# Formation of epitaxial metastable $NiGe_2$ thin film on Ge(100) by pulsed excimer laser anneal

Phyllis S. Y. Lim,[1] Dong Zhi Chi,[2] Poh Chong Lim,[2] Xin Cai Wang,[3] Taw Kuei Chan,[4] Thomas Osipowicz,[4] and Yee-Chia Yeo[1,a)]

[1]*Department of Electrical and Computer Engineering and NUS Graduate School for Integrative Sciences and Engineering (NGS), National University of Singapore (NUS), 10 Kent Ridge Crescent, Singapore 117576*
[2]*Institute of Materials Research and Engineering, Agency for Science, Technology, and Research (A*STAR), 3 Research Link, Singapore 117602*
[3]*Singapore Institute of Manufacturing Technology, Agency for Science, Technology, and Research (A*STAR), 71 Nanyang Drive, Singapore 638075*
[4]*Department of Physics, Centre for Ion Beam Applications (CIBA), National University of Singapore, 2 Science Drive 3, Singapore 117542*

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Epitaxial nickel digermanide ($NiGe_2$), a metastable phase, was formed by laser annealing Ni on (100) germanium-on-silicon substrates. The $NiGe_2$ formation was investigated using transmission electron microscopy, energy dispersive x-ray spectroscopy, x-ray diffraction, Rutherford backscattering spectroscopy, and first-principles calculations. The formation mechanism of $NiGe_2$ is discussed and is attributed to both the reduced interfacial energy at the $NiGe_2$/Ge(100) interface and the kinetic aspects of the laser annealing reaction associated with phase transformation and film agglomeration. © *2010 American Institute of Physics*. [doi:10.1063/1.3514242]

Germanium (Ge) has an electron mobility that is two times higher than that of Silicon (Si), and is an attractive channel material for high performance metal-oxide-semiconductor field-effect transistor (MOSFET).[1–3] However, realizing high-performance Ge n-MOSFETs is challenging. Annealing temperatures over 500 °C are typically required for n-type dopants activation but this leads to significant dopant diffusion[4] which aggravates short channel effects (SCEs) in aggressively scaled devices.[5] Metal germanides[6,7] with low formation temperatures and contact resistivity are also required as contact materials. To keep SCEs under control during contact formation, techniques such as laser annealing (LA) (Ref. 8) which can form germanide contacts without causing excessive diffusion of dopants would be attractive. However, nickel germanide ($NiGe_x$) formation using LA is not well investigated.

In this letter, we report a study of the formation of $NiGe_x$ via pulsed excimer LA. A continuous, epitaxial and Ge-rich nickel germanide ($NiGe_x$) film was formed, as observed from x-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDX), Rutherford backscattering spectroscopy (RBS), and transmission electron microscopy (TEM) analysis. The formation mechanism of $NiGe_2$ in the Ge-rich film, a phase not expected to exist in the Ni–Ge binary system, will be discussed.

15 nm of nickel (Ni) was sputtered on Ge-on-Si substrates formed by ultra-high vacuum chemical vapor deposition.[9] LA (wavelength $\lambda=248$ nm, pulse duration $=23$ ns) using 10 pulses, each at 0.3 J/cm$^2$, was performed under $N_2$ ambient to form nickel germanide. The laser spot size was $2\times2$ mm$^2$ and continuous stepping and scanning in the X and Y direction was performed for $2\times2$ cm$^2$ samples. Excess Ni was selectively removed, and material characterization was performed to examine the phase, interface morphology, and film composition. TEM images of $NiGe_x$ samples that were laser-annealed, and rapid-thermal-annealed (RTA) at 350 °C for 30 s are shown in Figs. 1(a) and 1(b), respectively. $NiGe_x$ formed by LA is thicker (~70 nm) than that formed by RTA (~33 nm). This large difference in thickness indicates that the film compositions differ from each other. Furthermore, unlike the $NiGe_x$ formed by RTA, where distinct grain boundaries are observable, the $NiGe_x$ film formed by LA is continuous and without grain boundaries. EDX analysis at localized spots for the laser-annealed film in Fig. 1(a) shows that a Ge-rich layer (with Ni:Ge atomic ratio of ~25:75 to 23:77) is formed closer to the Ge substrate and a mononickel germanide layer (with Ni:Ge ratio of 52: 48) is formed at the top surface. It should be noted that EDX is not an accurate method to identify the nickel germanide phase as scattering from Ge substrate may contribute to the Ge peak in the EDX spectrum.

RBS was performed to accurately determine the composition of the laser-annealed film. A collimated 2 MeV $He^+$ beam was perpendicularly incident to the sample under high vacuum, and ions backscattered at 160° were measured with an ORTEC Ultra detector. The measured spectrum and a simulation performed using SIMNRA code[10] (Fig. 2) shows a

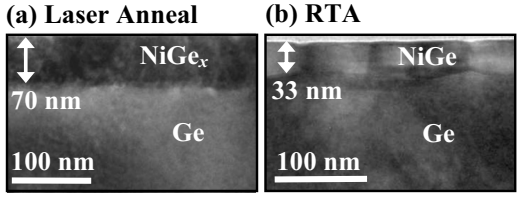


FIG. 1. Cross-sectional TEM images shows that (a) laser anneal at 300 mJ/cm$^2$ for 10 pulses gives a larger nickel germanide ($NiGe_x$) thickness than (b) RTA indicating a different composition from the mono-nickel germanide (NiGe) film obtained from RTA.

a)Author to whom correspondence should be addressed. Present address: Department of Electrical and Computer Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 117576. Electronic mail: yeo@ieee.org. Tel.: +65 6516-2298. FAX: +65 6779-1103.

 

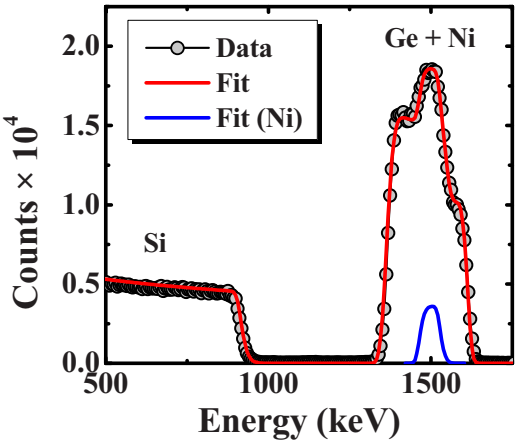


FIG. 2. (Color online) Rutherford backscattering spectrum of nickel germanide ($NiGe_x$) formed using a 10-pulse laser anneal, with 300 mJ/cm$^2$ per pulse. The simulation fitted to the experimental data indicates a 470 $\times 10^{15}$ atoms/cm$^2$ thick $Ni_{0.32}Ge_{0.68}$ has formed (Ni:Ge~1:2.1).

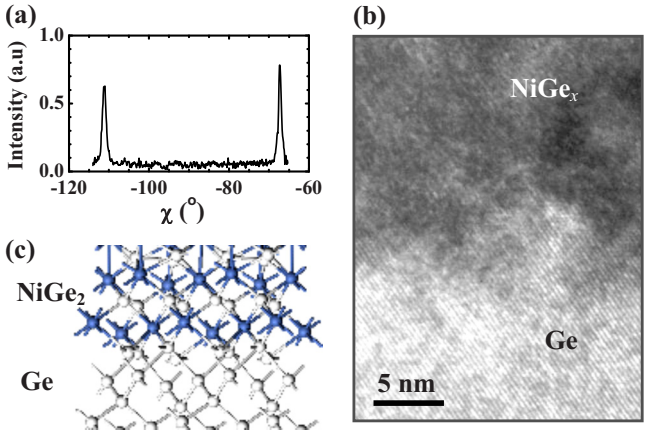


FIG. 4. (Color online) (a) XRD integrated intensity distribution as a function of $\chi$ of the laser-annealed nickel germanide ($NiGe_x$) film indicates that (511) planes are tilted. (b) High resolution TEM image of a highly epitaxial laser-annealed $NiGe_x$ film. (c) First principles simulation of the atomic structure at the $NiGe_2$/Ge(100) interface.

nonuniform Ge content and the presence of a Ni peak near the surface. The fit indicates that a $470\times10^{15}$ atoms/cm$^2$ thick $Ni_{0.32}Ge_{0.68}$ was formed. The Ni:Ge ratio is calculated to be 1:2.1, which is close to that of the digermanide phase.

XRD [Bruker D8 general area detector diffraction system (GADDS) equipped with a two-dimensional (2D) detector and Cu $K_\alpha$ radiation ($\lambda$=0.15 418 nm)] was also conducted. Figures 3(a) and 3(b) show 2D $\theta-2\theta$ XRD patterns obtained from films formed by LA and RTA, respectively. Each pattern, also known as Debye diffraction ring, is a plot of diffraction intensity for a given diffraction angle $2\theta$ ($x$-axis) and $\chi$ ($y$-axis). Figure 3(a) shows high intensity and well-defined bright spots located in the center of the Debye diffraction ring ($\chi=-90°$) and off-center positions, implying diffraction from an epitaxial film. In contrast, Fig. 3(b) exhibits rings with uniformly distributed intensity, a typical feature of polycrystalline films comprising randomly oriented grains.

The inset of Fig. 3(a) shows the integrated diffraction intensity as a function of $2\theta$. Two distinct $NiGe_2$ peaks[11] and a weak NiGe peak are identified. These results agree with the EDX analysis at localized spots. At $2\theta$ of 47.1°, the diffraction integrated intensity distribution as a function of $\chi$ is shown in Fig. 4(a). The two bright spots at $\chi$ equal to −111°

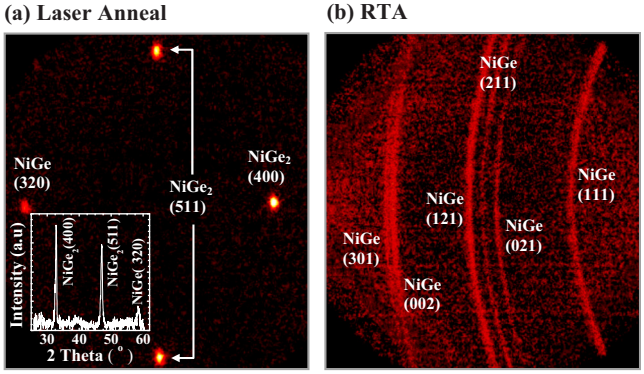


FIG. 3. (Color online) XRD GADDS scan of nickel germanide formed by rapid thermal annealing and by excimer LA. High intensity and well defined spots indicate an epitaxial film for the laser anneal process in (a) whereas rings of uniform distributed intensity indicate a polycrystalline film for the RTA process in (b).

and −67.3° indicate that 50% of the (511) planes are tilted at $\chi$ equal to −21.7° and 22° with respect to the (400) plane. Figure 4(b) shows the high resolution cross-sectional TEM image of the film formed by LA. Lattice fringes observed in the Ge substrate extend into $NiGe_2$, indicating the epitaxial relationship of Ge and $NiGe_2$.

Two following important observations have been made so far: (1) the presence of a metastable $NiGe_2$ phase and (2) the epitaxial nature of $NiGe_2$ on Ge. It is surprising to observe the $NiGe_2$ phase in the nickel germanide film as there exists no stable $NiGe_2$, although a previous study reported that metastable $NiGe_2$ can be synthesized under high pressure (5.5 GPa) and high temperature (700 °C).[11] Simulation of laser interaction with material (SLIM) (Ref. 12) shows that the maximum interfacial temperature generated in the sample during LA is 607 °C, less than the temperature used in Ref. 11. Hence, the phenomenon observed here is unexpected.

The absence of a stable $NiGe_2$ phase in Ni–Ge binary system is due to the fact that the phase transformation $NiGe+Ge\rightarrow NiGe_2$ is not thermodynamically favorable, i.e., the free energy change in the transformation is

$$\Delta G_f = \Delta G_{f\ \mathrm{NiGe_2}} - \Delta G_{f\ \mathrm{NiGe}} - \Delta G_{f\ \mathrm{Ge}} > 0, \tag{1}$$

where $\Delta G_{f\ \mathrm{NiGe_2}}$, $\Delta G_{f\ \mathrm{NiGe}}$, and $\Delta G_{f\ \mathrm{Ge}}$ are the free energies of formation of $NiGe_2$, NiGe, and Ge, respectively. While a positive $\Delta G_f$ is responsible for the absence of $NiGe_2$ in the bulk form, the case becomes different for phase transformation from a thin NiGe film on crystalline Ge substrate to a thin $NiGe_2$ film where the interfacial, surface, and strain energies become important additional thermodynamic parameters to consider. Here, the change in free energy for the total system $\Delta G_{\mathrm{total}}$ for a given thickness $t$ of $NiGe_2$ on a unit area can be expressed as

$$\Delta G_{\mathrm{total}} = t(\Delta G_{f\ \mathrm{NiGe_2}} - \Delta G_{f\ \mathrm{NiGe}} - \Delta G_{f\ \mathrm{Ge}}) + (\Delta\sigma_{\mathrm{NiGe_2}} - \Delta\sigma_{\mathrm{NiGe}}) + (\Delta G_{i\mathrm{NiGe_2/Ge}} - \Delta G_{i\mathrm{NiGe/Ge}}) + t(\Delta G_{\mathrm{strain}}), \tag{2}$$

where $\Delta\sigma_{\mathrm{NiGe_2}}$ and $\Delta\sigma_{\mathrm{NiGe}}$ are the surface energies of $NiGe_2$ and NiGe, respectively, $\Delta G_{i\mathrm{NiGe_2/Ge}}$ and $\Delta G_{i\mathrm{NiGe/Ge}}$ are the interfacial free energies for $NiGe_2$ and NiGe on Ge, respec-

tively, and $\Delta G_{\text{strain}}$ is the strain energy due to phase transformation. Assuming that the surface energies of $NiGe_2$ and NiGe are the same (both quantities are unknown) and the film is strain-free, the remaining two thermodynamic factors in the equation determine whether the phase transformation proceeds or is prohibited. From Eq. (2), one can conclude that a negative $\Delta G_{\text{total}}$ can be achieved (neglecting the second and forth terms) if the following two requirements are satisfied, i.e.,

$$t < -\frac{(\Delta G_{i\text{NiGe}_2/\text{Ge}} - \Delta G_{i\text{NiGe/Ge}})}{(\Delta G_{f\ \text{NiGe}_2} - \Delta G_{f\ \text{NiGe}} - \Delta G_{f\ \text{Ge}})} \tag{3}$$

and

$$\Delta G_{i\text{NiGe}_2/\text{Ge}} - \Delta G_{i\text{NiGe/Ge}} < 0. \tag{4}$$

It is important to note that the epitaxial $NiGe_2$ film has a (400) plane [from Fig. 3(a)] that is parallel to the Ge(100) surface and that an epitaxial relationship $NiGe_2(100)[010]//Ge(100)[010]$ can be constructed. For this epitaxial relationship, a simulation of the atomic structure at $NiGe_2/Ge$ interface using first-principles calculations shows that the interfacial atoms can be arranged such that there is no dangling or broken bond [Fig. 4(c)]. This simulation reinforces the fact that a thin metastable $NiGe_2$ film can be formed due to its ability to be constructed epitaxially on Ge(100) with a low interfacial energy. In other words, the significant reduction in interfacial energy between epitaxial $NiGe_2$ and Ge(100) (as compared to that of polycrystalline NiGe/Ge(100) interface) makes the two critical requirements, Eqs. (3) and (4), to be satisfied, consequently generating the thermodynamic driving force for NiGe to $NiGe_2$ phase transition. A further validation of this analysis is provided by an experiment where Ni films on Ge(111) substrates were laser-annealed under the same conditions, and the $NiGe_2$ phase was not formed. Here, epitaxial orthorhombic structure $NiGe_2$ simply cannot be constructed on the Ge(111) surface.

Apart from the influence of thermodynamics, the kinetics of the LA-initiated reaction also contributes to the formation of the continuous $NiGe_2$ film. It must be pointed out that a classical nucleation model may not be applicable here due to the positive $\Delta G_f$. Nevertheless, this phase transformation from NiGe to $NiGe_2$ is a thermally activated process and can be characterized by an activation energy $\Delta G^*$ which probably has a large value. RTA at low temperatures (e.g., 350 °C) will not provide a sufficiently large thermal energy to overcome the high activation energy barrier. At 500 °C and above, the activation energy may be surmounted, but the slow ramp-down rate during RTA will result in severe agglomeration of the film.[13] In an agglomerated film, the effective thickness of the individual $NiGe_2$ islands is much greater the critical thickness $t$ (by the conservation of mass) and therefore requirement, Eq. (3), is no longer satisfied. Also, with the reduced effective interfacial area, the influence of the free energies of formation becomes more dominant. Thus, epitaxial and continuous $NiGe_2$ film will not form from a RTA reaction even with high temperatures. On the contrary, LA overcomes this high activation energy barrier with its high interfacial temperature (607 °C). The fast heating and quenching of the film in nanoseconds also leaves little time for agglomeration to happen. Thus, the integrity of the NiGe film is retained, and a continuous $NiGe_2$ film is formed epitaxially.

In summary, pulsed excimer laser anneal of a nickel film on (100) germanium-on-silicon substrates resulted in an epitaxial, continuous, and germanium-rich nickel germanide ($NiGe_x$) film. A metastable phase, nickel digermanide ($NiGe_2$), was observed and is found to coexist with the mononickel germanide phase (NiGe) in the $NiGe_x$ film. The formation of the metastable $NiGe_2$ by LA is explained in terms of the ability of the orthorhombic structure of $NiGe_2$ to construct epitaxially on Ge(100) due to the reduced interfacial energy at $NiGe_2/Ge(100)$ interface, and the kinetic aspects of the LA reaction associated with phase transformation and film agglomeration.

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