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Interfacial reactions of Ni on $Si_{0.76}Ge_{0.24}$ and Si by pulsed laser annealing

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Abstract

Pulsed KrF laser annealing and vacuum annealing on the interfacial reactions of $Ni/Si_{0.76}Ge_{0.24}$ and Ni/Si were studied. For the $Ni/Si_{0.76}Ge_{0.24}$ films annealed at temperatures above 300°C, some Ge-rich $Si_{1-x}Ge_x$ grains were formed between the Ge-deficient Ni germanosilicide grains, resulting in the island structure. For Ni/Si films homogeneous epitaxial $NiSi_2$ films could be grown even at 600°C. Ni silicide (germanosilicide) associated with the amorphous overlayer was generally formed at lower energy densities for Ni/Si, NiSi/Si, $Ni/Si_{0.76}Ge_{0.24}$ and $Ni(Si_{1-x}Ge_x)/Si_{0.76}Ge_{0.24}$ systems, respectively. At higher energy densities constitutional supercooling occurred. The energy densities at which constitutional supercooling appeared were higher for NiSi and $Ni(Si_{1-x}Ge_x)$ than for Ni. For the continuous $Ni(Si_{1-x}Ge_x)$ films grown at 200°C in a vacuum furnace, subsequent laser annealing at an energy density of 0.6–1.0 J cm^{-2} have shown to render homogeneous $Ni(Si_{0.76}Ge_{0.24})_2$ and $Si_{0.76}Ge_{0.24}$ films without the island structure and Ge segregation.

Keywords: Interfacial reactions; Laser annealing

1. Introduction

The $Si_{1-x}Ge_x/Si$ heterojunction has significant potential applications in high-speed electronic and optoelectronic devices [1,2]. Interfacial reactions of metals such as Ni [3], Pt [4,5], Pd [5,6], Ti [7–12] and Co [13–16] on $Si_{1-x}Ge_x$ films have been studied for low-resistance ohmic contacts and as contacts for Schottky barrier infrared detectors. In these reactions the formation of a ternary phase was generally accompanied with Ge segregation. Additionally, for the Ti and Co on $Si_{1-x}Ge_x$ films an island structure also appeared at higher annealing temperatures [9,10,15,16]. These phenomena are presumably ascribed to the higher heat of formation for metal–Si than for metal–Ge [17]. Rapid thermal annealing could shorten the annealing time, resulting in a reduction of Ge segregation [9,10].

Pulsed laser annealing has been extensively used in growing thin films of silicides [18,19], $Si_{1-x}Ge_x$ [20], $Si_{1-x}C_x$ [21] and $Si_{1-x-y}Ge_xC_y$ [22]. In comparison with furnace annealing, pulsed laser annealing offers several advantages such as much shorter operational time, confinement of the heated area without causing changes in the pre-existing structure, reduction of contaminants, etc. For the growth of $Si_{1-x}C_x$ and $Si_{1-x-y}Ge_xC_y$, carbon at concentrations of some orders of magnitude above the equilibrium solubility can be incorporated into Si and $Si_{1-x}Ge_x$ by pulsed laser annealing due to the fast melt and resolidification process [21,22]. Similarly, it is expected that Ge segregation together with the formation of island structure, which commonly appears in the interfacial reactions of metal/$Si_{1-x}Ge_x$ by conventional furnace annealing, may be suppressed by pulsed laser annealing. In the present study, therefore, the effort was mainly focused on studying the interfacial reactions of the $Ni/Si_{0.76}Ge_{0.24}$ system as a function of the laser energy density. Meanwhile, similar studies were also carried out on the Ni/Si system for comparison.

2. Experimental

Relaxed epitaxial $Si_{0.76}Ge_{0.24}$ films about 0.15 μm thick were grown on n-type (100) Si at 550°C by ultra-high vacuum chemical vapor deposition. Prior to Ni deposition the substrates were cleaned by the RCA method and then immediately loaded into the chamber. An Ni overlayer about 250 Å thick was deposited on to the $Si_{0.76}Ge_{0.24}/Si$ and Si substrates, respectively, at room temperature by electron gun evaporation at a rate of 1 Å s^{-1}. The base pressure was around 1.0×10^{-6} Torr. Furnace annealing was carried out at a temperature of 200–600°C in a vacuum of $1–2\times10^{-6}$ Torr.

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Pulsed KrF laser annealing was performed at an energy density of 0.1–1.6 J cm^{-2} in a vacuum around 2×10^{-2} Torr. The duration time was 14 ns. The laser beam was focused on to an area of 4×4 mm^2. For each laser annealing the specimen was illuminated by one shot. Phase formation, microstructure and chemical compositions of the reacted layer were analyzed by energy dispersive spectrometry (EDS)/transmission electron microscopy (TEM) which was equipped with a field emission gun with an electron probe 12 Å in size. The variation of lattice parameters of $Si_{0.76}Ge_{0.24}$ films after annealing was examined by the X-ray diffraction (XRD) method with CuKα radiation. The areas of laser annealed samples used for XRD analysis were about 1×1 cm^2, which were composed of nine adjacent 4×4 mm^2 areas irradiated under identical conditions.

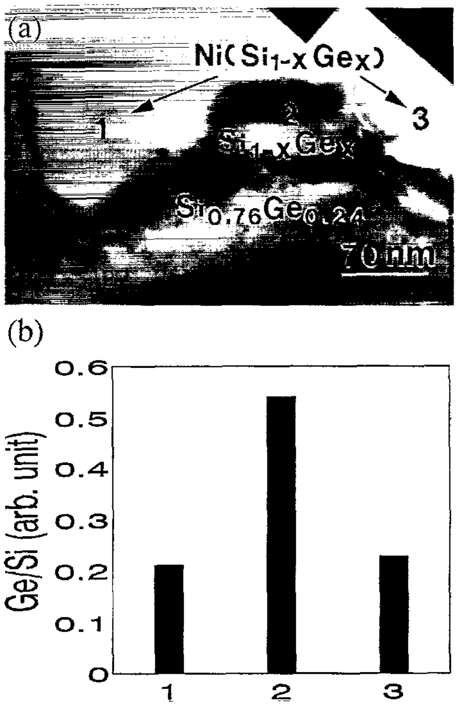

Fig. 1. (a) XTEM image and (b) the Ge/Si concentration ratio of an Ni/$Si_{0.76}Ge_{0.24}$ film after vacuum annealing at 300°C showing that the Ge-rich $Si_{1-x}Ge_x$ grains were formed between the Ge-deficient Ni($Si_{1-x}Ge_x$) grains.

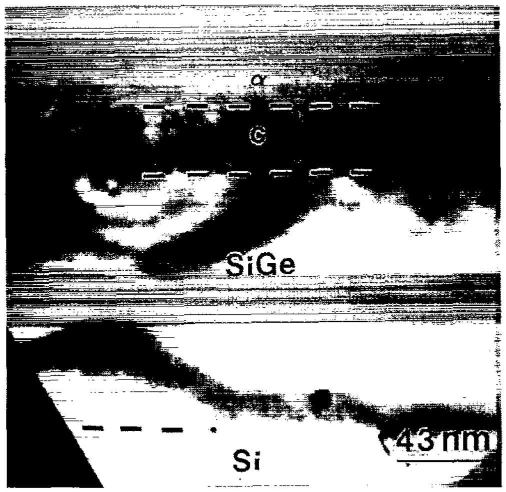

Fig. 2. XTEM image of an Ni/$Si_{0.76}Ge_{0.24}$ film after laser annealing at 0.3 J cm^{-2} showing that two layers of Ni germanosilicide were formed on the surface of the $Si_{0.76}Ge_{0.24}$ film. The upper layer is amorphous, while the lower layer is crystalline.

3. Results and discussion

3.1. Ni/$Si_{0.76}Ge_{0.24}$

For the Ni/$Si_{0.76}Ge_{0.24}$ films annealed at a temperature of 200–500°C in a vacuum furnace, an Ni($Si_{1-x}Ge_x$) layer was formed, which was confirmed to be a solid solution of NiSi and NiGe by EDS/TEM analysis. From EDS/cross-sectional TEM (XTEM) analysis of the sample annealed at 300°C some Ge-rich $Si_{1-x}Ge_x$ grains were formed between the Ge-deficient Ni($Si_{1-x}Ge_x$) grains as shown in Fig. 1. Ge segregation from the Ni($Si_{1-x}Ge_x$) layer to the $Si_{0.76}Ge_{0.24}$ substrate also appeared. The heats of formation for NiSi and NiGe have been determined to be about -45 and -32 kJ mol^{-1}, respectively [17]. These values suggest that Ni tends to react preferably with Si. It seems that Ge is repelled from the Ni($Si_{1-x}Ge_x$) grains and diffuses into the Ni($Si_{1-x}Ge_x$) grain boundaries to react with Si and Ge from the substrate, causing the formation of the Ge-rich $Si_{1-x}Ge_x$ grains. Similar results have been found in the Ti/$Si_{1-x}Ge_x$ system by Aldrich et al. [9,10]. Higher annealing temperatures yielded a greater Ge deficiency in the Ni($Si_{1-x}Ge_x$) layer. At 400°C the Ge-rich $Si_{1-x}Ge_x$ grains became connected, leading to the formation of the island structure. Meanwhile Ge was greatly enriched in the free surface of the $Si_{0.76}Ge_{0.24}$ film. The Ni$(Si_{1-x}Ge_x)_2$ phase started to form at 600°C, in which only a trace amount of Ge was present.

For the Ni/$Si_{0.76}Ge_{0.24}$ films annealed at an energy density of 0.1–0.3 J cm^{-2}, two layers were formed on the surface of the $Si_{0.76}Ge_{0.24}$ film. One example is shown in Fig. 2. From micro-diffraction analysis the upper layer was amorphous, while the lower layer was crystalline. From EDS/XTEM analysis the Ni/(Si+Ge) atomic ratios for the upper and lower layers were about 1:1 and 1:2, respectively. Generally, annealing at lower energy density favored the formation of an amorphous structure due to the higher cooling rate. At energy densities above 0.4 J cm^{-2} the constitutional supercooling occurred, resulting in the cellular structures of Ge-deficient $Si_{1-x}Ge_x$ island surrounded by Ni$(Si_{1-x}Ge_x)_2$ [23]. Poate et al. [18] and Tung et al. [19] observed the constitutional supercooling phenomenon in the Pt/Si system irradiated by Nd:YAG laser and indicated that interfacial instability and cell formation can be suppressed by melting mono- or disilicide layers.

A homogeneous Ni($Si_{1-x}Ge_x$) film without the island structure could be grown at 200°C. After pulsed KrF laser annealing at an energy density of 0.6–1.2 J cm^{-2}, it fully transformed into a homogeneous Ni$(Si_{1-x}Ge_x)_2$ film. One example of the film grown at 1.0 J cm^{-2} is shown in Fig. 3. It is worth noting that the island structure originally present

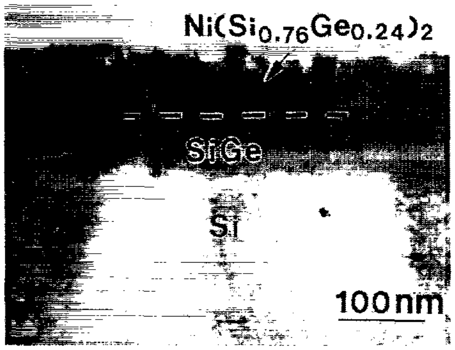

Fig. 3. XTEM image of an Ni/$Si_{0.76}Ge_{0.24}$ film after vacuum annealing at 200°C and subsequent laser annealing at 1.0 J cm^{-2}.

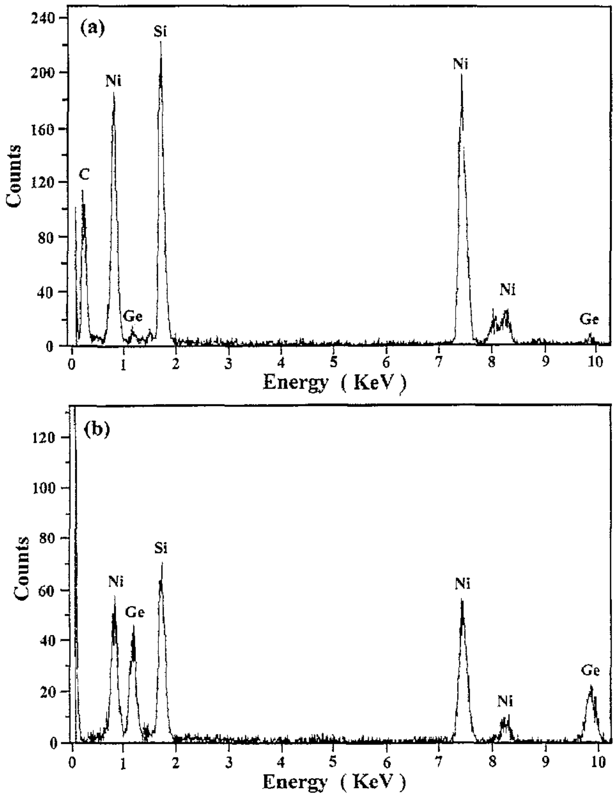

Fig. 4. EDS spectra of (a) an $Ni(Si_{1-x}Ge_x)$ grain grown at 500°C and (b) an $Ni(Si_{0.76}Ge_{0.24})_2$ film corresponding to that in Fig. 3.

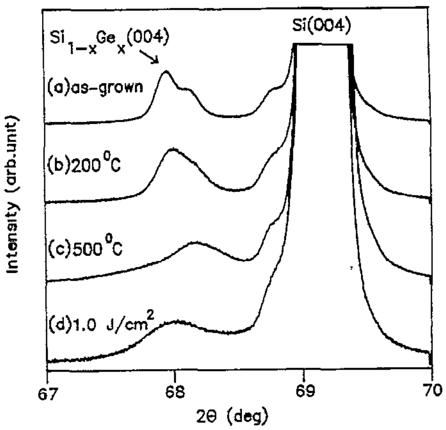

Fig. 5. XRD patterns of the as-grown $Si_{1-x}Ge_x$ film and the $Si_{1-x}Ge_x$ films after annealing at various conditions.

in the $Ni(Si_{1-x}Ge_x)$ films grown at temperatures above 400°C could not be removed by the subsequent laser annealing. From the EDS/XTEM analysis shown in Fig. 4 it is evident that in contrast to furnace annealing, pulsed KrF laser annealing allows a significant amount of Ge to be retained in the Ni germanosilicide, forming the $Ni(Si_{0.76}Ge_{0.24})_2$ films. In the Co/$Si_{0.76}Ge_{0.24}$ system studied previously Ge segregation during vacuum annealing might significantly increase and decrease the *c*-axis lattice parameters of the upper and lower layers of the $Si_{0.76}Ge_{0.24}$ film, respectively [16]. In the present study, the XRD patterns in Fig. 5 show that the *c*-axis lattice parameter of the $Si_{0.76}Ge_{0.24}$ film after laser annealing at 1.0 J cm^{-2} remained nearly unchanged, revealing that Ge segregation was effectively suppressed in the $Si_{0.76}Ge_{0.24}$ film. This XRD result is consistent with the EDS/XTEM analysis. However, the Ni concentration decreased as a function of the distance from the surface of the $Ni(Si_{0.76}Ge_{0.24})_2$ film. This result indicates that during one pulse irradiation, about 14 ns, the intermixing of the chemical species in the melt may not be completed due to fast resolidification. The higher Ni concentration on the surface of the $Ni(Si_{0.76}Ge_{0.24})_2$ film is ascribed to the incomplete reaction between the Ni film and the underlying $Si_{0.76}Ge_{0.24}$ film during the pre-annealing at 200°C for 0.5 h in the vacuum furnace. The $Ni(Si_{1-x}Ge_x)_2$ layer near the interface was epitaxially grown on the $Si_{0.76}Ge_{0.24}$ film, while part of the $Ni(Si_{1-x}Ge_x)_2$ layer near the surface was polycrystalline. The excess Ni on the surface of the $Ni(Si_{0.76}Ge_{0.24})_2$ film might hinder the $Ni(Si_{0.76}Ge_{0.24})_2$ grains from growing along the epitaxial orientations. Tung et al. [19] have reported similar results.

At energy densities above 1.2 J cm^{-2} both the $Ni(Si_{1-x}Ge_x)_2$ overlayer and the $Si_{1-x}Ge_x$ film showed Ge deficiency. An example of the $Ni(Si_{1-x}Ge_x)_2$ films grown at 1.6 J cm^{-2} is shown in Fig. 6. The trace of the melting depth is in the range of 0.22–0.25 μm from the film surface, which

Fig. 6. XTEM image of an Ni/$Si_{0.76}Ge_{0.24}$ film after vacuum annealing at 200°C and subsequent laser annealing at 1.6 J cm^{-2} showing that the $Si_{1-x}Ge_x$ film grew deep into the Si substrate.

is larger than the thickness, 0.15 μm, of the as-grown $Si_{0.76}Ge_{0.24}$ film. From EDS/XTEM analysis the Ge concentration decreased with the melting depth, indicating that the $Si_{1-x}Ge_x$ layer penetratedly grew into the Si substrate during laser annealing. Similar results have been observed in the pulsed laser annealing of $Si_{1-x}Ge_x$ and $Si_{1-x-y}Ge_xC_y$ films [22,24]. At 1.6 J cm^{-2} the cellular structure due to constitutional supercooling also appeared.

3.2. Ni/Si

For the Ni/Si samples annealed at 600°C homogeneous epitaxial $NiSi_2$ films without the island structure were formed. For the Ni/Si samples irradiated at 0.4 J cm^{-2} the NiSi layer associated with the amorphous overlayer was formed. From EDS/(XTEM) analysis the Ni:Si atomic ratio for the amorphous overlayer was about 1:1. At energy densities above 0.6 J cm^{-2} constitutional supercooling occurred.

For the NiSi films grown at 200°C subsequent laser annealing at energy densities above 0.6 J cm^{-2} caused the formation of homogeneous $NiSi_2$ films. From EDS/XTEM analysis the Ni concentration decreased as a function of distance from the surface of the $NiSi_2$ film. The $NiSi_2$ layer near the interface was epitaxial, while part of the $NiSi_2$ layer near the surface was polycrystalline. The constitutional supercooling appeared at 1.6 J cm^{-2}.

It is interesting to note that the energy densities at which constitutional supercooling occurs is much lower for Ni/Si and $Ni/Si_{0.76}Ge_{0.24}$ than for NiSi/Si and $Ni(Si_{1-x}Ge_x)/Si_{0.76}Ge_{0.24}$. This result may be explained in terms of the strong coupling of ultraviolet radiation with metals [25].

4. Conclusions

1. For the $Ni/Si_{0.76}Ge_{0.24}$ films annealed at temperatures above 300°C some Ge-rich $Si_{1-x}Ge_x$ grains were formed between the Ge-deficient Ni germanosilicide, resulting in the island structure. For Ni/Si films a homogeneous epitaxial $NiSi_2$ layer could be formed even at 600°C.

2. Ni silicide (germanosilicide) associated with the amorphous overlayer was generally formed at lower energy densities. Constitutional supercooling occurred at higher energy densities. The energy densities at which constitutional supercooling appeared were higher for NiSi/Si and $Ni(Si_{1-x}Ge_x)/Si_{0.76}Ge_{0.24}$ than for Ni/Si and $Ni/Si_{0.76}Ge_{0.24}$.

3. For the $Ni(Si_{1-x}Ge_x)$ films grown at 200°C in a vacuum furnace, subsequent laser annealing at an energy density of 0.6–1.0 J cm^{-2} have shown to render homogeneous $Ni(Si_{0.76}Ge_{0.24})_2$ and $Si_{0.76}Ge_{0.24}$ films without the island structure and Ge segregation.

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