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Laser-induced Ni(Pt) germanosilicide formation through a self-limiting melting phenomenon on $Si_{1-x}Ge_x/Si$ heterostructure

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Laser-induced Ni(Pt) germanosilicide formation on $Si_{1-x}Ge_x/Si$ substrate has resulted in the formation of smooth Ni(Pt) germanosilicide/Si interface with minimum interface roughness which is preferred as a contact material. A confined (self-limiting) melting phenomenon occurred during the laser-induced silicidation process at laser fluence of 0.4 J cm^{-2} (just at the melting threshold of the sample). This phenomenon is caused by significant differences in material properties of $Si_{1-x}Ge_x$ alloy and Si substrates. Formation of highly textured $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ phase was detected in the sample after 20-pulsed laser thermal annealing at 0.4 J cm^{-2}. The formation mechanism of the Ni(Pt) monogermanosilicide is discussed. © *2007 American Institute of Physics*.
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Innovative processes and materials need to be introduced in the fabrication of nanoscale metal-oxide-semiconductor field-effect transistor to further improve its performance. One of the present developments is the introduction of Ge in a form of $Si_{1-x}Ge_x$ alloy either as a channel material or a virtual substrate for strained Si based transistor.[1] As compared to Si, Ge offers a significant enhancement in bulk carrier mobilities. Therefore, implementation of $Si_{1-x}Ge_x$ substrate is essential in the fabrication of high-speed electronics and optoelectronics devices.[2,3] Solid-state interactions of Ni and $Si_{1-x}Ge_x$ substrates have been reported in several studies.[4–6] It was observed that Ge outdiffusion has been found to be the dominant mechanism which leads to a severe Ni germanosilicide agglomeration and interface roughening.[5,6] In recent years, laser thermal annealing (LTA) has gained interests and been researched more intensely in ultrashallow junction[7,8] and/or silicide contact formation[9–13] in nanoscale devices. Most studies on the laser-induced silicide formation, however, were focused on the interaction between pure metal and pure Si substrates.[9–13] In this letter, the reduction of Ni germanosilicide interface roughness under high energy laser annealing is studied. $Ni_{1-u}(Pt)_u$ was employed since Pt alloying has been reported to enhance the stability of the Ni(Pt) monogermanosilicide phase in the rapid thermal annealed (RTA) sample.[14,15]

A 960 Å compressively strained $Si_{1-x}Ge_x$ (x=0.15) epitaxial layer was directly grown on 200 mm p-Si(100) wafer by means of chemical vapor deposition. After surface cleaning using piranha solution ($H_2SO_4:H_2O_2$=4:1) for 10 min followed by 1 min dip in diluted HF (1:50) to remove the native oxide, a 50 nm thick $Ni_{1-u}(Pt)_u$ was sputtered from an alloy target of Ni with 5 wt. % Pt (u=0.032). Excimer laser irradiation (λ:248 nm; full width at half maximum of the pulse: 23 ns) was then carried out under continuous purified N_2 purging. Multiple-pulsed (5- and 20-pulsed) laser annealings using laser fluences of 0.2, 0.4, and 0.6 J cm^{-2} were performed to study the effect of repeated irradiation on Ni germanosilicidation. Identification of phase and crystallographic orientation was carried out using x-ray diffraction (XRD) with Cu $K\alpha$ radiation [average wavelength (λ): 1.5418 Å] in 2θ geometry. Cross-sectional transmission electron microscopy (XTEM) analyses using the JEM 2010 TEM were employed to evaluate the microstructure of the Ni germanosilicide formed, and nanoscale energy disperse x-ray spectroscopy (EDX) analysis as performed to investigate the elemental distribution across the sample thickness.

As shown in the XRD spectra depicted in Fig. 1, besides the presence of a significant amount of an unreacted $Ni_{1-u}(Pt)_u$, a small amount of Ni(Pt) germanosilicides (coexistence of $[Ni_{1-v}(Pt)_v]_2(Si_{1-y}Ge_y)$ and $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ was detected in the sample after 20-pulsed LTA at 0.2 J cm^{-2}. This is in contrast with the sample after five-pulsed LTA at 0.2 J cm^{-2} where no Ni(Pt) germanosilicide peaks could be observed in the XRD spectra (not shown). By comparing these phenomena, it is believed that during LTA at low laser fluence (below the melting threshold of the sample), the reaction occurs through a solid state reaction where an interdiffusion of elements happens at the $Ni_{1-u}Pt_u/Si_{1-x}Ge_x$ interface. Increasing the number of laser pulses to 20 pulses caused deeper diffusion of Ni atoms

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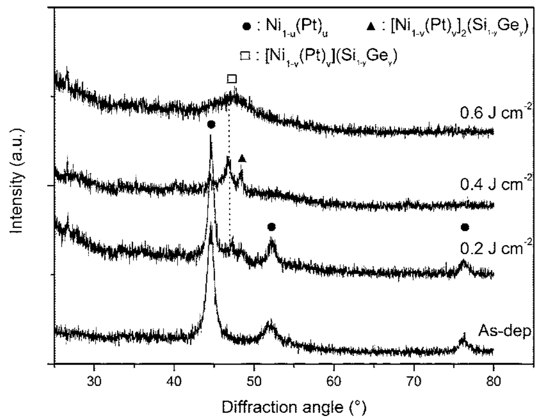

FIG. 1. XRD spectra of the $Ni_{1-u}Pt_u/Si_{1-x}Ge_x$ samples after 20-pulsed LTA process. The as-deposited sample has a composition of approximately 96.8 at. % Ni and 3.2 at. % Pt, which is symbolized as $1-u$ and u for simplicity. The initial Ge concentration in the $Si_{1-x}Ge_x$ layer was 15%. The y and v values in the germanosilicide phases formed are <0.15 and ≤0.032, respectively.

(compared to the one that occurred in the sample after five-pulsed LTA at 0.2 J cm^{-2}), resulting in the formation of a substantial Ni(Pt) germanosilicide film at the $Ni_{1-u}(Pt)_u/Si_{1-x}Ge_x$ interface. Increasing the laser fluence to 0.4 J cm^{-2} led to a formation of highly textured germanosilicides with a predominant $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ phase with some minute $[Ni_{1-v}(Pt)_v]_2(Si_{1-y}Ge_y)$ phase in the sample, indicated by the appearance of a strong peak at 46.73° and a weaker peak at 48.32°, respectively in the XRD spectra shown in Fig. 1(b). Simulation of laser interaction with material[16] (SLIM) shows that the temperature generated in the sample during LTA at 0.4 J cm^{-2} has reached the melting temperature (T_m) of the $Si_{1-x}Ge_x$ layer[17] but not of the underlying Si substrate. In a melt phase, the diffusion coefficient of an atom can reach five to eight orders in magnitude higher than that in solid,[18] thus allowing the elements to redistribute rapidly. Therefore, 20-pulsed LTA at 0.4 J cm^{-2} yielded in a more homogeneous elemental mixing, eliminated the unreacted $Ni_{1-u}(Pt)_u$, and resulted in the formation of predominant $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ phase.

Increasing the laser fluence to 0.6 J cm^{-2} has completely transformed the whole film to $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ phase. This was caused by a deeper melting induced by higher laser energy during LTA process. The melt depth of 20-pulsed LTA at 0.6 J cm^{-2} is believed to be deep enough to reach the Si substrate causing Si "enrichment" of the initially formed $[Ni_{1-v}(Pt)_v]_2(Si_{1-y}Ge_y)$ phase at 0.4 J cm^{-2}, resulting in a preferred formation of $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ phase. During solidification, rapid extraction of thermal energy from molten $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ layer to the Si substrate occurred. This resulted in a high solidification velocity which triggered the formation of nano-$[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ grains as detected as a broad peak in the XRD spectra shown in Fig. 1(a). The best condition for Ni(Pt) germanosilicide formation can be achieved by tailoring the initial thickness of the as-deposited film such that Ni(Pt)-rich germanosilicide phase $[[Ni_{1-v}(Pt)_v]_2(Si_{1-y}Ge_y)]$ formation can be completely avoided.

The interface roughening during RTA process can be clearly seen in inset I of Fig. 2(a) which shows the $Ni_{1-u}Pt_u/Si_{1-x}Ge_x$ sample after RTA at 600 °C for 60 s. Severe roughness at the Ni(Pt) germanosilicide/Si interface was

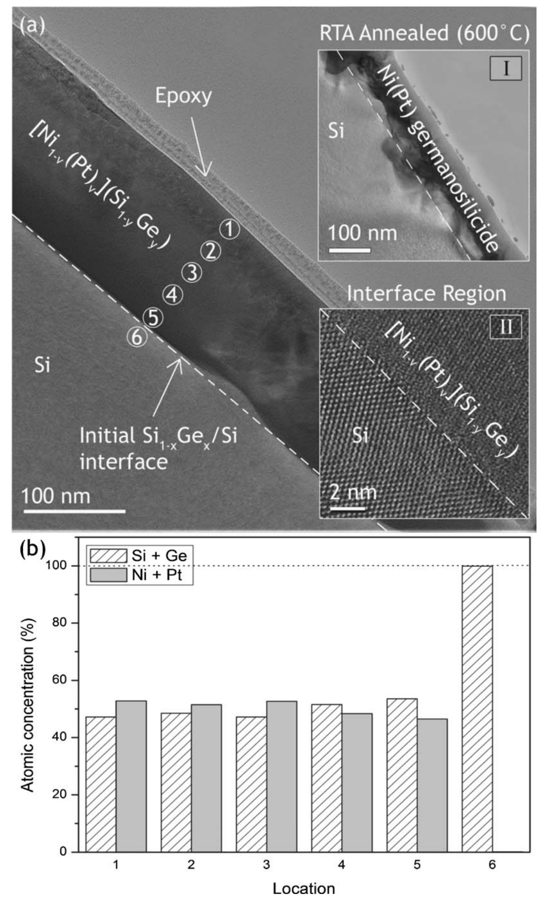

FIG. 2. (a) XTEM micrographs of the $Ni_{1-u}Pt_u/Si_{1-x}Ge_x$ sample after 20-pulsed LTA at 0.4 J cm^{-2}. Inset I depicts the XTEM micrograph of the sample after 60 s RTA at 600 °C. Inset II shows the HRTEM micrograph of the germanosilicide/Si interface of the sample after 20-pulsed LTA at 0.4 J cm^{-2}. (b) The EDX elemental analysis of the Ni(Pt) germanosilicide film shown in (a). Locations 1–6 indicate the acquisition location from the surface to the Si substrate, respectively. The average distance between each acquisition location was 25 nm.

evident with Ni atoms penetrating across the $Si_{1-x}Ge_x/Si$ interface, consuming some of the Si substrate during germanosilicide formation. This aggressive Ni diffusion into the bulk Si is caused by a larger absolute enthalpy of formation of Ni silicide as compared to Ni germanide phase[19] causing preferential reactions of Ni atoms with the Si. Figure 2(a) shows the low magnification TEM micrograph of a sample after 20-pulsed LTA at 0.4 J cm^{-2}. In contrast to the RTA samples, the laser annealed germanosilicide sample produced a significantly improved and smooth $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)/Si$ interface. Inset II of Fig. 2(a) shows a high resolution TEM micrograph of the interface of the sample after 20-pulsed LTA at 0.4 J cm^{-2}. The $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ film located at the upper part of the micrograph is highly textured and crystalline, which agrees with the XRD observation where only a single peak from $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ phase appeared. The interface is flat and smooth without significant roughness. A smooth interface is highly desirable for contact application as it can reduce scattering caused by interface roughness which in turn lowers the parasitic resistance of the contact region[20] and the junction leakage.[21]

The EDX analysis across the film is shown in Fig. 2(b). The EDX result is plotted based on the sum of Si–Ge and Ni–Pt atomic concentrations. Location 1 is the area at the surface, where as location 6 is at the area just below the

$[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ film. The average distance between EDX acquisition points was around 25 nm. EDX analysis has shown atomic concentration corresponding to $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ phase in the sample which agrees well with XRD analysis. It can be observed that the $[Ni_{1-v}(Pt)_v] \cdot (Si_{1-y}Ge_y)$ film is *slightly* Ni rich at the surface and becomes slightly Si rich towards the substrate which is expected in the LTA samples. We have also found a Ni-rich region on the surface at different acquisition locations (not shown), which is believed to arise from $[Ni_{1-v}(Pt)_v]_2(Si_{1-x}Ge_x)$ phase as found in the XRD analysis. Evaluation of the individual element atomic concentration has revealed that Pt distributed evenly in the $[Ni_{1-v}(Pt)_v] \cdot (Si_{1-y}Ge_y)$ film with the highest concentration of 4 at. % location 1 and around 3.3 at. % at location 5. Ge atomic concentration seems to undergo some loss during laser annealing process. The lowest concentration is at location 1 with Ge content of only 4.7 at. % and reaches its highest at locations, 4 and 5 with 7.1 and 6 at. %, respectively. It is believed that some Ge oxide was formed on the surface during multiple-pulsed LTA and dissolved during TEM sample preparation, which involves manual grinding with water as a coolant.

The formation of a smooth interface between Ni(Pt) germanosilicide and Si substrate in LTA samples was caused by intrinsic properties of $Si_{1-x}Ge_x$ film subjected to a tailored laser annealing process. From a thermodynamic point of view, it is known that Ge melts at a temperature almost 500 °C lower than that of Si (938 vs 1414 °C, respectively). Addition of Ge into Si to form $Si_{1-x}Ge_x$ epitaxial layer causes the T_m of $Si_{1-x}Ge_x$ alloy to be lower than that of the pure Si. In addition, it was reported that the thermal conductivity (k) of $Si_{1-x}Ge_x$ alloy is a function of composition with a broad maximum near the middle of the alloy system.[22] In terms of the volumetric specific heat (C_p) of the material, $Si_{1-x}Ge_x$ alloy should have a lower C_p than its Si counterpart since the pure Ge has generally lower C_p than pure Si.[23] Therefore, a lowly doped $Si_{1-x}Ge_x$ epitaxial layer with 15% of Ge used in this work is predicted to melt at temperature of ~1300 °C which is around 120 °C lower than that of Si,[17] with an approximately 20 times reduction of its thermal conductivity[22] and 1%–3% reduction of its volumetric specific heat value as compared to that of pure Si.[23] Due to significant differences in material properties of Si and $Si_{1-x}Ge_x$ alloy, especially its thermal conductivity, irradiating the $Ni_{1-u}(Pt)_u/Si_{1-x}Ge_x/Si$ sample with laser fluence that is sufficient to melt the $Si_{1-x}Ge_x$ layer will not melt the bulk Si underneath, hence preserving the interface smoothness. Similar to Ni silicides, Ni germanosilicides, especially $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$, have a lower melting temperature than either $Si_{1-x}Ge_x$ or Si. As a result, the initial Ni(Pt) germanosilicide which formed at the $Ni_{1-u}(Pt)_y/Si_{1-x}Ge_x$ interface during the first few LTA pulses will be remelted during subsequent laser pulses, affecting the surrounding $Si_{1-x}Ge_x$ layer to further react with the remaining Ni(Pt) film. Eventually, the whole $Si_{1-x}Ge_x$ layer was consumed and resulted in a formation of majority $[Ni_{1-v}(Pt)_v](Si_{1-y}Ge_y)$ phase.

Increasing the number of laser pulses may introduce enhancement of laser energy absorption induced by surface inhomogeneities formed during LTA at laser fluence higher than the melting threshold of the sample ($\geqslant 0.4$ J cm^{-2}). An UV-vis measurement of the sample reflectance after 20-pulsed LTA exhibited a reduction of surface reflectivity by as much as 9% as compared to the sample after 5-pulsed LTA. This reduction of surface reflectance may induce a higher temperature (~250 K, obtained from SLIM simulation) in the sample during LTA which resulted in a better melting and mixing of Ni(Pt) and $Si_{1-x}Ge_x$ layer underneath.

Laser-induced Ni(Pt) germanosilicides (of a highly textured $[Ni_{1-v}(Pt)_y](Si_{1-y}Ge_y)$) with excellent interfacial quality have been formed on an epitaxially grown $Si_{1-x}Ge_x$ layer on Si substrate. It was found that differences in material properties especially the melting temperature, thermal conductivity, and volumetric specific heat of Si and $Si_{1-x}Ge_x$ alloy have resulted in a confined (self-limiting) melting of just $Si_{1-x}Ge_x$ layer on top of Si substrate during LTA with a tailored laser processing. This has assisted the formation of a smooth Ni(Pt) germanosilicide/Si interface making it viable to alleviate the problem of interface roughness which is usually observed in the RTA Ni germanosilicide samples.

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