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Interfacial reactions of $Ni/Si_{0.76}Ge_{0.24}$ and $Ni/Si_{1-x-y}Ge_xC_y$ by vacuum annealing and pulsed KrF laser annealing

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Abstract

Interfacial reactions of Ni on $Si_{0.76}Ge_{0.24}$ and $Si_{1-x-y}Ge_xC_y$ films by vacuum annealing and pulsed KrF laser annealing were studied by transmission electron microscopy (TEM) in conjunction with energy dispersive spectrometry (EDS) and X-ray diffraction (XRD). For the $Ni/Si_{0.76}Ge_{0.24}$ and $Ni/Si_{1-x-y}Ge_xC_y$ films annealed at a temperature of 200–600°C Ge segregation and agglomeration occurred at an extent becoming more severe at higher temperatures. Upon pulsed KrF laser annealing the agglomeration structure was improved. The retardation of phase transformation in the $Ni/Si_{1-x-y}Ge_xC_y$ system was observed upon either vacuum annealing or pulsed laser annealing. Multiple-pulse annealing is an effective method to fabricate smooth $Ni(Si_{0.76}Ge_{0.24})_2$ and $Ni(Si_{1-x-y}Ge_xC_y)_2$ films without inducing Ge segregation to the remaining substrates and strain relaxation.

Keywords: Ni; $Si_{1-x}Ge_x$; $Si_{1-x-y}Ge_xC_y$; Pulsed KrF laser annealing

1. Introduction

Recently, $Si_{1-x}Ge_x$ on Si has been extensively studied for applications in the field of optoelectronics and high speed heterojunction bipolar transistors [1,2]. Since the lattice spacing of Ge is 4.2% larger than that of Si, compressive strains developed in the $Si_{1-x}Ge_x$ overlayer create stability problems that limit the thickness of the pseudomorphic $Si_{1-x}Ge_x$ overlayer. Carbon introduced substitutionally into $Si_{1-x}Ge_x$ reduces the lattice mismatch between $Si_{1-x}Ge_x$ and Si and then thicker pseudomorphic $Si_{1-x}Ge_x$ films with a high Ge content can be fabricated.

For device applications the formation of metal/$Si_{1-x}Ge_x$ and metal/$Si_{1-x-y}Ge_xC_y$ ohmic or rectifying contacts is required. Thus, the interfacial reactions of some metals such as Ni [3,4], Pt [5,6], Pd [6–8], Ti [9–12], Co [13–15], W [16], Cu [17,18], and Zr [19] on $Si_{1-x}Ge_x$, and Co [20], Zr [21], and Ti [11] on $Si_{1-x-y}Ge_xC_y$ by conventional furnace annealing and pulsed laser annealing have been studied, respectively. For conventional furnace annealing the formation of a ternary phase was generally accompanied with Ge segregation. Additionally, an agglomeration structure also appeared at higher annealing temperatures. These

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phenomena could be attributed to the higher heat formation for metal-Si than for metal-Ge [22]. Rapid thermal annealing and pulsed laser annealing can shorten the annealing time, resulting in a reduction of Ge segregation. Furthermore, multiple-pulse laser annealing can produce a smooth and continuous germanosilicide film without inducing strain relaxation in the unreacted $Si_{1-x}Ge_x$ film [8].

In the present study, the interfacial reactions such as phase transformation, Ge segregation, the formation of agglomeration, and strain relaxation in the $Ni/Si_{0.76}Ge_{0.24}$ and $Ni/Si_{1-x-y}Ge_xC_y$ systems upon vacuum annealing and pulsed KrF laser annealing were studied by using transmission electron microscopy (TEM) in conjunction with energy dispersive spectrometry (EDS) and X-ray diffraction (XRD).

2. Experimental

Strained and partially relaxed $Si_{0.76}Ge_{0.24}$ films about 1000 and 1500 Å thick were grown on n-type Si(1 0 0) at 550°C by ultra-high-vacuum chemical-vapor deposition (CVD), respectively. $Si_{1-x-y}Ge_xC_y$ films were prepared by C ions implanted into the partially relaxed $Si_{0.76}Ge_{0.24}$ films and subsequent pulsed KrF laser annealing at an energy density of 0.8–1.0 J/cm^2. Details of the preparation of $Si_{1-x-y}Ge_xC_y$ films and their characterization were described elsewhere [23]. Prior to deposition the substrates were cleaned by the RCA method and then immediately loaded into the chamber. Ni about 250 Å thick was deposited onto the $Si_{0.76}Ge_{0.24}$ and $Si_{1-x-y}Ge_xC_y$ films at room temperature by electron gun evaporation at a rate of 1 Å/s. The base pressure was around $1\text{–}2 \times 10^{-6}$ Torr. Furnace annealing was carried out at a temperature of 200–700°C in a vacuum of $1\text{–}2 \times 10^{-6}$ Torr. Pulsed KrF laser annealing was performed at an energy density of 0.1–0.3 J/cm^2 in a vacuum around 2×10^{-2} Torr. The pulse length is 14 ns. The laser beam was focused onto an area of 4×4 mm^2. Phase formation, the microstructures, and chemical compositions of the reacted layer were analyzed by EDS/TEM which was equipped with a field emission gun with an electron probe 12 Å in size. The strain relaxation of the unreacted $Si_{0.76}Ge_{0.24}$ films after annealing was analyzed by XRD.

3. Results and discussion

3.1. Vacuum annealing

For the $Ni/Si_{0.76}Ge_{0.24}$ films annealed at a temperature of 200–500°C $Ni(Si_{1-x}Ge_x)$ was formed. From EDS/cross-section TEM (XTEM) analysis Ge segregation from the $Ni(Si_{1-x}Ge_x)$ layer to the underlying $Si_{0.76}Ge_{0.24}$ substrate apparently appeared at temperatures above 300°C at an extent becoming more severe at higher temperatures. Agglomeration at 400°C occurred as shown in Fig. 1, in which the $Si_{1-x}Ge_x$ film exposed to the film surface is Ge-rich. The formation of heat for NiSi and NiGe has been determined to be about −45 and −32 kJ/mol, respectively [22]. These values suggest that Ni tends to react preferably with Si. Above 550°C $Ni(Si_{1-x}Ge_x)_2$ was formed, in which only a trace amount of Ge was present.

For the $Ni/Si_{1-x-y}Ge_xC_y$ films annealed at 200°C $Ni(Si_{1-x-y}Ge_xC_y)$ was formed concurrently with $Ni_2(Si_{1-x-y}Ge_xC_y)$. After annealing at a temperature of 250–550°C only $Ni(Si_{1-x-y}Ge_xC_y)$ was present. As seen in Fig. 2 the extent of agglomeration was significantly alleviated when compared with the $Ni/Si_{0.76}Ge_{0.24}$ system. From EDS/XTEM analysis the $Ni(Si_{1-x-y}Ge_xC_y)$ layer was also deficient in Ge with the extent being more severe at higher temperatures. One example is shown in

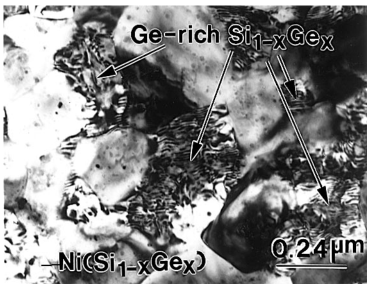

Fig. 1. Plan-view TEM image of the $Ni/Si_{0.76}Ge_{0.24}$ sample annealed at 400°C showing the agglomeration structures.

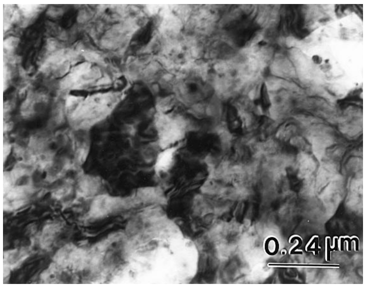

Fig. 2. Plan-view image of the $Ni/Si_{1-x-y}Ge_xC_y$ sample annealed at 400°C showing no agglomeration structures.

Fig. 3. At 600°C, $Ni(Si_{1-x-y}Ge_xC_y)_2$ was formed concurrently with the apparent appearance of agglomeration. Evidently, the phase transformation and appearance of agglomeration for the $Ni/Si_{1-x-y}Ge_xC_y$ system are sluggish in comparison with those for the $Ni/Si_{0.76}Ge_{0.24}$ system. The retardation of phase formation has also been observed in the $Ti/Si_{1-x-y}Ge_xC_y$ and $Co/Si_{1-x-y}Ge_xC_y$ systems [11,20]. It was suggested that C accumulation at the germanosilicide/epilayer interface blocked the interfacial reactions.

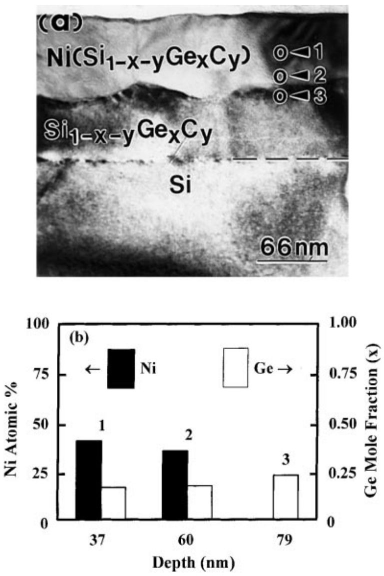

Fig. 3. (a) XTEM image and (b) the depth profiles of the chemical elements for the $Ni/Si_{1-x-y}Ge_xC_y$ sample annealed at 500°C showing that the $Ni(Si_{1-x-y}Ge_xC_y)$ film is deficient in Ge.

3.2. Pulsed KrF laser annealing

In our previous studies for the $Pd/Si_{0.76}Ge_{0.24}$ system [13] multiple-pulse annealing could homogenize the Pd concentration in the germanosilicide layer without inducing Ge segregation to the underlying $Si_{0.76}Ge_{0.24}$ films. For the $Ni/Si_{0.76}Ge_{0.24}$ films annealed at 0.2 J/cm^2 for 10 pulses $Ni(Si_{1-x}Ge_x)$ was formed concurrently with $Ni(Si_{1-x}Ge_x)_2$ as shown in Fig. 4. After annealing for 20 pulses a smooth $Ni(Si_{1-x}Ge_x)_2$ layer was formed as shown in Fig. 5, in which the upper layer is polycrystalline, while the lower layer is epitaxial. Meanwhile the EDS/XTEM data show that although some Ge segregate down to the lower part of the germanosilicide layer, they do not segregate out of the germanosilicide to the underlying $Si_{0.76}Ge_{0.24}$ film. Correspondingly, in Fig. 6 the XRD patterns of the sample annealed at

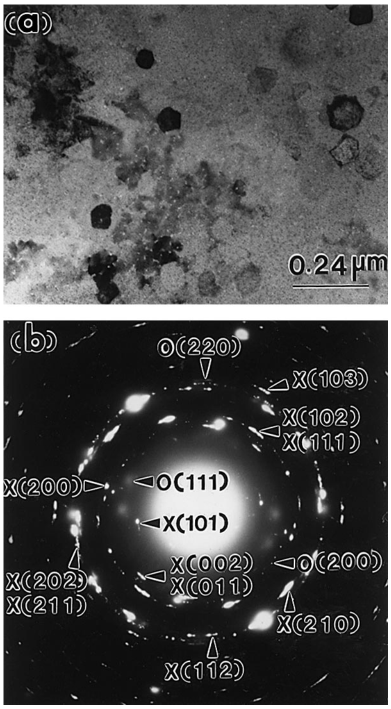

Fig. 4. (a) Plan-view image and (b) electron diffraction pattern (DP) of the $Ni/Si_{0.76}Ge_{0.24}$ sample annealed at 0.2 J/cm^2 for 10 pulses showing that $Ni(Si_{1-x}Ge_x)$ coexists with $Ni(Si_{1-x}Ge_x)_2$, where $Ni(Si_{1-x}Ge_x)$ and $Ni(Si_{1-x}Ge_x)_2$ are denoted as "X" and "O", respectively.

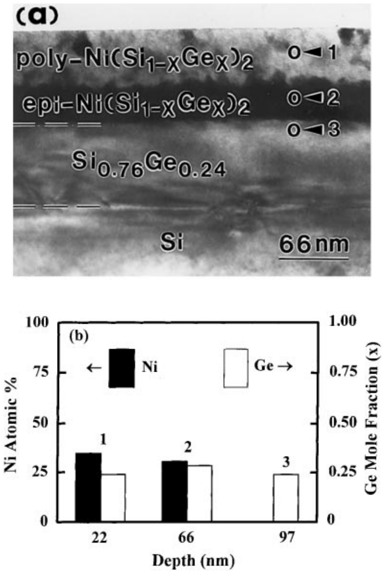

Fig. 5. (a) XTEM image and (b) the depth profiles of the chemical elements for the Ni/$Si_{0.76}Ge_{0.24}$ sample annealed at 0.2 J/cm^2 for 20 pulses showing that a continuous $Ni(Si_{1-x}Ge_x)_2$ film was formed without inducing Ge segregation to the underlying $Si_{0.76}Ge_{0.24}$ film.

0.2 J/cm^2 for 20 pulses show that the lattice constant of the unreacted $Si_{0.76}Ge_{0.24}$ film in the direction perpendicular to the film surface remains nearly unchanged in comparison with that of the as-grown $Si_{0.76}Ge_{0.24}$ film, revealing that no strain relaxation appears in the unreacted $Si_{0.76}Ge_{0.24}$ film. For the samples annealed at 0.3 J/cm^2 for 5 pulses a single $Ni(Si_{1-x}Ge_x)_2$ film was formed, however, Ge segregation to the underlying $Si_{0.76}Ge_{0.24}$ film occurred.

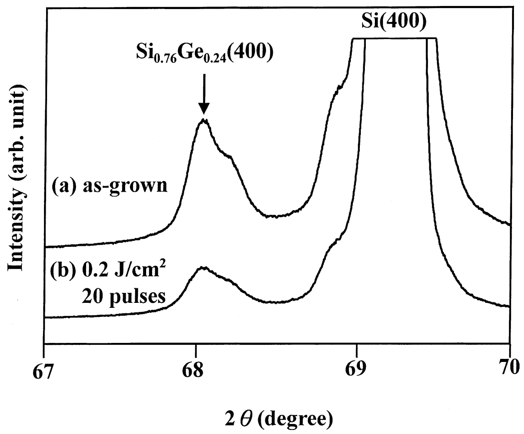

Fig. 6. XRD patterns of (a) the as-grown $Si_{0.76}Ge_{0.24}$ film and (b) the unreacted $Si_{0.76}Ge_{0.24}$ film after annealing at 0.2 J/cm^2 for 20 pulses.

For the Ni/$Si_{1-x-y}Ge_xC_y$ samples annealed at 0.2 J/cm^2 for 10 pulses only $Ni(Si_{1-x-y}Ge_xC_y)$ was formed as shown in Fig. 7. It is worth to note that for the Ni/$Si_{1-x}Ge_x$ samples annealed at 0.2 J/cm^2 for 10 pulses $Ni(Si_{1-x}Ge_x)_2$ has been formed already as shown in Fig. 4, indicating that upon pulsed laser annealing the sluggish phase transformation appears in the Ni/$Si_{1-x-y}Ge_xC_y$ system as well. $Ni(Si_{1-x-y}Ge_xC_y)_2$ was formed upon annealing at 0.2 J/cm^2 for 30 pulses. The $Ni(Si_{1-x-y}Ge_xC_y)_2$ layer was very smooth and no apparent Ge segregation into the underlying $Si_{1-x-y}Ge_xC_y$ film occurred.

It can be concluded that upon multiple-pulse laser annealing smooth $Ni(Si_{0.76}Ge_{0.24})_2$ and $Ni(Si_{1-x-y}Ge_xC_y)_2$ films can be grown without showing Ge segregation to the unreacted

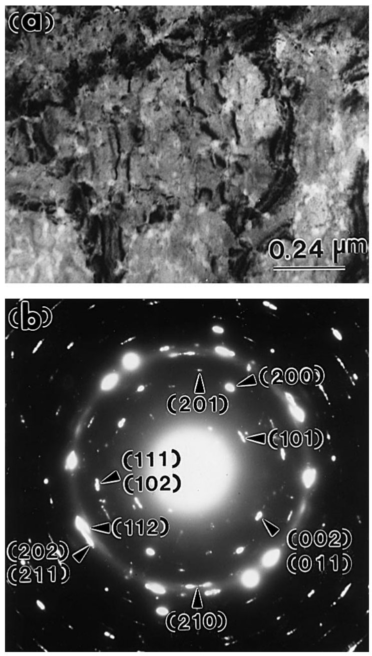

Fig. 7. (a) Plan-view image and (b) DP of the Ni/$Si_{1-x-y}Ge_xC_y$ sample annealed at 0.2 J/cm^2 for 10 pulses showing that only $Ni(Si_{1-x-y}Ge_xC_y)$ is present.

$Si_{0.76}Ge_{0.24}$ films and inducing strain relaxation. However, the addition of C to the $Si_{1-x}Ge_x$ films significantly retards the phase transformation.

4. Summary and conclusions

1. For the $Ni/Si_{0.76}Ge_{0.24}$ and $Ni/Si_{1-x-y}Ge_xC_y$ samples subjected to vacuum annealing Ge segregation to the underlying substrates and agglomeration occurred at an extent becoming more severe at higher annealing temperatures. The extent of agglomeration was significantly alleviated for the $Ni/Si_{1-x-y}Ge_xC_y$ system. When subjected to multiple-pulse laser annealing smooth $Ni(Si_{0.76}Ge_{0.24})_2$ and $Ni(Si_{1-x-y}Ge_xC_y)_2$ films could be grown without inducing Ge segregation to the unreacted substrates and strain relaxation.
2. C plays an important role in delaying phase transformation upon either vacuum annealing or pulsed KrF laser annealing.

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