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). 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 which aggravates short channel effects. Annealing at temperatures below 500 °C is required for n-type dopants activation but this leads to significant dopant diffusion which aggravates short channel effects. Laser annealing (LA) may offer a solution to this problem because it can be performed at low temperatures without causing excessive diffusion of dopants. Nevertheless, realizing n-type dopant diffusion which aggravates short channel effects.
nonuniform Ge content and the presence of a Ni peak near the surface. The fit indicates that a $470 \times 10^{15}$ 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 $K_a$ radiation ($\lambda=0.15418$ 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 the integrated intensity distribution as a function of 2$\theta$. The simulation fitted to the experimental data indicates a 470

![Image](https://via.placeholder.com/150)

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).

![Image](https://via.placeholder.com/150)

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 $-67.3^\circ$ indicate that 50% of the (511) planes are tilted at $\chi$ equal to $-21.7^\circ$ and $22^\circ$ 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). 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+$\text{Ge}\rightarrow\text{NiGe}_2$ is not thermodynamically favorable, i.e., the free energy change in the transformation is

$$\Delta G_f = \Delta G_f^\text{NiGe}_2 - \Delta G_f^\text{NiGe} - \Delta G_f^\text{Ge} > 0,$$

where $\Delta G_f^\text{NiGe}_2$, $\Delta G_f^\text{NiGe}$, and $\Delta G_f^\text{Ge}$ 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 $\Delta G_{\text{total}}$ for a given thickness $t$ of NiGe$_2$ on a unit area can be expressed as

$$\Delta G_{\text{total}} = t(\Delta G_f^\text{NiGe}_2 - \Delta G_f^\text{NiGe} - \Delta G_f^\text{Ge}) + (\Delta \sigma_{\text{NiGe}_2} - \Delta \sigma_{\text{NiGe}}) + (\Delta G_{\text{NiGe}_2/\text{Ge}}^\text{NiGe}_2 - \Delta G_{\text{NiGe}/\text{Ge}}^\text{NiGe}),$$

where $\Delta \sigma_{\text{NiGe}_2}$ and $\Delta \sigma_{\text{NiGe}}$ are the surface energies of NiGe$_2$ and NiGe, respectively, $\Delta G_{\text{NiGe}_2/\text{Ge}}^\text{NiGe}_2$ and $\Delta G_{\text{NiGe}/\text{Ge}}^\text{NiGe}$ 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.,

$$t < - \frac{(\Delta G_{\text{NiGe}_2\text{Ge}} - \Delta G_{\text{NiGe}/\text{Ge}})}{(\Delta G_{\text{fNiGe}_2} - \Delta G_{\text{fNiGe}} - \Delta G_{\text{fGe}})}$$  (3)

and

$$\Delta G_{\text{NiGe}_2\text{Ge}} - \Delta G_{\text{fNiGe}/\text{Ge}} < 0.$$  (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 $\Delta G_{\text{fNiGe}}$. 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., $350 \degree C$) will not provide a sufficiently large thermal energy to overcome the high activation energy barrier. At $500 \degree C$ and above, the activation energy may be surmounted, but the slow ramp-down rate during RTA will result in severe agglomeration of the film. In an agglomerated film, the effective thickness of the individual NiGe$_2$ islands is much greater than 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 ($607 \degree C$). 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$_2$) film. A metastable phase, nickel digermanide (NiGe$_3$), was observed and is found to coexist with the mononickel germanide phase (NiGe) in the NiGe$_2$ 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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