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Citation: [Appl. Phys. Lett.](#) **100**, 104101 (2012); doi: 10.1063/1.3692175

View online: <http://dx.doi.org/10.1063/1.3692175>

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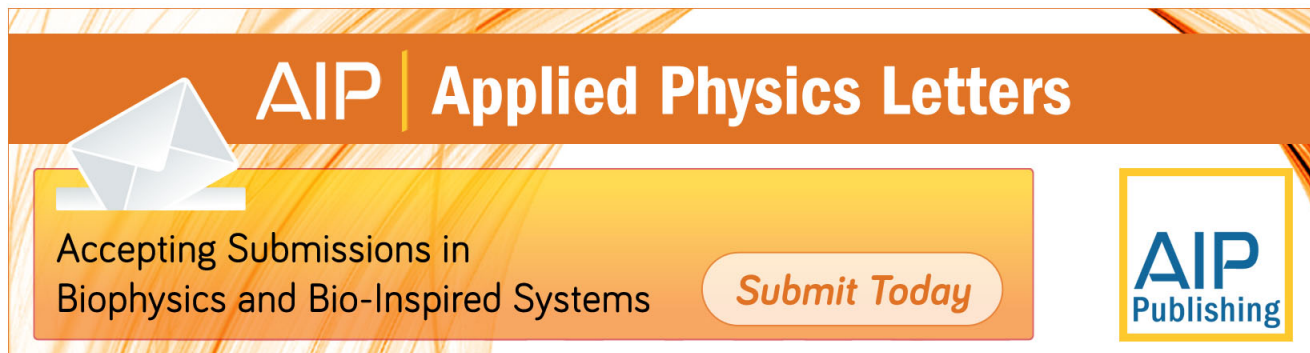
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Laser synthesis of germanium tin alloys on virtual germanium

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(Received 16 January 2012; accepted 15 February 2012; published online 6 March 2012)

Synthesis of heteroepitaxial germanium tin (GeSn) alloys using excimer laser processing of a thin 4 nm Sn layer on Ge has been demonstrated and studied. Laser induced rapid heating, subsequent melting, and re-solidification processes at extremely high cooling rates have been experimentally achieved and also simulated numerically to optimize the processing parameters. “*In situ*” measured sample reflectivity with nanosecond time resolution was used as feedback for the simulations and directly correlated to alloy composition. Detailed characterization of the GeSn alloys after the optimization of the processing conditions indicated substitutional Sn concentration of up to 1% in the Ge matrix. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3692175>]

Recent research on group IV direct band gap alloys for silicon-based infrared photonics and optoelectronics undoubtedly affirmed the germanium tin (GeSn) alloy as a valuable candidate for the convergence of Si based microelectronics and photonics.^{1,2} Due to the extreme low solubility of Sn in Ge (<1%),³ great efforts were directed to optimize the growth of such alloys with conventional techniques like chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) by tuning the deposition parameters for a non-equilibrium epitaxial growth.^{4–8} In the past, also alternative techniques involving laser annealing^{9–11} were proposed but not further developed.

In this work, we present the pulsed laser induced epitaxy (PLIE) as an alternative to CVD and MBE growth methods for synthesizing heteroepitaxial GeSn alloys on Si(001) substrates with virtual germanium buffer layer (v-Ge). The aim is to achieve epitaxial GeSn through fast non-equilibrium solid-liquid-solid phase transitions in order to overcome the extreme low solubility of Sn in Ge.³ Since the used ArF-excimer laser features pulse duration with 20–25 ns full width at half maximum (FWHM) and nanometer penetration depth, it becomes a useful annealing source capable to deliver very rapid melt/solidification cycles, if pulse energy density is well adjusted. To achieve a uniformly irradiated zone at 200 mJ/cm² pulse energy, a fly-eye beam homogenizer and a manual attenuator have been used.

A 100–110 nm v-Ge layer on Si(001) was first grown as a single step buffer (defect density > 10¹⁰/cm²) on Si(001) at 300 °C substrate temperature, followed by a 4 nm Sn layer, deposited at 85 °C in the same MBE reactor.⁷ Time resolved reflectivity (TRR) measurements using a HeNe (632.8 nm) probe laser beam, positioned at about 45° to the sample normal, was employed to monitor the melt duration¹² from the solid/liquid/solid phase transitions reflectivity changes during PLIE. The reflected beam was focused to a fast (<1 ns rise time) photodiode connected to a digital oscilloscope.

This signal supplied additional information on the surface roughness, which is directly correlated to the amount of scattered and reflected light, and was compared to surface roughness measurements obtained with a mechanical profiler (Dektak3ST). The melting depth and duration were calculated using a finite element method (FEM) solution of the heat conduction differential equation (HCDE).¹³ The direct relation between experiment and theory was provided by the liquid phase duration that was both calculated through FEM and extracted from the TRR experimental data.

Figure 1 compares the temporal evolution of the sample reflectivity, induced by the first 200 mJ/cm² laser pulse, with the maximum melting depth (MMD) and interface (Sn/v-Ge and v-Ge/Si) temperature, as estimated by FEM.

The reflectivity change during the phase transition (Figure 1(c)) mainly originates from the melting and solidification of the v-Ge substrate.¹⁴ The predicted onset of melting at the Sn/Ge interface (Figures 1(a) and 1(b)) at about 16 ns

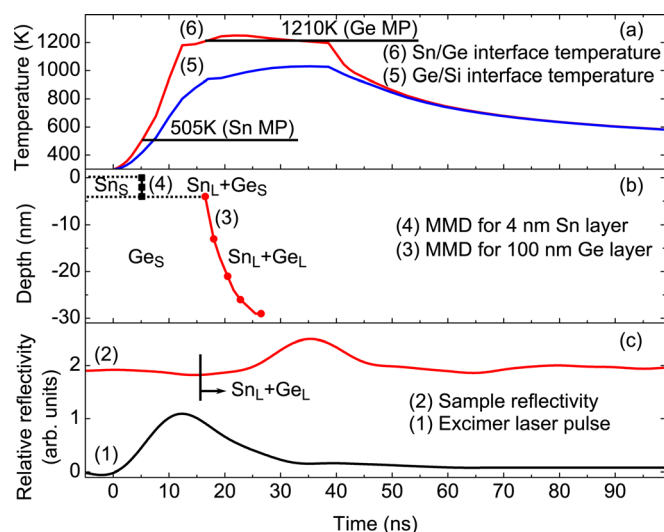


FIG. 1. (Color online) Temporal evolution of the (a) interface temperatures, (b) depth of solid-liquid transition, and (c) reflectivity, caused by the first laser pulse of 200 mJ/cm².

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after the laser pulse, is experimentally confirmed by TRR. Similar reflectivity change behavior for laser energy close to the Ge melting threshold was reported by Jellison *et al.*¹⁵ and Solis and Afonso.¹⁶ The increase of the final reflectivity after the irradiation indicates the GeSn compound formation.¹⁰ However, the model used to calculate MMD and the temperature profiles at the interfaces does not simulate diffusion, thus static interfaces are assumed, to evaluate when the melting point (MP) is reached.

The influence of the number of pulses, an important PLIE processing parameter, can be extracted by monitoring the TRR data (melting duration, relative reflectivity change) and surface roughness measurements during multiple pulses (up to 100 laser pulses at 1 Hz).

Melt duration increases with the number of pulses from 28 ns for 1 pulse to a maximum of 50 ns for 50 pulses and then drops below 37 ns (Figure 2(a)). On the other hand, the reflectivity and roughness as a function of the number of pulses (Figure 2(b)) show that, after the tenth pulse, surface reflectivity decreases almost linearly but roughness remains constant. Therefore, the surface roughness does not contribute to the reflectivity change, indicating only an alloy composition change relation, with dependence of the number of laser pulses. Assuming that best (homogenous) intermixing is achieved at high number of pulses, characterization of the sample irradiated with 100 pulses of 200 mJ/cm² will be presented in the following.

To quantify the Sn content in the sample and evaluate the GeSn film quality, Rutherford backscattering spectrometry (RBS) (1.4 MeV He⁺ ions at 170° backscattering angle) of the untreated Sn/v-Ge/Si(001) structure and the GeSn alloy obtained after laser treatment was performed (Figure 3). The random spectrum of the untreated structure reveals a 100 nm Ge layer and a Sn deposition with an areal density of 2.9×10^{15} atoms/cm². The corresponding channeling spectrum exhibits a minimum yield value of about 5% and a significant peak at the low energy edge of the Ge signal, which

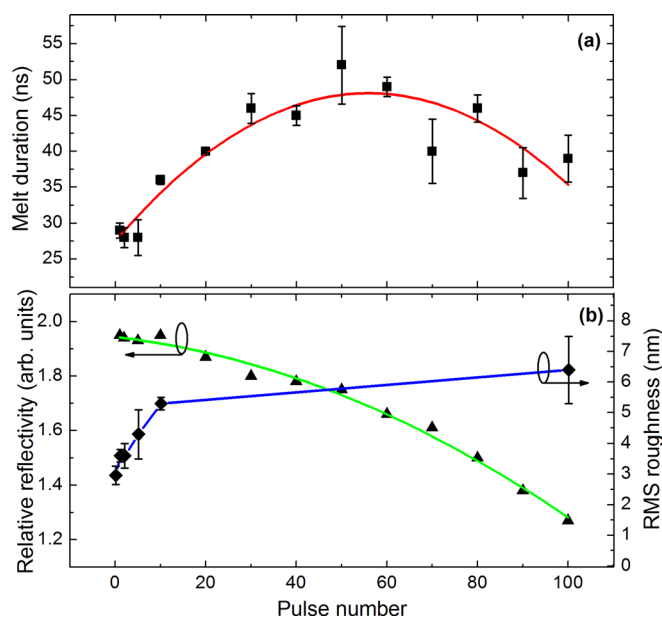


FIG. 2. (Color online) Melt duration extracted from the TRR spectra (a) and surface reflectivity and RMS roughness (b) of the sample surface for different number of 200 mJ/cm² pulses. All lines are guide for the eye.

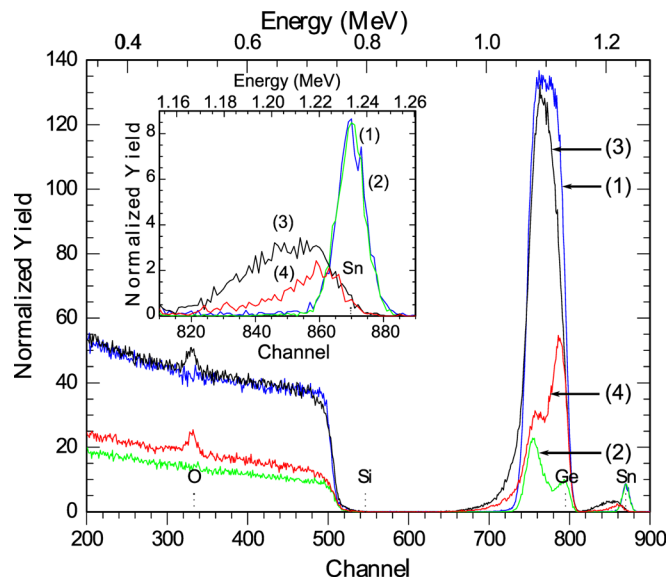


FIG. 3. (Color online) Random (1) and [001] channeling (2) spectra of the untreated structure in comparison to the random (3) and [001] channeling (4) spectra of a sample treated with 100 pulses of 200 mJ/cm². The inset shows a magnification of the backscattering signal of Sn.

could be ascribed to the misfit dislocation network at the interface due to the lattice mismatch of 4.2% between Ge and Si. The Sn signal shows the same intensity both in random and channeling mode indicating that the deposited Sn is either polycrystalline or amorphous. After laser treatment, the deposited Sn is distributed within the Ge layer. In the upper 50 nm of the v-Ge layer, a concentration of about 1 at. % Sn was determined that decrease almost linearly towards the interface. In addition, oxidation of the Ge (and probably Sn) surface was observed, indicated by the existence of an O surface peak and a change in the shape of the Ge signal. The channeling spectrum of the laser treated sample shows that a substantial part of the Sn atoms is on substitutional lattice sites. However, the channeling yield of the Ge signal is rather high due to the formation of an amorphous oxide on the surface.

To obtain a more precise evaluation of the layer structure as well as of the Sn concentration profiles, time of flight secondary ion spectroscopy (TOF-SIMS) and transmission electron microscopy (TEM) analysis of the laser treated samples have been performed. The TEM images (Figure 4(a)) confirm the RBS results, revealing a sample structure with a thin oxide cap (about 2 nm) on top of a 40 nm GeSn layer that does not show any Sn precipitates or clusters. The GeSn alloy is epitaxial to the v-Ge (inset of Figure 4(a)) and separated by a dot-like structured interface of light atomic weight (probably voids). Moreover, it can be observed, that threading dislocations present in the v-Ge continue through the GeSn alloy, suggesting similar dislocations density as for the untreated sample. The interface between the v-Ge layer and the Si substrate is well defined with no Si/Ge intermixing, thus melting has not taken place at this interface. The TOF-SIMS analysis of the Sn depth distribution (Figure 4(b)) indicates that the Sn content is almost uniform in the first 35 nm, although the Sn intensity slightly fluctuates and increases, probably due to knock-on effects of Sn in the Ge matrix and matrix changes between amorphous surface, crystalline GeSn, and v-Ge. In the remaining v-Ge, Sn diffusion due to

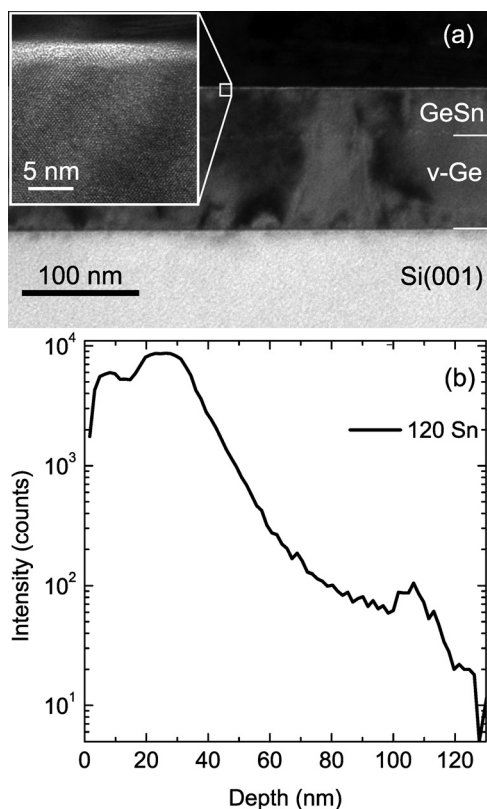


FIG. 4. TEM image (a) taken in tilted geometry to better visualize threading dislocations with a high resolution image of the sample surface (inset) and (b) TOF-SIMS depth profile of the Sn content in the GeSn/v-Ge/Si(001) structure.

residual temperature gradient after each of the 100 laser pulses is observed.^{5,17} Slight increase of signal intensity at the v-Ge/Si interfaces can also be attributed to matrix effects caused by changing crystal lattice.

Finally, Raman analysis using a 632.8 nm excitation source in backscattering configuration has been performed to confirm the composition and crystalline structure of the alloy^{11–13} by analyzing the frequency shift, given by composition and strain variation.¹⁸ The vibrational modes of fully strained and relaxed GeSn alloys^{19,20} show a decreasing Ge-Ge phonon frequency and an increasing peak asymmetry with increasing Sn concentration. Figure 5 shows the Raman spectra of the as-deposited (black dotted line) and the laser treated (red continuous line) Sn/v-Ge structures. The typical peak position of the Ge-Ge mode at 301 cm^{-1} shifts to 299.5 cm^{-1} after PLIE, indicating compressive strain build-up in the layer.¹⁹ Moreover, a vibrational mode around 263 cm^{-1} , reported for excitation closer to the resonance frequency of the $E_1/E_1 + \Delta_1$ optical transitions,²⁰ is clearly observed for the laser treated structure, confirming substitutional Sn from Ge-Sn bonds. The peak around 186 cm^{-1} is assigned to the Sn-Sn vibration mode.

In conclusion, we have presented the synthesis of epitaxial GeSn alloy from a Sn/Ge layer system by pulse laser induced epitaxy. TRR was used for “*in situ*” monitoring of surface properties and composition changes during laser treatment. The GeSn layer thickness may be adjusted by varying the number of laser pulses. 40 nm thick layer of high crystalline quality was obtained for 100 laser pulses. RBS,

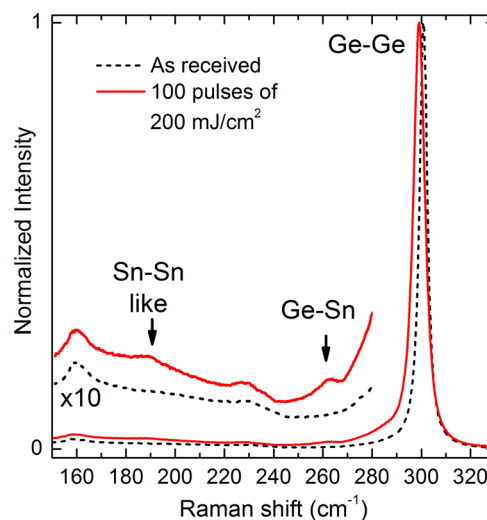


FIG. 5. (Color online) Raman spectra of the Ge-Ge vibration mode from v-Ge/Sn before and after laser treatment with magnified ($\times 10$) Ge-Sn and Sn-Sn modes region.

TOF-SIMS, TEM and Raman analysis clearly demonstrate the formation of homogenous GeSn alloys with up to 1% substitutional Sn in the Ge matrix.

Research on PLIE has been partially financed by Spanish (MAT2008-02350, MAT2011-24077) and Galician (2010/83) Grants. Research at IHT was supported by the Deutsche Forschungsgemeinschaft (SCHU2496/4-1).

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