_y$) film after annealing at 600°C is shown in Fig. 3a. The Ni(Pt)(Si$_{1-y}$Ge$_y$) grains were in the form of big crystals and appeared to be highly textured. This observation agrees well with the XRD results shown in Fig. 2b. Because the Si$_{1-z}$Ge$_z$ substrate has a varying Ge content, it is of interest to evaluate whether the Ge and/or Pt atoms inside the Ni(Pt)(Si$_{1-z}$Ge$_z$) sample were distributed evenly throughout the germanosilicide grain. The grain was aligned to a [110] zone axis to facilitate lattice spacing measurement. The normalized lattice spacing of the Ni(Pt)(Si$_{1-z}$Ge$_z$) grain as a function of depth at the location near the grain boundary (■) and in the middle of the germanosilicide grain (▲) was measured, as shown in Fig. 3b. The measurement location “near the grain boundary” was around 5 atomic spacings away from the grain boundary, whereas the “middle of the grain” was at the middle area of the grain, which, in this case, was around 30 nm away from the grain boundaries. It is apparent that the lattice spacing inside a single-crystal Ni(Pt)(Si$_{1-z}$Ge$_z$) decreases as a function of depth. The secondary-ion mass spectrometry depth profiling analysis of the sample (not shown) revealed that the Pt atoms did not diffuse as fast as the Ni atoms and were accumulated near the surface region, which resulted in the variation observed in the lattice parameter of the germanosilicide film. The fact that the Ni(Pt)(Si$_{1-y}$Ge$_y$) grains are textured and large plays an important role in preventing the out-diffusion of Ge atoms to the grain boundaries (due to a limited grain boundary area).

To further evaluate the effect of the Pt alloying during Ni(Pt) germanosilicidation, another set of samples with a 20 atom % Pt alloying was prepared. The annealing conditions were similar to other sets of samples described previously. The XRD spectra of the Ni$_{1-z}$(Pt)$_z$/Si$_{1-x}$Ge$_x$ ($u = 0.2$) samples before and after RTA annealing processes are shown in Fig. 4. The sample with higher Pt alloying exhibits an even more textured Ni$_{1-z}$(Pt)$_z$/Si$_{1-x}$Ge$_x$ film [where $z \approx 0.2$ and $y \approx 0.4$, it will be written as Ni(Pt)$_{0.2}$(Si$_{0.8}$Ge$_{0.2}$) for simplicity]. Again the $y$ value here might or might not be exactly the same as the one in the Ni(Pt)(Si$_{1-z}$Ge$_z$) sample, especially for the high temperature annealing processes. No formation of PtSi or PtGe could be observed from the XRD analysis. This indicates that the Pt atoms were still incorporated inside the germanosilicide grains even at the 20 atom % of Pt alloying. This result is expected because all NiSi, NiGe, PtSi, and PtGe phases have a similar orthorhombic $pmma$ structure, and hence a complete miscibility is possible throughout the whole range of atomic composition.

After 400°C annealing, the XRD spectra of the Ni$_{1-z}$(Pt)$_z$/Si$_{1-x}$Ge$_x$ ($u = 0.2$) is dominated by the appearance of high intensity double peaks at around 2θ angle of 29–31°. The peaks could be attributed to the (011) and (002) peaks of the Ni(Pt)$_{0.2}$(Si$_{0.8}$Ge$_{0.2}$) phase. As the annealing temperature increases, the (002) peak becomes dominant, and eventually only the diffraction peak from this plane is observable in the XRD spectra. These
set of agglomeration of the Ni/H2O849 rhombic crystal structure. Adding Pt resulted in texturing in the internal symmetry, which is expected from the crystal with an ortho-
grains detected/H2O849 manosilicide film.18 The compressive stress in a Si 1−x
which at the same time affects the mechanical stability of the ger-
mination along the its a twofold rotational symmetry with an appearance of grain tex-
substrate. Pt addition has altered the interfacial energy and the lattice dimension of the germanosilicide, thus allowing it to form a textured film on the substrate.

**Morphology of germanosilicide on condensed SiGe.**—The onset of agglomeration of the Ni/Si1−xGey/Si sample could be detected after annealing at temperatures as low as 500°C. Annealing at higher temperatures, i.e., 600°C, resulted in a severe islanding of the Ni(Si1−xGey) film (see Fig. 6a). As reported previously, the agglomeration of Ni(Si1−xGey) formed on Si1−xGey substrate is affected both thermodynamically and mechanically.16,18 From the thermodynamic point of view, the explanations used for the agglomeration of Ni germanosilicide with low Ge content are still valid as Si is still the majority element in the Si1−xGey substrate used. Compressive stress adversely affects the agglomeration in the Ni germanosilicide through a stress release mechanism. Ni germanosilicide acts as a fast diffusion medium of both Si and Ge atoms for releasing the stress, which at the same time affects the mechanical stability of the germanosilicide film.18 The compressive stress in a Si1−xGey layer is directly affected by the amount of Ge in the Si1−xGey. The presence of a Ge concentration gradient inside the condensed Si1−xGey layer, as observed by the AES depth profiling analysis (Fig. 1) especially after a depth of 50 nm, results in a varying compressive stress with a maximum stress very near to the surface area (highest Ge content and then diminishes as a function of depth). The presence of the Ge gradient in the Si1−xGey film is beneficial in alleviating the adverse

![Figure 4](image4.png)

**Figure 4.** (Color online) XRD spectra of the Ni(Pt)0.2/Si1−xGey/Si sample ($u = 0.2$) after RTA at different temperatures starting from 400 to 700°C. The XRD spectrum from the as-deposited sample is also plotted for comparison.

![Figure 5](image5.png)

**Figure 5.** (Color online) Pole figures of (a) Ni(Si1−xGey), (b) Ni(Pt)0.1/Si1−xGey, and (c) Ni(Pt)0.2/Si1−xGey after RTA at 500°C. The pole figures were taken at 20 value of 30.13°, which corresponds to the (002) plane of the NiSi-based phase.

![Figure 6](image6.png)

**Figure 6.** SEM micrograph of (a) the Ni(Si1−xGey) sample, (b) the Ni(Pt)0.1/Si1−xGey/Si sample ($u = 0.1$), and (c) the Ni(Pt)0.2/Si1−xGey/Si sample ($u = 0.2$) after annealing at 600°C. There is enhanced improvement in the morphological stability of the sample with increasing Pt concentration.
improves the morphological stability of the germanosilicide through the elimination of the compressive stress. Slow diffusion of Pt atoms during the Ni(Pt) germanosilicide formation resulted in the formation of Ni(Pt) germanosilicide film with varying lattice parameters, with its biggest near the surface and its smallest nearest the substrate. Alloying with higher Pt concentration resulted in highly textured grains with a better morphological stability of the Ni(Pt) germanosilicide sample. The dominant texturing orientation of the Ni(Pt) germanosilicide grain was in the (002) direction, which is parallel to the substrate surface Si(001).

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