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Laser-induced Ni(Ti) silicide formation

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Effects of Ti alloying during laser-induced Ni silicide formation is studied. Unique triple layer microstructures were found with the presence of supercell in the NiSi₂ grains formed at the interface. This supercell formation was caused by a local ordering of Ni and Si atoms that favor lower free energy during rapid solidification. Ti rapidly segregates from the alloy melt and forms a protective TiO_x overlayer on the surface during solidification. Melt front progressing towards the Ni-rich region leads to quenching of an amorphous layer sandwiched between NiSi₂ grains and the TiO_x overlayer. © 2006 American Institute of Physics. [DOI: 10.1063/1.2186073]

Laser thermal annealing (LTA) poses as an attractive annealing method that can be employed to form a silicide in ultrashallow junction devices for sub-65 nm technology and beyond. The laser can provide ultrafast annealing with a very limited thermal energy that is just enough to form silicide and minimize change in the overall diffusion profile of the junction. In almost all previous experiments performed with pulsed laser irradiation, only pure metal-silicon interactions were studied.^{1–4} In the conventional rapid thermal annealing process, the presence of an interfacial oxide between metal (like Ni or Co) and the Si substrate has been found hindering the silicidation reaction. Adding a Ti cap or impurity/alloying engineering have been proven effective to reduce the oxygen contamination.^{5–7} It was recently found that using a laser to anneal Ti capped Co film has resulted in Co silicide formation.⁸ In this letter the effects and roles of Ti alloy in Ni silicide formation using excimer laser irradiation with an aim of minimizing oxidation issue are presented.

A *p*-Si(100) wafer was used in the study. It was cleaned using a standard Radio Corporation of America (RCA) solution followed by a diluted HF (1:50) dip for 60 s just before loading the wafer into a sputtering chamber. A layer of 100-nm Ni_{1–x}(Ti)_x was sputtered from an alloy target with a Ni and Ti composition of 76.5 and 23.5 at. %, respectively. Excimer laser irradiation (λ : 248 nm; full width at half-maximum: 23 ns) was then carried out on the as-deposited samples using a Lambda Physik laser generator under continuous purified N₂ purging. Laser fluences ranging from 0.2 to 0.5 J cm^{–2} were used to study the effect of laser fluence on Ni silicidation. X-ray diffraction (XRD) analysis was employed to determine the phases formed in the sample, Auger electron spectroscopy (AES) was carried out to evaluate the interdiffusion of elements after LTA, and cross-sectional

transmission electron microscopy (XTEM) analyses were done using the JEM2010 TEM system.

As observed in XRD spectra in Fig. 1, LTA using 0.2 and 0.3 J cm^{–2} laser fluence did not initiate any silicidation. On the other hand, the appearance of the NiSi₂ peak was observed after LTA at 0.5 J cm^{–2} without the formation of the undesirable high resistivity (70–90 $\mu\Omega$ cm) (Refs. 9–11) ternary Ni-Ti-Si silicide in the film. Even though no or minimum silicide formed at low laser fluences, grain growth and interdiffusion of Ni-Ti-Si are believed to have occurred. Selected area electron diffraction (SAED) from the sample after 0.2 J cm^{–2} laser irradiation (not shown) clearly shows more

FIG. 1. XRD spectra of single-pulsed laser annealed samples. The as-deposited sample has a composition of approximately 80 at. % Ni and 20 at. % Ti, which is symbolized as 1–*x* and *x* for simplicity. However, upon laser annealing with 0.2 J cm^{–2}, Ti atoms out-diffused and the composition of Ni and Ti in the film became 1–*y* and *y*, respectively, where *y* < *x*.

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distinct spots in the diffraction pattern, which indicates more textured and bigger grains were present in the film. In addition, a sudden decrease in the sheet resistance (from 50 to 15 $\Omega/\square$) after a single-pulsed LTA at 0.2 J cm⁻² fluence was observed. This can be attributed to the grain growth (reduced grain boundary scattering) and Ti out-diffusion from Ni lattice (reduced lattice scattering). The latter phenomenon can be observed in the XRD spectra shown in Fig. 1 in which the Ni_{1-x}Ti_x peak shifted toward a larger 2θ angle after LTA at 0.2 J cm⁻². In addition, an electron dispersive x-ray spectroscopy (EDX) analysis of the film has shown more than 8% increment in the Ti concentration at the surface after LTA at 0.2 J cm⁻². This Ti segregation occurred due to a high affinity of Ti to oxygen (at 700 °C, $\Delta G_{fNi_3Ti} = -126.05$ kJ/mol; $\Delta G_{fTiSi_2} = -129.39$ kJ/mol; $\Delta G_{fTiO_2} = -815.93$ kJ/mol).¹² Although no distinct TiO_x layer formed after LTA at 0.2 J cm⁻², its formation can be easily observed at melt regime at a high laser fluence of 0.5 J cm⁻² whose AES depth profile is shown in Fig. 3. The TiO_x formation suggests that Ti alloying is useful in preventing the film from oxygen contamination during single-pulsed LTA.

Simulation of laser interaction with material (SLIM)¹³ was carried out to approximate the maximum surface temperature of the sample during laser irradiation at 0.4 J cm⁻². A reflectivity of 0.45 for the Ni_{1-x}(Ti)_x as-deposited film (versus 0.52 for pure Ni) was measured with UV-VIS spectroscopy and adopted in the simulation. It was approximated that the temperature of the sample could be as high as ~1400 °C ($\pm 10\%$) during LTA at 0.4 J/cm², which might have caused a complete melting of the Ni_{1-x}(Ti)_x film, indicating the threshold energy of melting of this system. Since the maximum temperature of the melt was only about tens of degrees higher than the solidification temperature of Ni_{1-x}(Ti)_x (~1350 °C), an amorphous phase resulted upon rapid solidification of the melt. This phenomenon can be observed in XRD spectra in Fig. 1, which shows a significant reduction of the Ni_{1-y}Ti_y peak intensity with no formation of new phases after LTA at 0.4 J cm⁻². The XTEM micrograph has also verified the formation of the amorphous overlayer with a small number of newly nucleated NiSi₂ grains at the interface (not shown). Taking the analogy from Si amorphization,¹⁴ the solidification velocity is usually in the range of 15–20 m/s to create an amorphous Si phase. However, the minimum solidification velocity required to create amorphous Ni-Si compound could be smaller than this value (maybe in the range of 10–15 m/s). This is because in a multielement system, the atoms need a longer time to rearrange themselves in a crystal as compared to a single element system. Therefore, even in a slower solidification velocity, the amorphization of the film in the multielement system can still occur.

Increasing the laser fluence to 0.5 J cm⁻² resulted in the formation of a layered structure (Fig. 2) consisting of TiO_x at the surface, followed by a Ni-rich amorphous Ni-Si layer, and polycrystalline NiSi₂ at the Si interface. On the onset of laser-induced melting, there was a Si-rich region near the original Ni_{1-x}(Ti)_x/Si interface with a Ni-rich Ni-Si overlayer. A Si-rich compound like NiSi₂ has a melting temperature (T_m) at around 993 °C, whereas the Ni-rich compound like Ni₂Si has a high T_m at around 1310 °C.¹⁵ During the solidification process, these two layers, which have different T_m , were in contact with one another. Most of the thermal

FIG. 2. XTEM showing a formation of layered structure in a sample after single-pulsed laser irradiation at 0.5 J cm⁻². The insets show the SAED pattern from the Ni-rich amorphous Ni-Si(α -Ni-Si) layer and the polycrystalline NiSi₂ grains.

energy in the molten film was then liberated or transferred to the substrate as it has a larger volume (as compared to the thin molten layer at the surface) and will act as a heat sink in the system during the solidification process. It can now be imagined that the inner layer has cooled down to a temperature lower than the T_m of the outer layer. But since the Si-rich inner layer has a T_m lower than the Ni-rich outer layer, it will stay in the liquid phase whereas the outer layer will be severely undercooled. During the solidification of the film, the thermal energy from the outer layer will be transferred to the inner layer and hence it will be able to maintain its liquid phase. This makes the solidification velocity of the inner layer to be significantly slower (in the range of 1.5–<10 m/s), hence allowing the Ni and Si atoms to rearrange themselves in a NiSi₂ crystal.

The compositional distribution of the sample after single-pulsed LTA at 0.5 J cm⁻² fluence can be observed in the AES depth profiling analysis shown in Fig. 3. Almost all of the Ti atoms out-diffused to the surface forming TiO_x after

FIG. 3. AES depth profiling of the sample after single-pulsed LTA at 0.5 J cm⁻² fluence.

the laser irradiation. Besides a high affinity of Ti to oxygen, this phenomenon might be due to a lower solid solubility of Ti in the NiSi_2 crystal than that in the Ni lattice; hence during rapid NiSi_2 nucleation and growth, Ti atoms were being pushed toward the surface. Furthermore, the large diffusion distance traveled by the Ti atoms in a very short annealing time can only be possible in a melt phase where the diffusion coefficient of the atoms can be 5–8 orders in magnitude higher than that in solid.¹⁶ In addition, due to a significant variation in the thickness of both amorphous Ni-rich Ni-Si and polycrystalline NiSi_2 layers, as can be observed in Fig. 2, the correlation between AES and XTEM results could not be precisely established.

A meshlike SAED pattern was observed in the epitaxially grown NiSi_2 grains of the 0.5 J cm^{-2} LTA sample, indicating that the NiSi_2 grains were heavily twinned in alternating manners. As there are four possible (111) twinning directions of NiSi_2 on the Si(100) substrate,¹⁷ a combination of these twinning types might be present at the interface. In addition, an appearance of additional diffraction spots located between subcell reflections was also observed in the SAED pattern. These additional spots appeared due to the formation of a supercell in the NiSi_2 grains, which were caused by local ordering of Ni and Si atoms that favors lower free energy during rapid solidification. The Ti presence in the film or stress generated during rapid cooling could have also affected the arrangement of Ni and Si atoms in the NiSi_2 crystals, which resulted in tripling of the crystal in a [111] direction.

Laser annealing of the $\text{Ni}_{1-x}(\text{Ti})_x$ alloy on the Si substrate has been studied. It was found that Ti started to out-diffuse from the Ni lattice toward the surface at 0.2 J cm^{-2} laser irradiation. Rapid quenching that is attributed to the formation of the amorphous phase was observed at 0.4 J cm^{-2} annealing. Laser irradiation at 0.5 J cm^{-2} has caused an out-diffusion of the Ti atoms to the surface, forming a TiO_x compound and making it viable to prevent oxygen

incorporation during LTA. Furthermore, formation of a layered structure with the Ni-rich amorphous Ni-Si layer being sandwiched between TiO_x and heavily twinned NiSi_2 grains with supercell formation was found.

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