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LASER-INDUCED CRYSTALLIZATION OF Ge/Sn MULTILAYER AMORPHOUS FILMS

A comparative analysis of the structural, morphological, and optical properties of 150-nm-thick polycrystalline GeSn films formed by laser annealing of amorphous multilayer heterostructures on a Ge/Si(100) buffer layer using two types of radiation – pulsed nanosecond ($\lambda = 355$ nm) and femtosecond ($\lambda = 800$ nm) was carried out. According to Raman spectroscopy and X-ray diffraction data, pulsed nanosecond UV annealing within a narrow pulse energy density range of 0.2–0.3 J/cm² is most effective for preserving surface planarity and achieving maximum substitutional incorporation of tin (up to 10.3 at.% Sn). Femtosecond annealing provides a lower level of tin incorporation (7.5 at.%) due to intermixing of Sn and Ge elements at the interface between the film and the buffer layer, as confirmed by secondary ion mass spectrometry profiles. It is shown that the surface morphology of the films under these two types of laser processing also differs substantially; in particular, femtosecond annealing causes self-organization of laser-induced periodic surface structures (LIPSS), which are promising for application in specialized optoelectronic devices.

Keywords: GeSn thin films, laser annealing, nanosecond laser, femtosecond laser, XRD, SEM, SIMS, Raman spectroscopy, segregation.

1. Introduction

In recent years, GeSn thin films grown on silicon substrates have been intensively studied [1–3]. Significant interest in these materials is driven by the ability to transform indirect-bandgap germanium into a direct-bandgap GeSn solid solution by incorporating approximately 8–10 at.% of tin atoms into the Ge lattice [4, 5]. Since Si, Ge, and Sn belong to Group IV of the periodic table, GeSn materials are easily integrated into well-developed Si technology, opening broad prospects for creating efficient optoelectronic devices. The choice of GeSn for such a transformation is explained by the fact that the energy

gap between the conduction band minima at the center of the Brillouin zone (Γ -point) and at its edge (L-valley) in Ge is only 140 meV, whereas in Si this value exceeds 2 eV [4]. Tin is a semimetal in which the valence band maximum is located above the conduction band minimum at the Γ -point. The incorporation of Sn atoms into the Ge crystal lattice sites leads to a restructuring of its electronic spectrum: the Γ -minimum of the conduction band shifts downward much faster than the L-minima. As a result, at an Sn concentration of 8–10 at.%, the GeSn solid solution becomes a direct-bandgap semiconductor. Under equilibrium conditions at room temperature, the solubility of Sn in Ge does not exceed 1 at.% [6]. Therefore, nonequilibrium growth methods such as molecular beam epitaxy (MBE) [2, 7] and chemical vapor deposition (CVD) [8] are usually used to form GeSn films with a high tin content (≥ 8 at.%). However, these methods are expensive and primarily used to produce laboratory samples, which highlights the relevance of developing more accessible

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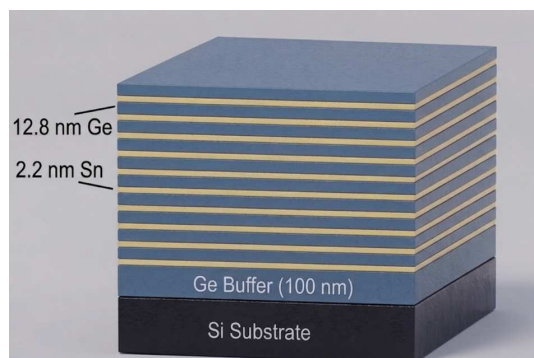


Fig. 1. Schematic representation of the initial 10-period Ge/Sn structure on a 100-nm Ge buffer layer grown on a Si substrate

and scalable technological approaches. In addition to the aforementioned MBE and CVD methods, other approaches are applied to achieve nonequilibrium Sn incorporation into Ge, including co-doping of Ge with Sn and carbon atoms [9]. Local mechanical stresses arising in the Ge lattice during Sn incorporation due to the significant difference in their atomic radii can be partially compensated for by the joint introduction of Sn and C atoms. At the same time, strain compensation via carbon incorporation is limited by its extremely low solubility in Ge, and any deviation from the optimal Sn/C ratio leads to phase separation of carbon, triggering heterogeneous tin segregation. In view of this, it is advisable to maintain the carbon concentration at a level deliberately below the threshold of full strain compensation. It is known that metastable homogeneous amorphous $\text{Ge}_{1-x}\text{Sn}_x$ films can be obtained over a fairly wide composition range ($x \leq 0.25\text{--}0.35$). At the same time, to form crystalline films from them with a high content of tin incorporated into the lattice sites, it is necessary to implement a nonequilibrium process – ultrafast annealing, which enables film crystallization while “freezing” Sn atoms in the crystal lattice sites. As shown in [9–11], pulsed laser annealing is an effective tool for this purpose, allowing for rapid heating of the near-surface layer and ensuring swift cooling of the material. Despite the high efficiency of femtosecond laser annealing demonstrated in [10, 12, 13], the high cost and operational complexity of such systems significantly limit their widespread technological application. The use of nanosecond (ns) laser annealing ($\lambda = 355$ nm) can serve as a well-grounded alternative in certain cases. Due to the small optical absorption depth in

GeSn, ns-ultraviolet radiation can generate high temperature gradients, providing a crystallization front velocity sufficient to reach the Sn atom solute trapping threshold. If, under these conditions, the substitutional tin content in the Ge lattice remains comparable to that obtained with femtosecond (fs) annealing, the use of ns lasers will make it possible to significantly reduce the cost and simplify the technology for forming polycrystalline GeSn films.

The aim of this work is to study the features of amorphous $\text{Ge}_{1-x}\text{Sn}_x$ film annealing using pulsed ns and fs lasers, to perform a comparative study of the properties of the formed coatings, and to establish the optimal laser processing regimes for achieving maximum incorporation of Sn atoms into the Ge crystal lattice sites.

2. Experimental

GeSn films with a thickness of 150 nm were grown by thermal evaporation of Ge and Sn targets in vacuum (6.7×10^{-4} Pa) onto a 100-nm-thick Ge buffer layer deposited on a Si(100) substrate. The deposition of Sn and Ge was carried out not simultaneously but through a layer-by-layer alternation of Sn and Ge intermediate layers (10 periods, Fig. 1). Laser annealing was performed using a Seal-355-5SE nanosecond DPSS laser (wavelength $\lambda = 355$ nm, pulse duration $\tau \approx 22$ ns, pulse repetition rate $f = 130$ kHz, source power $P_{\text{laser}} = 5.0$ W). To prevent film ablation and ensure a solid-phase crystallization regime, the radiation was attenuated by a glass plate. The laser beam was focused into a spot with a diameter $d = 20$ μm . Scanning was performed using a galvanometric system at a speed $v = 2000$ mm/s. The pulse energy density was varied from 0.1 to 0.6 J/cm². During femtosecond annealing of the samples, a Ti: sapphire laser system was used ($\lambda = 800$ nm, $\tau = 150$ fs, $f = 1$ kHz, average power $P_{\text{avr}} = 135$ mW). The laser spot diameter was varied within the range of 840–1040 μm , and the scanning speed was maintained in the range of 0.1–1 mm/s. The structure and properties of the resulting films were investigated using secondary ion mass spectrometry (SIMS), X-ray diffraction (XRD), Raman scattering spectroscopy, and scanning electron microscopy (SEM). Raman scattering spectra were recorded using an MDR-23 spectrometer equipped with a cooled iDus 401A BR-DD CCD detector (Andor). The spectra were excited by

a solid-state laser with a wavelength $\lambda = 532$ nm; the power density of the radiation on the sample surface did not exceed 10^3 W/cm², which prevented thermal heating and structural modification of the samples. X-ray diffraction analysis was carried out using Cu $K\alpha$ line radiation ($\lambda = 0.15406$ nm) on a Philips X'Pert PRO-MRD diffractometer in symmetric geometry ($2\theta - \omega$) with a scan step of 0.025° . The surface morphology and elemental composition were studied using a Zeiss Sigma 500 VP FE-SEM scanning electron microscope equipped with a Smart-EDX EDS detector. Elemental depth profiles in the films were obtained using time-of-flight secondary ion mass spectrometry on a TOF-SIMS IV instrument (Germany) in dual-beam mode, utilizing a 25 keV Bi⁺ primary ion beam (1 pA) as the analytical beam and a 1 keV O₂⁺ beam (250 nA) for sputtering. The angles of incidence for both ion beams were 45° . TOF-SIMS spectra were acquired from an area of 101.56×101.56 μm^2 within a 300×300 μm^2 crater bottom. The depth resolution was ≈ 1 nm.

3. Results and Discussion

Typically, laser annealing of semiconductor structures is applied to achieve ultrafast local thermal processing without heating the entire substrate [14]. This is critically important for submicron manufacturing in modern microelectronics, where conventional furnace annealing or rapid thermal annealing leads to degradation or significant property changes in ultra-small elements due to undesirable dopant diffusion. In our case, the key objective was to locally crystallize the amorphous GeSn film and “freeze” Sn atoms at substitutional sites in the Ge crystal lattice. To realize this process, the cooling time of the laser-heated film must be shorter than the diffusion time of Sn atoms during their segregation. A number of other requirements are also imposed on laser annealing, notably the prevention of the formation of an overly developed surface morphology (melting, capillary waves, Marangoni effects), a requirement that is critical for the subsequent formation of contacts or heterostructures. However, in this work, we focus primarily on the efficiency of Sn incorporation into the Ge crystal lattice. A direct comparison between nanosecond (ns) and femtosecond (fs) annealing is complex, as physically distinct processes occur in the film during the interaction with ns and fs radiation. Nevertheless, their influence on the final properties of the processed

material can be fully characterized. For the crystallization of an amorphous GeSn film by ns radiation, the main parameters are the pulse energy density ($F = E_p/S$, where E_p is the pulse energy and S is the laser spot area) and the peak power ($P_{\text{peak}} = E_p/\tau$, where τ is the pulse duration). During the interaction of fs radiation with the film, a more critical parameter is the cumulative (absorbed) energy density, as the energy density of a single pulse is insufficient to induce crystallization. Therefore, to achieve maximum incorporation of Sn atoms into the Ge lattice, this work experimentally determined the ns pulse energy density sufficient to heat the amorphous GeSn film to its crystallization temperature and incorporate Sn atoms, as well as the cumulative energy density for the interaction of fs radiation with the film.

Fig. 2 shows SEM images of the surface of GeSn films processed by ns laser radiation ($\lambda = 355$ nm) with energy densities (F) of 0.1 (a) and 0.35 J/cm² (b), as well as films processed by fs laser radiation ($\lambda = 800$ nm) with cumulative energy densities of 150 (c) and 190 J/cm² (d). From Fig. 2, a, b, it can be seen that increasing the ns radiation energy density from 0.1 to 0.35 J/cm² significantly modifies the film morphology. At $F = 0.1$ J/cm² (Fig. 2, a), no distinct laser pulse spots are present on the film surface; instead, only dark dendritic structures are observed. These may result from surface atom diffusion and represent a manifestation of the Soret effect (thermodiffusion). After surface processing at $F = 0.35$ J/cm² (Fig. 2, b), laser pulse spots become clearly visible, with their surfaces covered by a network of corrugations. These represent compressive strain waves formed during rapid structural reorganization under high axial and radial temperature gradients. Surface morphology changes in the film processed by fs laser radiation ($\lambda = 800$ nm) when the cumulative energy density is varied from 150 to 190 J/cm² are less prominent. In both cases, a fine-grained periodic relief structure is observed, resulting from laser pulse overlap and the formation of laser-induced periodic surface structures (LIPSS) [15] (see insets in Fig. 2, c, d). With an increase in the cumulative energy density, higher-magnification SEM images reveal that pores begin to form within the film under these conditions.

Raman scattering spectroscopy is an effective method for quantitatively evaluating the content of Sn atoms incorporated into the Ge crystal lattice [3,

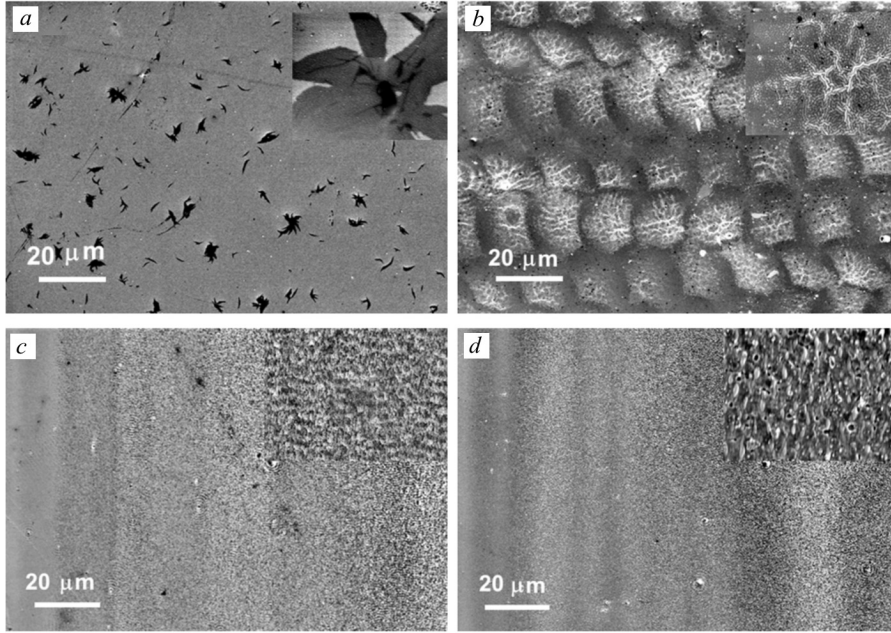


Fig. 2. Representative SEM images of the surface of GeSn films treated with nanosecond laser radiation ($\lambda = 355$ nm) at energy density of 0.1 J/cm^2 (a) and 0.35 J/cm^2 (b); and treated with femtosecond laser radiation ($\lambda = 800$ nm) at absorbed energy density of 150 J/cm^2 (c) and 190 J/cm^2 (d). The insets show magnified areas of the film surface. Images were acquired at a beam energy of 1 keV and a working distance of 3 mm using an in-lens detector

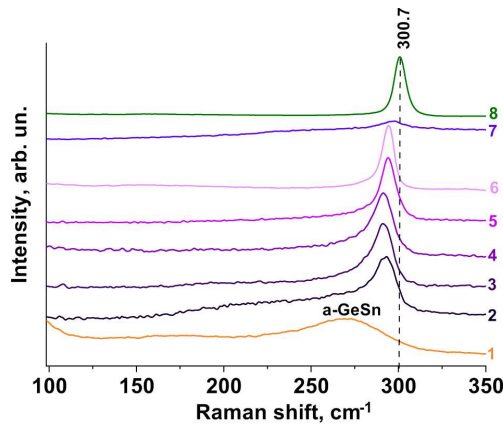


Fig. 3. Raman spectra of GeSn films: initial film (1); annealed by nanosecond laser radiation ($\lambda = 355$ nm) at pulse energy densities of 0.1 (2); 0.2 (3); 0.3 (4); 0.35 (5); 0.45 (6); 0.6 J/cm^2 (7). For comparison, the Raman spectrum of single-crystal Ge is shown (8)

9–11, 15, 16], as spectral analysis allows one to determine specifically the substitutional tin concentration, rather than the total tin content measured by many other techniques.

Fig. 3 shows the Raman scattering spectra of the initial GeSn film and films annealed using a pulsed laser at energy densities ranging from 0.1 to 0.6 J/cm^2 . The spectra were recorded at the center of

the laser-annealed spots. The spectrum of the initial GeSn sample corresponds to a completely amorphous phase. Analysis of the Raman scattering spectra of the annealed polycrystalline GeSn film indicates a strong dependence of the microstructural characteristics of the material, particularly the efficiency of Sn atom incorporation into lattice sites, on the laser processing parameters (pulse energy density F). Based on the frequency shift of the Ge–Ge vibrational mode, the content of Sn atoms incorporated into the Ge lattice can be estimated using the following expression [16]:

$$\omega_{\text{GeSn}(x,\varepsilon)}^{\text{Ge-Ge}} = \omega_{\text{Ge bulk}}^{\text{Ge-Ge}} - \alpha \cdot x + \beta \cdot \varepsilon, \quad (1)$$

where $\alpha = 82 \pm 4 \text{ cm}^{-1}$, $\beta = -563 \pm 34 \text{ cm}^{-1}$, and ε is the elastic strain. During cooling from the onset temperature of crystallization ($T_{\text{GeSn}} \approx 598 \text{ K}$) to room temperature ($\approx 298 \text{ K}$), the GeSn film tends to contract much more strongly than the bulk Si substrate, which holds the film and prevents it from shrinking to its equilibrium volume. As a result, in-plane biaxial thermal tensile strain arises at the interface. Since the film is polycrystalline, strains caused by the lattice mismatch between the GeSn film and the Si substrate relax almost completely at grain boundaries and dislocations. Therefore, thermal stresses become the dominant source of residual macro-stresses [17],

which can be evaluated using the following expression [18]:

$$\varepsilon = (\Delta\alpha \cdot \Delta T), \quad (2)$$

where $\Delta\alpha$ is the difference between the thermal expansion coefficients of the GeSn film and the Si substrate (in our case, $\Delta\alpha \approx 5.1 \times 10^{-6} \text{ K}^{-1}$; ΔT is the temperature difference between the crystallization onset and room temperature, amounting to 300 K). In addition to the substitutional Sn content in the Ge lattice and the tensile elastic strain (ε), spatial confinement effects (size effects) can also affect the frequency position of the Ge–Ge mode if the size of the formed GeSn nanocrystals is significantly smaller than 20 nm [19]. To estimate the average size of the GeSn nanocrystals, X-ray diffraction (XRD) patterns were recorded.

Fig. 4 shows the XRD patterns of the $\text{Ge}_{1-x}\text{Sn}_x$ film immediately after deposition (curve 1) and after ns laser annealing at $\lambda = 355 \text{ nm}$ ($F = 0.2 \text{ J/cm}^2$) (curve 2). The XRD patterns demonstrate that the initial as-deposited film is amorphous (curve 1). The pattern after laser annealing (curve 2) represents a superposition of signals from the annealed and unannealed surface regions of the GeSn film. The size of the coherent scattering domains (corresponding to the average nanocrystal size) was determined using Scherrer's equation [20]:

$$D = (k \cdot \lambda) / (\beta \cdot \cos(\theta)), \quad (3)$$

where λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the reflection in radians, θ is the Bragg angle, and k is a dimensionless shape factor ($k \approx 0.9$). The average nanocrystal diameter determined from Eq. (3) using the parameters of the (111) reflection for this film is $\approx 13 \text{ nm}$. For GeSn nanocrystals of this average size, the low-frequency shift of the Ge–Ge Raman mode due to the spatial confinement effect does not exceed 0.2 cm^{-1} , which was taken into account when determining the substitutional tin content in the lattice. Estimation of the substitutional Sn content incorporated into the Ge lattice using Eq. (1) yields the following values: for $F = 0.2 \text{ J/cm}^2$, $x = 10.3 \text{ at.}\%$; for $F = 0.3 \text{ J/cm}^2$, $x = 9.7 \text{ at.}\%$; for $F = 0.35 \text{ J/cm}^2$, $x = 6.8 \text{ at.}\%$; for $F = 0.45 \text{ J/cm}^2$, $x = 6.3 \text{ at.}\%$. The maximum incorporation of Sn into the lattice is observed for ns laser annealing (355 nm) with a pulse energy density

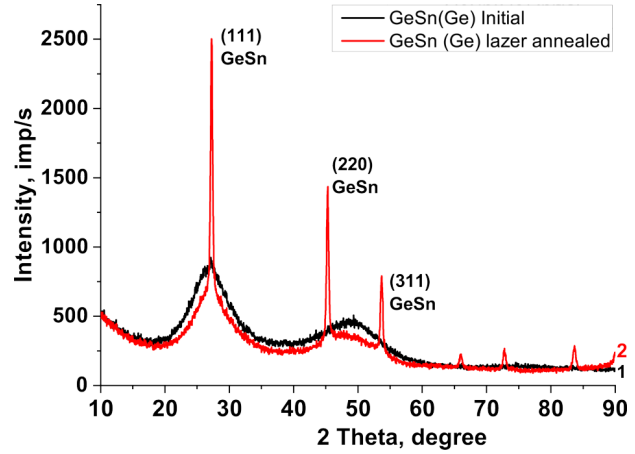


Fig. 4. X-ray diffraction (XRD) patterns of the as-deposited $\text{Ge}_{1-x}\text{Sn}_x$ film (1) and the $\text{Ge}_{1-x}\text{Sn}_x$ film annealed by laser radiation with $\lambda = 355 \text{ nm}$ at a pulse energy density of 0.2 J/cm^2 (2)

in the range of $0.2\text{--}0.3 \text{ J/cm}^2$. A further increase in the radiation energy density leads to progressive Sn atom segregation. With an increase in pulse energy density up to 0.6 J/cm^2 , the GeSn film completely evaporates (ablation occurs), resulting in only a low-intensity second-order band (2TA) at 297 cm^{-1} from the Si substrate being detected in the Raman spectra (Fig. 3, curve 7). Note that for nanosecond annealing at an energy density of $F = 0.1 \text{ J/cm}^2$, a band is observed in the Raman spectrum (Fig. 3, curve 2), which is a superposition of contributions from the amorphous and crystalline phases.

As revealed by Raman scattering studies (spectra not shown), due to the lateral propagation of the thermal front, regions of the GeSn film not directly exposed to the laser beam were also annealed up to a distance of $2\text{--}3 \mu\text{m}$ from the boundary of the laser spot. The lateral distance to which the thermal front propagates can be estimated using the following expression:

$$L \approx \sqrt{D_{\text{th}} \cdot t_{\text{eff}}}, \quad (4)$$

where D_{th} is the thermal diffusivity of the material, and t_{eff} is the effective thermal relaxation time of the heterostructure following the laser pulse. The value of D_{th} for the thin GeSn film and Ge buffer layer at high temperatures lies within the range of $0.1\text{--}0.25 \text{ cm}^2/\text{s}$. Although the nanosecond laser pulse duration is 22 ns , the effective dissipation time (t_{eff}) of the thermal field in the film during thermal re-

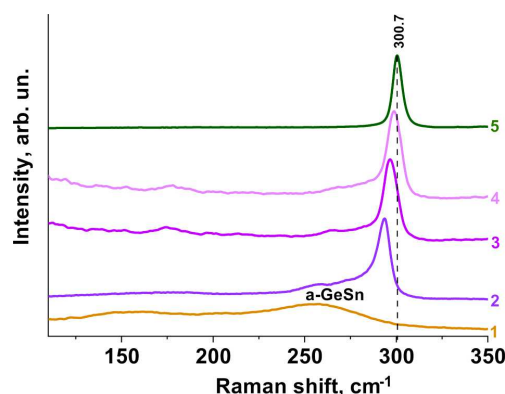


Fig. 5. Raman spectra of the 10-layer Ge/Sn structure in the as-deposited structure (1) and after femtosecond laser annealing at accumulated energy densities of 150 J/cm² (2), 170 J/cm² (3), 190 J/cm² (4). For comparison, the Raman spectrum of single-crystal Ge is shown (5)

laxation is in the range of 100–250 ns. Substituting these values into Eq. (4) yields $L \approx 3.2 \mu\text{m}$, which is in good agreement with the experimental data. Thus, the temperature of the thermal wave up to $\approx 3 \mu\text{m}$ from the laser spot boundary exceeds the solid-phase crystallization threshold of GeSn ($T > 300\text{--}350^\circ\text{C}$), but remains well below the melting threshold. This is supported by SEM morphological observations: the film surface remains atomically smooth, and its crystallization proceeds purely due to the propagation of the lateral thermal front.

Fig. 5 presents the Raman scattering spectra of the 10-period Ge/Sn structure after fs laser annealing as a function of the cumulative energy density. It should be noted that while studying the Ge/Sn structures annealed by the ns laser, we analyzed the Raman spectra as a function of the single-pulse energy density, as one pulse was sufficient to crystallize the amorphous layer. For femtosecond annealing, a regime with a significantly lower energy density per pulse was selected; therefore, approximately 10^4 pulses must strike the same area to achieve crystallization. As a result, the cumulative effect drives film crystallization, with the total cumulative energy density being the governing parameter. The initial as-deposited film, as mentioned above, is amorphous, as evidenced by a broad featureless band centered at 256 cm^{-1} in the spectrum (Fig. 5, curve 1). Under fs laser annealing at a cumulative energy density of 150 J/cm^2 , an asymmetric Ge–Ge band characteristic of crystalline GeSn appears at

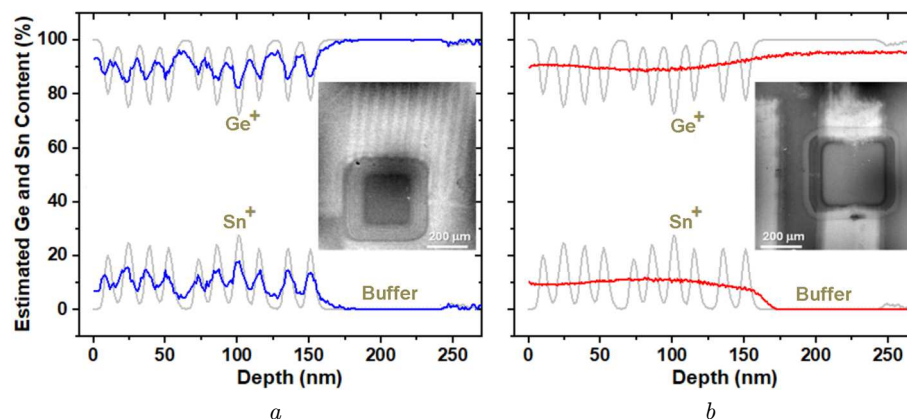
293.5 cm^{-1} . Note that for femtosecond annealing at a total energy density of less than 150 J/cm^2 , the Raman spectrum is a superposition of contributions from the amorphous and crystalline phases (spectrum not shown). An estimate of the tin content incorporated into the Ge crystal lattice, using spectrum 2 (Fig. 5) and Eq. (1), yields a value of $\sim 7.5 \text{ at.}\%$. A further increase in the total energy density leads to a gradual shift of the Ge–Ge band. Increasing the cumulative energy density causes a gradual shift of the Ge–Ge band toward higher frequencies, signaling enhanced Sn segregation processes. At a cumulative energy density as low as 170 J/cm^2 , the Ge–Ge peak shifts to 296.6 cm^{-1} , corresponding to a substitutional tin content of $3.7 \text{ at.}\%$ according to Eq. (1). Further increases in total energy lead to further Sn segregation.

Comparing the maximum substitutional Sn incorporation achieved via ns versus fs annealing indicates that the former yields a higher substitutional tin fraction: $10.3 \text{ vs. } 7.5 \text{ at.}\%$. This contrasts with theoretical expectations, according to which fs annealing should “freeze” Sn atoms into Ge lattice sites more effectively. To elucidate the reasons for this behavior, mass spectrometry measurements using secondary ion mass spectrometry were performed on initial, ns-annealed, and fs-annealed samples.

In Fig. 6, *a*, *b*, the profiles of Ge and Sn in GeSn films treated with ns (*a*) and fs (*b*) lasers are shown (blue and red curves, respectively), along with their distributions in the initial GeSn film (gray curves). All profiles were obtained from the ratio of ToF-SIMS signal intensities of Ge^+ and Sn^+ , normalized to the average Sn content according to EDS analysis.

In Fig. 6, *a*, an alternation of Ge and Sn layers is clearly observed in the initial film. After ns-laser annealing, the distribution profiles of Ge and Sn atoms remain similar, and at first glance it appears that complete intermixing of the elements does not occur; however, the oscillation amplitude of the Sn atomic concentration in adjacent layers decreases significantly. Furthermore, despite the absorption depth of ns-laser radiation with a wavelength of 355 nm in the GeSn film being only $10\text{--}20 \text{ nm}$, comparison of the profiles indicates that the distribution of Ge and Sn atoms undergoes changes throughout the entire thickness of the film. This indicates that the directed thermal front from the laser pulse reaches the inter-

Fig. 6. Profiles of Ge and Sn in the GeSn films treated with ns (a) and fs (b) lasers. Profiles of the initial film are also shown as gray curves. The profiles were obtained from the ratio of ToF-SIMS signal intensities of Ge^+ and Sn^+ , normalized to the average Sn content according to EDS analysis. The insets show the positions of the ToF-SIMS craters relative to the laser-treated areas of the film



face with the Si substrate. The incomplete intermixing of elements between layers observed in the profiles is because the crater formed during SIMS analysis partially covers the unannealed area of the film. As a result of the superposition of signals from the annealed and unannealed regions, such an averaged profile is obtained.

A different pattern of Ge and Sn atomic distribution is observed after fs-laser annealing (Fig. 6, b). In this case, the etching raster during SIMS measurements almost completely fell within the fs-treated area (see inset in Fig. 6, b), as a result of which interlayer oscillations of the Ge and Sn profiles are only weakly pronounced. At the same time, blurring of the interface between the film and the Ge buffer layer is observed: some Sn atoms diffuse into the buffer, while Ge atoms, conversely, diffuse into the film. Consequently, the effect of an increased number of Sn atoms at the lattice sites during fs-processing of the film – due to their ultrafast “freezing” – is compensated for by their intermixing with Ge atoms from the buffer layer.

The Ge content in Fig. 6, b does not reach 100% due to the diffusion of silicon into the buffer. Note that the diffusion of Si from the substrate or buffer layer into the GeSn film could induce a shift in the Ge–Ge mode. However, according to literature data, Si contributes noticeably to the shift in the frequency of the Ge–Ge vibrational mode only at concentrations $x_{\text{Si}} \geq 1$ at.%. At lower Si contents, this shift does not exceed the spectral resolution of the spectrometer (0.5 cm^{-1}). Furthermore, the recorded Raman spectra show no bands characteristic of local Si–Ge ($390\text{--}400 \text{ cm}^{-1}$) and Si–Si

($500\text{--}520 \text{ cm}^{-1}$) vibrations, confirming the absence of significant interfacial silicon intermixing in the studied active GeSn layer.

4. Conclusions

Polycrystalline GeSn films were fabricated and investigated by nano- and femtosecond laser annealing of amorphous layers grown on a Ge buffer layer on a Si(100) substrate, varying the pulse energy density for ns-radiation and the total energy density for fs-radiation. A comparative analysis of the obtained films was carried out, establishing that for ns-radiation, the most effective pulse energy density range for maximum incorporation of Sn atoms into Ge crystal lattice sites is $0.2\text{--}0.3 \text{ J/cm}^2$, with the substitutional tin content reaching 10.3 at.%, which agrees well with EDS analysis. A further increase in energy density leads to enhanced tin segregation, as the increased energy delivered to the material extends the cooling time and, accordingly, increases the duration of Sn diffusion. For fs-radiation, the most effective total energy density for Sn lattice incorporation is 150 J/cm^2 . The advantages provided by ultrafast heating and crystallization processes of the film during fs-annealing are somewhat offset by interfacial intermixing of atoms with the Ge buffer layer and Si substrate, as evidenced by SIMS profiles. On the other hand, fs-laser annealing makes it possible to obtain a film morphology substantially different from that obtained by ns processing. In particular, fs-laser processing is characterized by the formation of laser-induced periodic surface structures (LIPSS), which are promising for application in specialized optoelectronic devices.

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1. J.M. Carmona-Sanchez, J. Tiscareno-Ramirez, V. Aca-Aca, A. Hern'andez-Flores *et al.* Formation and structural characterization of amorphous GeSn thin films via solid-state Sn diffusion into hydrogenated amorphous germanium. *J. Alloys and Compounds* **1074**, 189195 (2026).
2. S. Gougam, M.A. Schubert, G. Capellini, M.H. Zoellner. Delayed epitaxial breakdown in MBE-grown GeSn epitaxial layers by high deposition rate and temperatures. *J. Phys. D: Appl. Phys.* **59**, 275106 (2026).
3. A.A. Corley-Wiciak, I. Zaitsev, O. Concepcion, D. Buca *et al.* Shedding light on epitaxial SiGeSn alloys with Raman spectroscopy: local order and thermomechanical properties. *J. Phys.: Condens. Matter.* **37**, 493002 (2025).
4. S. Gupta, B. Magyari-Kope, Y. Nishi, K.C. Saraswat. Achieving direct band gap in germanium through integration of Sn alloying and external strain. *J. Appl. Phys.* **113**, 073707 (2013).
5. S. Zaima, O. Nakatsuka, N. Taoka *et al.* Growth and applications of GeSn-related group-IV semiconductor materials. *Sci. Technol. Adv. Mater.* **16**, 043502 (2015).
6. R.W. Olesinski, G.J. Abbaschian. The Ge–Sn (Germanium-Tin) system Bull. *Alloy Phase Diagrams* **5**, 265 (1984).
7. S.V. Kondratenko, Y.V. Hyrka, Y.I. Mazur, A.V. Kuchuk *et al.* Photovoltage spectroscopy of direct and indirect bandgaps of strained $\text{Ge}_{1-x}\text{Sn}_x$ thin films on a Ge/Si (001) substrate. *Acta Mater.* **171**, 40 (2019).
8. S. Acharya, A. Fischer, N. Rosson, A. Said, H. Stanchu *et al.* High-quality GeSn grown in foundry mode via chemical vapor deposition enabling lasing up to 235 K. *J. Appl. Phys.* **138**, 173101 (2025).
9. V.O. Yuhymchuk, G.G. Tarasov, M.Ya. Valakh, P.M. Lytvyn *et al.* Synthesis of $\text{Ge}_{1-x}\text{Sn}_x$ and $\text{Ge}_{1-x-y}\text{Sn}_xC_y$ films by magnetron sputtering followed by laser annealing. *Semicond. Phys., Quantum Electron. & Optoelectron.* **29** (1), 019 (2026).
10. V.O. Yuhymchuk, P.M. Lytvyn, A.A. Korchovyi, O.Yo. Gudymenko *et al.* Laser-induced crystallisation of amorphous GeSn and GeSn:C films. *Mater. Res. Express* **12**, 115004 (2025).
11. V.O. Yuhymchuk, O.Yo. Gudymenko, T.M. Sabov, O.V. Dubikovskiy *et al.* Formation and properties of GeSn:C films on silicon substrates. *Semicond. Phys., Quantum Electron. & Optoelectron.* **27** (4), 412 (2024).
12. X. Wang, D. Qi, W. Zhou, H. Deng, Yu. Liu *et al.* Effect of Laser Pulse Width and Intensity Distribution on the Crystallographic Characteristics of GeSn Film. *Coatings* **13**, 453 (2023).
13. J. Zhang, S. Shangguan, W. Wang, W. Shi *et al.* Study on the Periodic Structure of Polycrystalline GeSn Prepared by Femtosecond Pulse Laser Direct Writing. *SSRN Electronic Journal*, <http://dx.doi.org/10.2139/ssrn.4402223> (2023).
14. O. Aktas, A.C. Peacock. Laser thermal processing of group IV semiconductors for integrated photonic systems. *Adv. Photonics Res.* **2**, 2000159 (2021).
15. J. Bonse. Quo vadis LIPSS? – Recent and future trends on laser-induced periodic surface structures. *Nanomaterials* **10**, 1950 (2020).
16. H. Lin, R. Chen, Yi. Huo *et al.* Raman study of strained $\text{Ge}_{1-x}\text{Sn}_x$ alloys. *Appl. Phys. Lett.* **98**, 261917 (2011).
17. T. Imajo, T. Suemasu, K. Toko. Strain effects on polycrystalline germanium thin films. *Sci. Rept.* **11**, 8333 (2021).
18. L.B. Freund, S. Suresh. *Thin Film Materials* (Cambridge Univ. Press, 2010).
19. Yi. Jie, A.T.S. Wee, C.H.A. Huan, Z.X. Shen, W.K. Choi. Phonon confinement in Ge nanocrystals in silicon oxide matrix. *J. Appl. Phys.* **109**, 033107 (2011).
20. J.I. Langford, A.J.C. Wilson. Scherrer after sixty years: A survey and some new results in the determination of crystallite size. *J. Appl. Crystallogr.* **11** (2), 102 (1978).

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ЛАЗЕРНО-ІНДУКОВАНА КРИСТАЛІЗАЦІЯ БАГАТОШАРОВИХ АМОРФНИХ ПЛІВОК Ge/Sn

Проведено порівняльний аналіз структурно-морфологічних та оптичних властивостей полікристалічних плівок GeSn товщиною 150 нм, сформованих методом лазерного відпа-лу аморфних багатошарових гетероструктур на буферному шарі Ge/Si(100) з використанням двох типів випромінюван-ня: імпульсного наносекундного ($\lambda = 355$ нм) і фемтосекун-дного ($\lambda = 800$ нм). За даними спектроскопії раманівського розсіювання світла та X-променевої дифрактометрії (XRD) встановлено, що імпульсний наносекундний УФ-відпал у вузькому діапазоні густини енергії імпульсу 0,2–0,3 Дж/см² є найефективнішим для збереження планарності поверхні та досягнення максимального замісного вбудовування оло-ва у вузли ґратки германію (до 10,3 ат.% Sn). Фемтосекун-дний відпал забезпечує дещо нижчий рівень інкорпорації олова (7,5 ат.%) унаслідок міжфазного перемішування еле-ментів Sn та Ge між плівкою та буферним шаром, що під-тверджено профілями SIMS. Показано, що морфологія по-верхні плівок за умов використання цих двох типів лазер-ної обробки також суттєво відрізняється: зокрема, фемто-секундний відпал спричиняє самоорганізацію поверхневих періодичних структур (LIPSS), які є перспективними для використання в спеціальних оптоелектронних пристроях.

Ключові слова: плівки GeSn, лазерний відпал, наносе-кундний лазер, фемтосекундний лазер, XRD, CEM, SIMS, раманівська спектроскопія, сегрегація.