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Suppression of oxidation in nickel germanosilicides by Pt incorporation

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The effect of oxidation of 10 nm $Ni/Si_{0.75}Ge_{0.25}$ and 10 nm Ni(10 at. % Pt)/$Si_{0.75}Ge_{0.25}$ thin films at annealing temperatures ranging from 400 to 800 °C has been studied in detail by Rutherford backscattering spectrometry analysis, cross-sectional transmission electron microscopy, energy dispersive x-ray, and sheet resistance measurements. It is observed that for the films without Pt incorporation, almost two-thirds of the germanosilicide is oxidized. The incorporation of a Pt(10 at. %) into Ni not only dramatically reduces the oxidation of the germanosilicides, but also improves the interfacial roughness and morphology. The integral amount of oxygen found in the germanosilicide in the Ni(10 at. % Pt)$Si_{0.75}Si_{0.25}$ films [$(1.1\pm0.17)\times10^{17}$ at./cm^2] is approximately four times less than that of $NiSi_{0.75}Si_{0.25}$ [$(4.0\pm0.28)\times10^{17}$ at./cm^2]. This result is explained in terms of the roles of the higher melting point and bond energy of PtSi in NiSi and NiGe, and much lower free energy of the formation of platinum oxide. *© 2005 American Institute of Physics*. [DOI: 10.1063/1.2120902]

NiSi is an attractive material to replace $CoSi_2$ for nanoscale complementary metal-oxide semiconductor (CMOS) devices because of its well known advantageous properties.[1–3]

Since $Si_{1-x}Ge_x$ films will be present in the gate (polycrystalline)[4] and source/drain (single crystal)[5] areas of metal-oxide-semiconductor field-effect transistors (MOSFETs), understanding the solid-state interactions of Ni and Ni(Pt) with $Si_{1-x}Ge_x$ and O_2 is very important. Typically, considerable amount of oxygen is present[6] in the silicide even though the reaction takes place in a high-vacuum environment. The oxygen contamination during silicidation may come from the following sources: (1) the annealing ambient, (2) oxygen incorporated within the as-deposited metal layer, and (3) interfacial oxide at the metal/silicon interface.

It is also well established that the oxidation rate of SiGe is higher than that of the pure Si.[7] This enhanced oxidation of SiGe is of technological concern, and therefore it is important to study the oxidation in the $Ni/Si_{1-x}Ge_x$ thin-film system. In this letter, we study the effect of Pt in Ni(Pt) alloy on the oxygen incorporation into nickel germanosilicides at different annealing temperatures.

$Si_{1-x}Ge_x$ 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 $Si_{1-y}Ge_y$ ($y=0\rightarrow0.25$) layer of thickness of 3.0 μm, and a uniform relaxed $Si_{1-x}Ge_x$ layer ($x=0.25$) of thickness of 3.0 μm were subsequently grown over the substrate. The samples were subjected to the standard RCA-I and RCA-II cleaning processes followed by a dip in a 10% HF for oxide removal. After the native oxide removal, the wafers were loaded in a sputtering chamber. A layer of 10 nm Ni or 10 nm Ni(10 at. % Pt) was sputter deposited on the $Si_{0.75}Ge_{0.25}$ samples at a deposition pressure of 10^{-6} Torr. The Ni- and Ni(Pt)-deposited samples were rapid thermal process (RTP) annealed in a N_2 ambient to form germanosilicide layers at different temperatures of 400, 500, 600, 700, and 800 °C each for 1 min.

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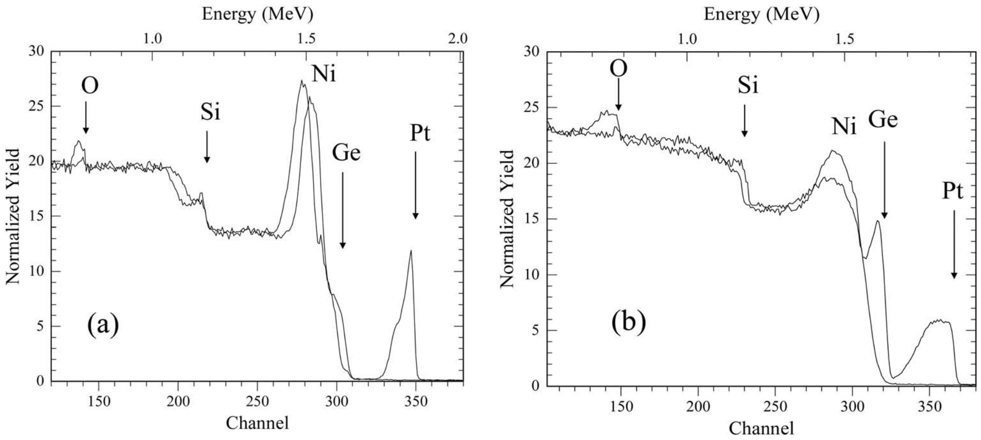

FIG. 1. 2 MeV 4He$^+$ RBS spectra of 10 nm Ni/Si$_{0.75}$Ge$_{0.25}$ and of 10 nm Ni(10 at. %Pt)/Si$_{0.75}$Ge$_{0.25}$ films annealed at (a) 400 °C and (b) 800 °C using RTP after 1 min.

Rutherford backscattering spectrometry (RBS) analysis was carried out using a 3.5 MV Singletron accelerator to determine the layer thickness, elemental distributions, and interfacial roughness of the germanosilicide films. The RBS spectra were analyzed using the simulation code RUMP.[8] Cross-sectional transmission electron microscopy (XTEM) with energy dispersive x-ray (EDX) was done for getting the internal structure and stoichiometry of the samples. A Keithley Instruments four-point probe system was employed for sheet resistance measurements.

Figure 1(a) shows the RBS spectra of a 10 nm Ni/Si$_{0.75}$Ge$_{0.25}$ and 10 nm Ni(10 at. % Pt)/Si$_{0.75}$Ge$_{0.25}$ films RTP annealed at 400 °C. The RBS analysis confirms that without Pt incorporation, almost two-third of the germanosilicide is oxidized and the integral amount of oxygen in the layer is $\sim 4.0 \times 10^{17}$ at./cm^2. In addition, the interface between the germanosilicide and the Si$_{0.75}$Ge$_{0.25}$ substrate is relatively sharp even though a considerable amount of Ge has migrated to the surface as shown in Fig. 1(a). In the Pt-alloyed samples, the migration of Ge to the surface is suppressed and the stoichiometric amounts of Ge are present in the germanosilicide layer. It is important to observe that the oxidation is greatly suppressed in the Ni(Pt)SiGe samples. The total amount of oxygen in the germanosilicide layer is $\sim 1.1 \times 10^{17}$ at./cm^2, as can be derived from the presence of the small oxygen peak in the spectra for all the 10 nm Ni(Pt)/Si$_{0.75}$Ge$_{0.25}$ thin films.

As shown in Fig. 2, the total amount of oxygen for the 10 nm Ni(10 at. % Pt)/Si$_{0.75}$Ge$_{0.25}$ thin films remains constant between 400 and 800 °C. On the other hand, for the 10 nm Ni/Si$_{0.75}$Ge$_{0.25}$ annealed thin films, the concentration of oxygen incorporated into the germanosilicide films between 400 and 500 °C is low, and increases considerably with annealing temperature. The oxygen content remains constant ($\sim 4.6 \times 10^{17}$ at./cm^2) at 600 and 700 °C as shown in Fig. 2.

With increasing annealing temperature, two other phenomena are observed from the RBS spectra: (i) agglomeration and/or interface roughening leading to an increasing slope of the Ni edge, and (ii) an increasing amount of Ge migration towards the surface which is consistent with the results reported in Ref. 9. Furthermore, no Ni is found within the first ~40 nm of the Ni/Si$_{0.75}$Ge$_{0.25}$ annealed films, implying that a pure oxide with a stoichiometry of SiGe$_{0.55}$O$_2$ is present near the surface. This stoichiometry clearly demonstrates that Ge migration towards the surface is much more pronounced than that of the Si migration. For the Ni(Pt)/Si$_{0.75}$Ge$_{0.25}$ annealed films, Ni and Pt are always found at the surface. However, only a small amount of oxide with a stoichiometry of NiPt$_{0.14}$SiGe$_{0.25}$O is present.

Figures 3(a) and 3(b) show the XTEM images of a 10 nm Ni on Si$_{0.75}$Ge$_{0.25}$(100) substrate and 10 nm Ni(Pt =10 at. %) film on Si$_{0.75}$Ge$_{0.25}$(100) substrate both annealed at 600 °C. It is observed that agglomeration and Ge outdiffusion of germanosilicide film occur in the pure Ni system at 600 °C resulting in Ge-enriched SiGe grains and Ge-deficient Ni-germanosilicide grains. On the other hand, the Ni$_{0.9}$Pt$_{0.1}$(Si$_{1-x}$Ge$_x$) film is relatively uniform and continuous with the Ge concentration similar to that of the Si$_{0.75}$Ge$_{0.25}$ substrate at 600 °C and Ge only starts to outdiffuse at 700 °C.

Figure 4 shows the sheet resistance of the germanosilicide films annealed at various temperatures for both 10 nm Ni/Si$_{0.75}$Ge$_{0.25}$ and 10 nm Ni(10 at. % Pt)/Si$_{0.75}$Ge$_{0.25}$ films. It is observed that the sheet resistance of the 10 nm Ni/Si$_{0.75}$Ge$_{0.25}$ films is always higher than that of the 10 nm Ni(10 at. % Pt)/Si$_{0.75}$Ge$_{0.25}$ films and the difference increases with increasing annealing temperature.

The large difference of oxygen incorporation between the 10 nm Ni/Si$_{0.75}$Ge$_{0.25}$ and the 10 nm Ni(10 at. % Pt)/Si$_{0.75}$Ge$_{0.25}$ thin films can be explained as follows. As the melting point of NiGe, NiSi, PtSi, and PtGe is 860, 980, 1230, and 1075 °C, respectively,[10] the melting

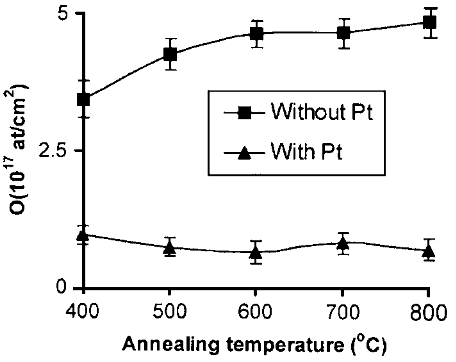

FIG. 2. Oxygen incorporation into the 10 nm Ni/Si$_{0.75}$Ge$_{0.25}$ and 10 nm Ni(10 at. %Pt)/Si$_{0.75}$Ge$_{0.25}$ films after 1 min of RTP annealed at various temperatures.

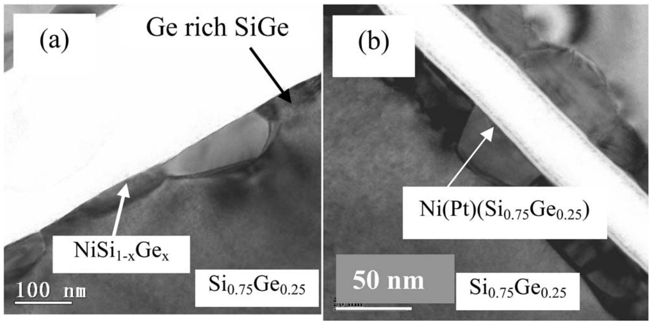

FIG. 3. (a) Cross-sectional TEM micrographs of 10 nm Ni on $Si_{0.75}Ge_{0.25}$ and (b) of 10 nm Ni(10 at. %Pt) on $Si_{0.75}Ge_{0.25}$ both annealed 600 °C. In (a) x is less than 0.25.

point of $NiSi_{1-x}Ge_x$ is anticipated to be lower than that of NiSi. Therefore, one would expect a worsened morphological stability for $NiSi_{1-x}Ge_x$ as compared to NiSi. As a result, the outdiffusion of Ge and possibly Si from $NiSi_{1-x}Ge_x$ is expected to increase at low temperature. On the other hand, as the melting point of $Ni(Pt)Si_{1-x}Ge_x$ is anticipated to be higher than that of $NiSi_{1-x}Ge_x$, the morphological stability of the $Ni(Pt)Si_{1-x}Ge_x$ would be better which in turn reduces Ge and Si outdiffusion towards the surface, leading to less oxide formation. It was reported that[11] morphology being improved by around 150 °C if a 10–20-Å-thick Pt interlayer is included between a 100 Å Ni and B-doped $Si_{1-x}Ge_x$.

The free energy of formation of $SiO_2(\Delta H=-70$ kcal/g at.) and $GeO_2(\Delta H=-44$ kcal/g at.) is much larger than that of the metal oxides $[\Delta H(PtO)=-8.5$ kcal/g at. and $\Delta H(Ni_2O_3)=\Delta H(NiO)=$ Ni oxide $=-29$ kcal/g at.].[12] Therefore, the formation of SiO_2 and GeO_2 is more favorable than the formation of NiO or PtO. As the outdiffusion of Ge and Si to the surface with increasing annealing temperature is evident [Figs. 1(a) and 1(b)], in this surface Ge and Si are eventually oxidized with oxygen ambient.

Another factor contributing to the reduced oxidation of the $Ni(Pt)/Si_{0.75}Ge_{0.25}$ thin films could be the effect of Pt acting as a barrier for oxygen diffusion from the surface to the bulk region of the germanosilicide. Since Pt has a large atomic radius as compared to Ni, it can inhibit the diffusion of Ge and Si to the surface and oxygen into the bulk region resulting in a reduced oxidation. One very important property of PtSi is that the bond energy of PtSi is 118.72 kcal/mol (Ref. 13) which is much larger than that of NiSi (75.2 kcal/mol) (Ref. 14) and NiGe (68.5 kcal/mol).[15] Due to this strong bond strength of PtSi, the probability of dissociation of the bond is less compared to the NiSi and NiGe bonds which in turn improves the overall stability of the germanosilicide as NiSi, NiGe and PtSi are orthorhombic MnP structure and completely miscible.[16,17] The XTEM results shown in Fig. 3 unambiguously confirm much better germanosilicide stability with the Pt addition.

The observed sharp rise in the sheet resistance for the 10 nm $Ni/Si_{0.75}Ge_{0.25}$ sample at 600 °C and the 10 nm $Ni(Pt)/Si_{0.75}Ge_{0.25}$ sample at 700 °C are attributed to agglomeration and oxidation effects. In the 10 nm $Ni/Si_{0.75}Ge_{0.25}$ thin films, the germanosilicide films suffer severe agglomeration as early as 600 °C. The slight increase in the sheet resistance for the 10 nm $Ni/Si_{0.75}Ge_{0.25}$ films at 400 and 500 °C is attributed to the incorporation of a higher amount of oxygen, as compared to the 10 nm $Ni(Pt)/Si_{0.75}Ge_{0.25}$ films. As the integral amount of oxygen does not increase sharply, the sharp increase in the sheet resistance of the NiSiGe samples at 600 °C is due to the agglomeration rather than oxidation. On the other hand, as very little oxygen is incorporated in the Ni(Pt)SiGe film, the sheet resistance does not vary much up to 700 °C of the annealed $Ni(Pt)/Si_{0.75}Ge_{0.25}$ films.

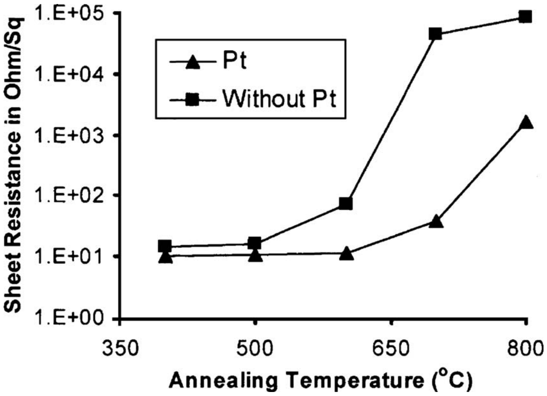

FIG. 4. Sheet resistance of the 10 nm $Ni/Si_{0.75}Ge_{0.25}$ and of 10 nm Ni(10 at. %Pt)/$Si_{0.75}Ge_{0.25}$ thin films as a function of annealing temperatures.

In conclusion, around four times larger amount of oxygen incorporation occurs in Ni-germanosilicide at an annealing temperature range of 400–800 °C as compared to that of Ni(Pt)-germanosilicide. This large amount of the oxygen contamination in the Ni-germanosilicide films is due to the increasing trends of Ge and Si outdiffusions towards the surface at elevated temperatures.

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