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Carrier dynamics in thin Germanium Tin epilayers

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The Si-based mid-infrared silicon photonics is an emerging technology in which group-IV Germanium Tin ($\text{Ge}_{1-x}\text{Sn}_x$) binary alloy can play a fundamental role in development of a Si-compatible photonic components including monolithically integrated coherent light sources and detectors, on the same Si or SOI substrate. Although the GeSn-on-Si lasers, at low temperatures, have already been demonstrated, the knowledge of the material properties necessary for such device optimization and real life usage is very limited. In particular, carrier relaxation kinetics, relaxation pathways, and accompanied physical mechanisms, important for the laser's dynamics, have not been subjected to in depth research and understanding. In this work, we present detailed spectroscopic studies on photo-injected carrier dynamics in $\text{Ge}_{1-x}\text{Sn}_x$ epilayers, as a function of Sn content ($\sim 6\text{--}12\%$) and temperature ($20\text{--}300\text{ K}$), by utilizing time-resolved differential reflectivity and photoluminescence. While the latter technique allowed to track separated electron and hole dynamics with a femtosecond time resolution, the former experiment exploited a joined electron-hole recombination. This experimental approach allowed to identify: (i) two initial electron relaxation processes after photo-excitation; (ii) radiative electron-hole recombination on below-bandgap-states; (iii) non-radiative carrier recombination involving the Shockley-Read-Hall mechanism; (iv) non-radiative recombination through the surface states. The research results significantly expand the knowledge on the initial carrier relaxation dynamics in the $\text{Ge}_{1-x}\text{Sn}_x$ epitaxial material. It provides unknown up-to-date kinetic parameters of the initial stage of electron relaxation and further carrier recombination dynamics, unveils the critical role of bandgap inhomogeneity for the relaxation dynamics, and highlights the role of below-bandgap states that can participate in the light generation process in $\text{Ge}_{1-x}\text{Sn}_x$ epilayers.

Introduction

The development of silicon (Si) photonic devices operating in the mid-infrared (MIR) spectral region ($3 - 50\text{ }\mu\text{m}$) of electromagnetic spectrum has achieved remarkable progress. Waveguides, splitters, resonators, modulators, switches, light detectors, and light sources are the key elements of the photonic integrated circuits that now can be merged into a single Si-based platform achieving new functionalities and better performance at a reduced price and lower energy consumption. This should open vast application possibilities from free-space data communication and MIR imaging of biological structures to portable MIR lab-on-a-chip spectroscopic measurements or tracing chemical elements in different states of matter using a sensor-in-a-chip platform. Nevertheless, one of a major problem is a lack of the Si-compatible light source operating in the mid-infrared spectral region. Currently considered solutions include III-V (GaSb, InP and others) and group-IV ($\text{Ge}_{1-x}\text{Sn}_x$)

semiconductor materials epitaxially grown directly on Si or via a relaxed Ge buffer. The latter one, employing the $\text{Ge}_{1-x}\text{Sn}_x$ binary alloy is a very attractive solution, because it permits creation of all group-IV (Si, Ge, $\text{Si}_{1-x}\text{Ge}_x$ and $\text{Ge}_{1-x}\text{Sn}_x$) monolithically integrated photonic platform on Si. Since the first demonstration of the $\text{Ge}_{1-x}\text{Sn}_x$ lasing at low-temperature in 2015, the number of reports on the lasing in the bulk-like $\text{Ge}_{1-x}\text{Sn}_x$ material has been expanding rapidly, giving a spark for further development of this technology.

Unstrained or bulk Ge is an indirect-gap semiconductor with a bandgap energy $E_{\text{L,Ge}} \approx 0.66 \text{ eV}$ at a room temperature (RT) between the conduction band minimum at the L-point of the Brillouin zone and the valence band maximum at the Γ -point. The direct energy gap is shifted up of $\sim 0.14 \text{ eV}$ and located at the Γ -point. Incorporation of Sn and formation of the $\text{Ge}_{1-x}\text{Sn}_x$ alloy causes the faster energy down shift of the Γ -point conduction band minimum with the Sn content than that for the L-point. It results in the conversion from indirect to, the favorable for optical devices, direct gap semiconductor at $x \sim 0.08$ and yields the direct energy gap tuning range between 0.6 eV ($2.066 \text{ }\mu\text{m}$) to 0.29 eV ($4.275 \text{ }\mu\text{m}$) at RT with the x varied from 0.08 to 0.23. This picture can be strongly modified by the existence of strain originating from the $\sim 15\%$ lattice mismatch between α -Sn and Ge, which shifts the indirect-to-direct band crossover to the higher Sn content. Additionally, the strain relaxation at the higher Sn content may induce a large density of misfit dislocations, e.g., edge and threading dislocations, stacking faults, and twin boundaries that can strongly imprint radiative and non-radiative processes in $\text{Ge}_{1-x}\text{Sn}_x$, affecting the device performance. One would expect that this can as well imprint carrier relaxation dynamics important for dynamic parameters of devices.

Carrier relaxation dynamics in $\text{Ge}_{1-x}\text{Sn}_x$ epitaxial layers have not been studied in-depth, mostly due to a problematic spectral range for the most suitable time-resolved experiments to be performed. The initial information comes from Ref. . Kinetic parameters were extracted not from time-resolved studies but indirectly evaluated from temperature-dependent PL experiments after applying a many-parameters physical model. In this case, the low-temperature ($T = 10 \text{ K}$) carrier lifetime was estimated to $\sim 2.1 \text{ ns}$ and decreased to $\sim 0.35 \text{ ns}$ at RT following the temperature-dependent Shockley-Read-Hall (SRH) recombination process. Kinetic parameters were revealed only for a single, more than 200-nm-thick GeSn layer. Later, in Ref. , the time-resolved photoluminescence (TRPL) technique was applied to measure T -dependent PL dynamics for a thin $\text{Ge}_{0.95}\text{Sn}_{0.05}$ layer. Data analysis yielded the carrier lifetime of $\sim 2.0 \text{ ns}$ at $T = 10 \text{ K}$ decreasing with temperature to $\sim 0.8 \text{ ns}$ at $T \approx 150 \text{ K}$. Furthermore, in this case, the SRH recombination processes were suggested as dominating the observed PL dynamics. Finally, a very recent study utilized time-gated PL via the up-conversion process in a non-linear crystal and at $T = 20 \text{ K}$ revealed of $\sim 217 \text{ ps}$ carrier lifetime for a 350-nm-thick $\text{Ge}_{0.875}\text{Sn}_{0.125}$ layer arguing that the SRH recombination is nearly temperature independent, which is a strike difference to the conclusions derived from the previous research. The common drawback of the mentioned experiments is that the interpretation of

experimental data comes from the PL, assuming to be originated from the direct-gap transition in GeSn at a high-enough Sn content. However, it is already proved that the PL can have its origin in point and extended defects at dislocations energetically located in the GeSn bandgap. Therefore, the interpretation of carrier relaxation processes in GeSn is an issue demanding more advanced research. This work aims to expand the knowledge on minority carrier dynamics in GeSn epilayers with a variable Sn content ranging from $\sim 6\text{--}12\%$. The research is based on the complementary experimental techniques: PL, TRPL, photoreflectance ($\Delta R/R$), and time-resolved differential reflectivity (TRDR), revealing emission and absorption properties of the system in question and giving insights into radiative and non-radiative relaxation and recombination pathways. Based on both experiments' nature, we identify the separated contribution of defect-related radiative and trap-related non-radiative states into the overall carrier kinetics evolving differently in the temperature range between $10\text{--}300\text{ K}$.

Results and discussion

Low-temperature PL and photoreflectance experiments

[fig:PRandPL] (a) $\Delta R/R$ (solid black line) and PL spectra (a shaded grey area) for the virtual Ge substrate (v-Ge) on Si. A solid red line indicates the fitting function as described in Supporting information, S2. (b)-(f) $\Delta R/R$ (solid black line) and PL spectra (a shaded grey area) for GeSn/v-Ge structures with various Sn content. A Gaussian fit to the high-energy-side PL peak is plotted in blue. A solid red line depicts the fits to the GeSn-related $\Delta R/R$ feature. The obtained direct energy gap ($E_T = E_T^{HH}$) is indicated by an arrow, as well as the estimated indirect energy gap for the strained material (E_L^s), and the light-hole energy transition (E_L^H). γ is a spectral broadening of the $\Delta R/R$ feature. $T=20\text{ K}$, $P_{\text{PL}}=100\text{ mW}$, $d_{\text{spot}}=150\text{ }\mu\text{m}$. (g)

E_F (red points) and PL peak energies (blue points) plotted with the Sn content in $\text{Ge}_{1-x}\text{Sn}_x$ epilayers. (h) Sketch of a GeSn bandstructure in the momentum(k)-vector space with inhomogeneously broadened conduction bands (Γ_c and L). Γ_v is the valence band. Blue areas indicate below-bandgap states for electrons and holes.

The results of low-temperature PL and $\Delta R/R$ experiments presented in Fig. 1 give a relevant background prior to discussing carrier dynamics in the $\text{Ge}_{1-x}\text{Sn}_x$ epilayers. Fig. 1(b)–(f) (solid black line) present $\Delta R/R$ features spread around ~ 0.87 eV. These optical transitions are devoted to the absorption process involving the edges of valence and conduction bands at the Γ point of the Brillouin zone in germanium. It is confirmed by a similar type of $\Delta R/R$ feature shown in Fig. 1(a) for the reference v-Ge substrate. In this case, the $\Delta R/R$ line-shape was fitted to the low-field electro-modulation formula (see Supporting information, S2). The extracted direct gap energy for the v-Ge epilayer is $E_{\Gamma,\text{Ge}}^S = 0.87 \pm 0.02$ eV, informing on the existence of residual strain. Raman spectroscopy (see Supporting information, S1) revealed that the build-in residual biaxial tensile strain is $\sim 0.23\%$ originating from the mismatch of the thermal expansions between v-Ge and Si. The same conclusion holds for the v-Ge substrates with $\text{Ge}_{1-x}\text{Sn}_x$ epilayers on top.

Fig. 1(b)–(f) reveals other $\Delta R/R$ features on the low-energy part of absorption-like spectra, shifting towards lower energy with the increase of Sn mole fraction. They are attributed to the absorption-like direct-gap optical transitions involving top-most, strain-split heavy-hole (HH) valence (Γ_v^{HH}) and conduction (Γ_c) bands at the Γ point of the Brillouin zone in $\text{Ge}_{1-x}\text{Sn}_x$ epilayers. The transition is sketched in Fig. 1(h) as an up-pointed red arrow. The role of the strain-split light-hole (LH) valence band in optical transitions is omitted due to the sizable HH-LH splitting energy (> 75 meV) and low oscillator strength of the $\Gamma_v^{\text{LH}} - \Gamma_c$ optical transition (see Supporting information, S2). The effective direct gap energy (E_F) is extracted from $\Delta R/R$ features according to the fitting procedure described in the Supporting information, S2. The fitting curves are plotted in Fig. 1(b)–(f) (solid red line) with arrows indicating E_{Γ}^{HH} and E_{Γ}^{LH} energies. In the article, we refer to E_{Γ}^{HH} as E_F , if not other stated. Please note, the $\Delta R/R$ features representing the direct gap optical transition in GeSn are spectrally broad. The extracted broadening parameter (γ) equals around ~ 50 meV for all the structures (see Supporting information, S2). It reflects the bandgap inhomogeneity due to strain variation, electric field conditions, and fluctuation of chemical composition across the surface area from which the optical signal was derived. It is justified to assume that the spatial inhomogeneity of the Γ band is translated on-to the L band and any other bands in GeSn with significant consequences for the observed carrier dynamics. The spectral overlapping of the inhomogeneously broadened bands indicated in Fig. 1(b)–(f) (superimposed grey-shaded rectangle areas centred at the E_F and E_L^S) may suggest the multi-component character of the time-resolved optical response taken from a different spectral region.

The extracted E_F plotted as a function of the Sn content in Fig. 1(g) provides further information on the band structure of $\text{Ge}_{1-x}\text{Sn}_x$ epilayers. The figure contains calculated curves representing theoretically-estimated changes in the direct and indirect gap energy for the case of unstrained and compressively strained $\text{Ge}_{1-x}\text{Sn}_x$ material (see Supporting information, S3). The comparison of E_F and theoretical values demonstrates that the

examined epilayers are truly strained (see also Supporting information, S1, S2, and S5). The expected crossover between indirect-to-direct gap GeSn should occur at $x > 0.20$. It means that in the considered range of chemical composition, the $\text{Ge}_{1-x}\text{Sn}_x$ epilayers remain indirect-gap semiconductors with poor abilities for light emission. However, this conclusion stays in contrast to the results of PL experiments presented in Fig. 1(b)–(f) (grey and blue shaded areas).

The PL response consists of two superimposed emission bands. The lower-energy PL band located near 0.51 eV is unchanging with the Sn mole fraction and matches PL emission from the reference $\nu\text{-Ge}$ substrate presented in Fig. 1(a). This PL band is attributed to the electron-hole recombination at a defect-on-dislocation in germanium. The higher-energy PL band was fitted by a Gaussian-line profile plotted as a blue-shaded area in Fig. 1(b)–(f). The extracted PL peak energies (E_{PL}) are presented in Fig. 1(g) (blue points), showing that the E_{PL} is shifting with the Sn mole fraction towards low energies. The observation suggests that the PL band is originated from a $\text{Ge}_{1-x}\text{Sn}_x$ epilayer. Moreover, the E_{PL} shows a sizable $>39\text{ meV}$ down-shift in respect to E_{r} (see Supporting information, Tab. S1), and apparently, it is lower than a theoretically-estimated indirect energy gap (E_{L}^{s}) for the compressively strained GeSn. These findings suggest that the considered PL emission can have similar nature as the one observed for $\nu\text{-Ge}$ at 0.51 eV . It can come from the electron-hole recombination at optically active defects-on-dislocations driven by the plastic strain relaxation in the $\text{Ge}_{1-x}\text{Sn}_x$ epilayers grown on the $\nu\text{-Ge}$ substrate. The defects are associated with the Lomer 90° or 60° -type dislocations. In the latter case, it would form a band-like distribution of electronic states even up to 150 meV below the Γ_{v} . Other reports suggest the existence of point-like dislocation-related defects, they may also be optically active. These defects are found $20\text{--}30\text{ meV}$ below the Γ_{v} . They are partially energetically superimposed with the Sn-related acceptor-type multi-vacancy complexes spanning the range of $5\text{--}20\text{ meV}$ below the Γ_{v} . These types of Sn-related shallow acceptors are seemed to be responsible for the p-type of unintentionally-doped GeSn epilayers. These states are sketched as N_{h} in Fig. 1(h). Assuming the presence of donor states near the conduction band and depicting them as N_{e} in Fig. 1(h), the PL can be plotted as the optical transition between the N_{e} and N_{h} (down-pointed blue arrow).

The conclusions from steady-state experiments are the following: (i) the examined $\text{Ge}_{1-x}\text{Sn}_x$ epilayers are indirect-gap semiconductors with the lack of PL emission from the direct gap; (ii) PL emission comes from the below-bandgap states; (iii) the $\text{Ge}_{1-x}\text{Sn}_x$ bandgap structure suffers spatial variations across the surface area of a sample indicated by the substantial ($>39\text{ meV}$) broadening of the $\Delta R/R$ feature.

Low-temperature TRDR and TRPL experiments

[fig:RelvsE] Energy dispersion of extracted kinetic parameters for $\text{Ge}_{1-x}\text{Sn}_x$ epilayers at $T = 20 \text{ K}$ and $P_{\text{pump}} = 7 \text{ mW}$: (f)–(j) PL lifetime – τ_{PL} (yellow circles), short TRDR lifetime component – $\tau_{DR,S}$ (red squares), long TRDR lifetime component – $\tau_{DR,L}$ (open black squares). (a)–(e) fast TRDR rise time component – τ_f (blue triangles), slow TRDR rise time component – τ_s (green triangles). Vertical dashed lines the E_Γ energy. (k) Sketch of the GeSn band structure with possible relaxation pathways indicated by solid arrows.

The discussion on carrier dynamics in the $\text{Ge}_{1-x}\text{Sn}_x$ epilayers begins with presenting the results of TRDR experiment at $T = 20 \text{ K}$. The TRDR traces are recorded as a function of the probe pulse energy (E_{probe}) with a fixed pump pulse energy ($E_{\text{pump}} = 1.49 \text{ eV}$) (see Supporting information, S4). The analysis yielded that the ascendant amplitude of TRDR is contributed by two processes having different time scales. The fitting procedure to the double exponential rise function provides two characteristic time constants nearly independent on the Sn mole fraction and E_{probe} : the fast one (τ_f), falling into the range of $1\text{--}7 \text{ ps}$, and the slow one (τ_s) being within the $23\text{--}40 \text{ ps}$ range. These results are summarized in Fig. 2(a)–(e). The lack of τ_f for the $\text{Ge}_{0.94}\text{Sn}_{0.06}$ epilayer is due to a small amplitude of an underlying process that could not be trustfully recovered by the fit. Since the structures are p-type, one can assume that relaxation mechanisms and possible relaxation pathways, which are behind the extracted kinetic parameters, are related to photo-generated minority carriers, namely electrons.

In the beginning, we consider the building-up of the carrier population at the states addressed by the E_{probe} above the effective E_Γ ($E_{\text{probe}} > E_\Gamma$), where the overlap of Γ_c and L bands is negligible. The electron population photo-injected much above the minimum of the

Γ_c band is rapidly thermalizing to the bottom of the Γ_c band and to the X-band and finally to the L-band, through the interaction with optical and acoustic phonons. This is sketched by blue arrows in Fig. 2(k). The discussion skips Auger processes due to the insufficient photo-injected carrier population density, roughly $9 \times 10^{13} \text{ cm}^{-2}$ per pulse. For the reference case of germanium, the measured electron relaxation at $T = 300 \text{ K}$ is varied from 0.1 ps and includes: electron relaxation within the Γ_c band ($\sim 0.1 \text{ ps}$), hot electrons transfer from Γ_c to L (0.2 ps), cold electrons transfer from Γ_c to L (1.2 ps), X to L transition (0.4 ps), and Γ_c to X transfer (0.1 ps). At low temperatures, these time constants are expected to be slightly higher due to the lower phonon states density, and thus relaxation times end up in a few ps range. One can conclude that the τ_f component extracted here for the $\text{Ge}_{1-x}\text{Sn}_x$ epilayers can have the same origin as the above-mentioned for germanium.

The existence of the τ_s component of the ascending TRDR amplitude at $E_{\text{probe}} > E_\Gamma$ is more puzzling. While the carrier relaxation process among 3D densities of states to the bottom of the Γ_c should be relatively fast, as indicated by τ_f , it is hard to find other processes that could slow down the relaxation. However, we can propose the mechanism that emerges from the observed spatial inhomogeneity of the GeSn band-structure represented by the γ parameter. During the relaxation, carriers can be trapped by local confining potential islands spatially distributed within the spot area of an excitation pulse. Thus, the τ_s can represent a carriers redistribution or a tunnelling process between these confining potentials, similar to the carrier relaxation among spatially localized states in the 2D wetting layer of Stranski-Krastanow quantum dots. This scenario seems to be supported by the temperature-dependent TRDR experiment that will be later discussed in the article.

For the case, when $E_L^S \leq E_{\text{probe}} \leq E_\Gamma$, the τ_f and τ_s are nearly unchanged as compared to the case when $E_{\text{probe}} > E_\Gamma$, which is nothing unexpected. A surprising finding is the lack of changes when the E_{probe} is below the L bands' spectrally-broad distribution (see Fig. 2(b)). It can suggest that fast building-up of the carrier population at the bands' edges is equally efficient for some below bandgap states, or the inhomogeneity of L bands is more extensive.

Let us move to discuss the slowly decaying TRDR amplitude, which is related to the depopulation of a density of states addressed by the E_{probe} . The TRDR decay curve analysis implies that at least two decay components contribute to it (see Supporting information, S4). Therefore, the decay is characterized by the fast ($\tau_{d,f}$) and slow ($\tau_{d,s}$) decay time constants plotted in Fig. 2(f)–(j) as a function of E_{probe} .

First, we discuss the results when $E_{\text{probe}} < E_L^S$. Please note the spectral overlapping of the PL band (blue-shaded Gaussian profile) with the spectrally-broadened E_L^S (grey-shaded rectangle) presented in Fig. 2(f)–(j). In this spectral range, the probe pulse measures a carrier population decay in at least two families of states: (a) below-bandgap states associated with defects in GeSn and partially contributing to the observed PL emission, and (b) the L band states due to the band structure inhomogeneity. The extracted $\tau_{d,f}$ and $\tau_{d,s}$ are shifted apart, pointing to two different carrier relaxation pathways present in all the structures. For the $E_{\text{probe}} < E_L^S$, the $\tau_{d,s}$ is saturated at a maximum value without exhibiting a clear dispersion

across the energy scale, reaching 0.9 ± 0.1 ns for the $\text{Ge}_{0.94}\text{Sn}_{0.06}$ epilayer and 1.1 ± 0.1 ns for the rest of the structures. Conversely, the $\tau_{d,s}$ shows a strong dispersion ($\tau_{d,f}(E_{\text{probe}})$) in the discussed energy range. For the $\text{Ge}_{0.94}\text{Sn}_{0.06}$ epilayer, the $\tau_{d,f}(E_{\text{probe}})$ increases from ~ 520 ps at $E_{\text{probe}} \approx E_{\Gamma}$ to ~ 730 ps at $E_{\text{probe}} < E_{\Gamma}$ defining the $\tau_{d,f}(E_{\text{probe}})$ variation range: $\Delta\tau_{d,f} \approx 210$ ps. When the Sn content increases, the high-energy value of $\tau_{d,f}(E_{\text{probe}})$ decreases accompanied by the decrease in $\Delta\tau_{d,f}$.

It is instructive to compare the results of TRDR with these from the TRPL experiment to identify the relaxation processes that stay behind the $\tau_{d,f}$ and $\tau_{d,s}$ kinetic parameters. These cases are limited to the $\text{Ge}_{1-x}\text{Sn}_x$ epilayers with $x = 0.06, 0.085$, and 0.095 , for which the PL emission band is within the spectral range of the superconducting detector. The TRPL traces are recorded as a function of emission energy. Each TRPL trace is characterized by a resolution-limited rise and a slow, mono-exponential decay (see Supporting information, S4). The extracted PL decay time (τ_{PL}) is plotted in Fig. 2(f)–(h) (yellow points) as a function of emission energy. The $\tau_{\text{PL}}(E)$, which clearly starts below the E_{L}^{S} edge, is nearly identical to the $\tau_{d,f}(E_{\text{probe}})$. This observation allows ascribing the $\tau_{d,f}$ measured for the $E_{\text{probe}} < E_{\Gamma}$ as contributed by the effective radiative lifetime of electron-hole pairs at a defect band in GeSn. Whereas the $\tau_{d,s}$ is attributed to the purely non-radiative recombination of presumable electrons in the L band within the trap states N_{T} which are contributed either by the bulk traps or surface states. The energy dispersion of τ_{PL} and $\tau_{d,f}$ reminds the dispersion for optically-active localized states in disordered semiconductor alloys or quantum wells, which could also be the case for the examined GeSn epilayers. From this standpoint, the dispersion can be considered as generated by a carrier migration among optically active higher- to lower-energy states additionally affected by the non-radiative recombination channels. non-radiative recombination impact is reflected in the damping of the dispersion curve seen through the $\Delta\tau_{d,f}$ parameter. The $\Delta\tau_{d,f}$ steadily decreases with the increase of Sn content, from ~ 294 ps for the $\text{Ge}_{0.915}\text{Sn}_{0.085}$ to ~ 109 ps for the $\text{Ge}_{0.88}\text{Sn}_{0.012}$ epilayer and would be correlated with the increased number of non-radiative states generated by strain or point defects which are induced by the incorporation of tin atoms into the Ge matrix. While the possible nature of radiative states has already been discussed for the steady-state experiments, it is hard to point to the specific non-radiative recombination centres. However, the $\tau_{d,s}$ measured in the energy range around the E_{L}^{S} edge can be tentatively assigned to the SRH recombination lifetime.

It is interesting to compare the TRPL results with those previously published. The ~ 2 ns PL lifetime reported in Ref. for a thin $\text{Ge}_{0.95}\text{Sn}_{0.05}$ layer is longer than ~ 0.5 ns obtained here. From the one hand side, it could be related to a high excitation condition specific for the performed experiment. On the other hand, the reported epilayer could have good optical quality, translating to reduced non-radiative recombination. The results presented in Ref. seem to be more consistent with ours. The ~ 217 ps PL lifetime for the 350-nm-thick $\text{Ge}_{0.875}\text{Sn}_{0.125}$ is comparable to ~ 320 ps for the 36-nm-thick $\text{Ge}_{0.88}\text{Sn}_{0.12}$ epilayer. The lifetime difference can be attributed to the thick epilayer's deteriorated crystal quality due to a bit higher Sn content and strain

relaxation above the critical thickness leading to the enlargement of defect states density. Note that literature data did not provide any other kinetic parameters related to non-radiative recombination channels.

Now, we shift the discussion towards $\tau_{d,f}$ and $\tau_{d,s}$ obtained at energy states above the GeSn conduction band minimum ($E_{\text{probe}} > E_L^s$). In this case, Fig. 2(f)–(j) show that the $\tau_{d,s}$ is relatively little affected when the E_{probe} approaches the E_L^s , but it suffers a huge drop when crossing the E_Γ . To interpret this observation, one needs to recall the substantial inhomogeneity of the L and Γ bands resulting in a spectral overlap of related densities of states. Thus, for the $E_{\text{probe}} > E_\Gamma$, the contribution of rapid relaxation phenomena represented by τ_f and τ_s overcomes the non-radiative relaxation that occurs on the decreasing number of states at the high-energy tail of the L-band distribution. Conversely, when the E_{probe} approaches the low-energy tail of the inhomogeneously-broadened L band distribution, the rapid relaxation processes' contribution is reduced. Thus, the $\tau_{d,s}$ is governed by a relatively slow non-radiative relaxation at the L-band. It is also affected by the carrier relaxation at the high-energy tail of the defect distribution.

The more puzzling behaviour concerns the $\tau_{d,f}$. As it was already stated, for $E_{\text{probe}} < E_L^s$, the $\tau_{d,f}$ is partially related to radiative recombination at below-bandgap states and suffers the characteristic energy dispersion. However, when the E_{probe} is shifting above the E_L^s , the $\tau_{d,f}(E_{\text{probe}})$ is getting nearly dispersionless even above the effective E_Γ . The $\tau_{d,f} \approx 200 \text{ ps}$ obtained for the structures at $E_{\text{probe}} > E_L^s$ is close to the value of surface recombination lifetime ($\sim 500 \text{ ps}$) estimated from the $\tau_{\text{surf}} = W/2s$ expression. Here, the surface recombination velocity $s = 4000 \text{ cm/s}$ obtained for the Ge/Si interface, and the layer thickness W is taken from Tab. 1. A similar surface recombination velocity of $170 \pm 35 \text{ ps}$ was measured for the 220-nm-thick $\text{Ge}_{0.875}\text{Sn}_{0.125}$ epilayer on Ge. Therefore, we believe that $\tau_{d,f}$ at $E_{\text{probe}} > E_L^s$ is getting dominated by the surface recombination at the GeSn/Ge or GeSn/air interface.

Temperature-dependent TRDR and TRPL experiments

[fig:Tdep] Temperature dependence of (a) - TRDR rise times (τ_f , τ_s), and (b) - TRDR decay times ($\tau_{d,f}$, $\tau_{d,s}$) extracted for the Ge_{1-x}Sn_x epilayers with $x=0.06$ (open and full triangles and squares in red), $x=0.095$ (open and full triangles and squares in green), $x=0.11$ (open and full triangles and squares in blue). Red, green and blue lines in (a) represent the fitting curves for a phonon-mediated relaxation process. Red, green and blue dashed lines in (b) are guides to the eye. $E_{\text{pump}}=1.52$ eV, $E_{\text{probe}} \approx E_{\Gamma}$, $P_{\text{pump}}=7$ mW.

The temperature-dependent TRDR experiment provides additional arguments supporting the stated hypothesis on existing carrier relaxation channels and mechanisms in the studied Ge_{1-x}Sn_x epilayers. Three Ge_{1-x}Sn_x epilayers were selected for these studies having the Sn content of 6%, 9.5%, and 11%. In the experiment, the $E_{\text{probe}} \approx E_{\text{L}}^{\text{S}}$ (see orange points in Fig. 2(f), (h), and (i)) and accounts for the temperature-driven GeSn bandgap evolution. The extracted TRDR amplitude rise ($\tau_f(T)$, $\tau_s(T)$) and decay times ($\tau_{d,f}(T)$, $\tau_{d,s}(T)$) from the TRDR traces are plotted in Fig. 3. Fig. 3(a) shows that both rise times are getting shorter with T . While the overall decrease in the τ_f reaches a few picoseconds between low and high temperature, the reduction in the τ_s is a few tens of picoseconds. The behaviour of the $\tau_s(T)$ function can be interpreted with the postulated picture that includes spatial fluctuation of the GeSn bandgap. The decline of $\tau_d(T)$ with T can be governed by the smearing of spatially-distributed inhomogeneous confining potentials by the $k_{\text{B}}T$ energy, where k_{B} is the Boltzmann constant. Besides, the increasing phonon population at elevated temperatures accelerates carrier-phonon scattering and increases energy relaxation and carrier transfer efficiency among localized sites. It leads to the diminishing of the role of spatial localization promoting the fast carrier relaxation typical for bulk material over the carrier-hopping-like processes among localized sites in inhomogeneous GeSn.

The temperature evolution of decay time constants presented in Fig. 3(b) shows that the observed carrier recombination channels identified by $\tau_{d,s}$ and $\tau_{d,f}$ have a different origin due to the very different temperature characteristics. In the temperature range $10\text{--}100\text{ K}$, the $\tau_{d,s}(T)$ decreases almost twice with T . This behaviour is consistent with the bulk-like SRH process. The carrier capture efficiency by trap states N_T increases with temperature. Interestingly, the speed-up of non-radiative recombination is accompanied by the T -enhanced carrier population at the examined states reflected in the increase of $\tau_{d,s}(T)$ for $T > 100\text{ K}$. The activation temperature at which the states located near the E_L^S are getting populated varies from $\sim 80\text{ K}$ for the $\text{Ge}_{0.89}\text{Sn}_{0.11}$ epilayer to $\sim 160\text{ K}$ for the $\text{Ge}_{0.905}\text{Sn}_{0.095}$ and $\text{Ge}_{0.94}\text{Sn}_{0.06}$ epilayers. The smallest activation temperature for the highest-Sn-content structure can be attributed to the larger population of trap states with their wider energy distribution in the GeSn bandgap. It is interesting to correlate this specific $\tau_{d,s}(T)$ function with the published results of electrical measurements performed on GeSn, looking for a possible origin for the carrier activation source at elevated temperatures. have investigated temperature-dependent electrical transport characteristics extracted from the dark current-voltage curves of a GeSn/Ge device. The dark resistance of a device stops decreasing at $T \approx 160\text{ K}$ with increasing temperature, attributed to the increasing number of carriers in the conduction band originated from the unspecified surface or bulk-like defect states. have used conventional Deep Level Transient Spectroscopy (DLTS) to study defects in a GeSn/Ge diode. The temperature-controlled DLTS experiment allowed to identify minority carrier (electrons) traps in the diode showing pronounced DLTS deeps at $\sim 100\text{ K}$ and $\sim 150\text{ K}$. These were attributed to defects at the hetero-junction and the bulk-like-traps in the GeSn epilayer and/or the virtual Ge substrate, respectively. However, the exact origin of defects was not clarified. Finally, in Ref. the DLTS experiment has also been used to investigate the GeSn/Ge junction diode. The DLTS spectra have revealed deeps smeared between 100 K and 150 K . The deeps were attributed to the extended-defect-like-states identified as the deep, repulsive-like donor centres with a band-like distribution in the GeSn bandgap. In the same studies, the T -dependent reverse-bias current density increased significantly at $T > 160\text{ K}$, suggesting that these defects may be a source of minority carriers in the conduction band at elevated temperatures.

The above-mentioned temperature-driven carrier dynamics can be completed by the discussion on the $\tau_{d,f}(T)$ function. Figure 3(b) shows the $\tau_{d,f}(T)$ is nearly temperature-independent up to $T \approx 150\text{ K}$, which is in high contrast to the $\tau_{d,s}(T)$ function. At $T > 150\text{ K}$, the $\tau_{d,f}$ slightly increases with T but not as much as the $\tau_{d,s}$. While the SRH recombination involves the deep, bulk-like traps, the $\tau_{d,f}$ obtained at E_L^S must describe another recombination channel. Since it is weakly temperature-dependent, it could be indeed related to the surface recombination.

Conclusions

In conclusion, we investigated carrier dynamics in compressively strained and indirect bandgap $\text{Ge}_{1-x}\text{Sn}_x$ epilayers grown on Ge/Si(001) virtual substrate. Sn content, x , was varied

between 6% and 12%. The use of complementary optical methods, including TRDR and TRPL and supported by data obtained from the steady-state spectroscopic experiments (PL, $\Delta R/R$, Raman), allowed us to measure carrier kinetics and to identify possible carrier relaxation pathways and recombination mechanisms. Our results show some similarities to previous reports on carrier dynamics in $\text{Ge}_{1-x}\text{Sn}_x$ epilayers, but they considerably expand knowledge on newly observed carrier recombination channels, unveiled by the TRDR experiment.

We found that initial electron relaxation, just after the photo-excitation at $T = 20$ K, is contributed by two processes: fast one characterized by the ~ 1 ps relaxation time, and slow one falling into the range of ~ 23 – 40 ps. This was not previously reported for $\text{Ge}_{1-x}\text{Sn}_x$ epilayers. While the fast relaxation process is related to electron thermalization through interaction with phonons to the bottom of the Γ band and further to the L band, the slower process is attributed to the postulated carrier transfer between spatially localized potential landscapes, generated by the inherent inhomogeneities of $\text{Ge}_{1-x}\text{Sn}_x$ epilayers. Thermal averaging of confining potentials with increasing temperature leads to a substantial speed-up of the slow component towards the values of the fast relaxation time. The initial electron relaxation is followed by its radiative and non-radiative recombination reflected in the composite optical response. Because the band gap in the researched $\text{Ge}_{1-x}\text{Sn}_x$ epilayers is indirect, the observed PL process is related to the electron-hole recombination at below-bandgap localized states, in a vicinity of the non-radiative recombination. The strong dispersion of PL lifetime across the PL energy band suggests carrier transfer within optically-active below-bandgap states. The non-radiative recombination at the mobility edge of $\text{Ge}_{1-x}\text{Sn}_x$ epilayers is due to two processes: the SRH one identified by its strong temperature dependence and the surface recombination process is almost temperature-independent. The low-temperature SRH lifetime is nearly 1 ns, while the surface recombination time is close to ~ 200 ps, with negligible dependence on Sn content in the $\text{Ge}_{1-x}\text{Sn}_x$ epilayers.

These findings allow us to put a perspective on $\text{Ge}_{1-x}\text{Sn}_x$ -based applications. On one side, the rapid intraband relaxation time, up to a few ps, is plausible for a high modulation speed of a laser and an optical amplifier, quick changes of a device's state in the case of optical switches, and a fast response time of a photodetector. On another side, the apparent high efficiency of non-radiative processes observed in the investigated $\text{Ge}_{1-x}\text{Sn}_x$ epilayers can be unfavorable for optoelectronic devices. In $\text{Ge}_{1-x}\text{Sn}_x$ -based photodetectors, the relevant time scale heavily relies on rapid intraband relaxation, which is at least two orders of magnitude faster than surface recombination time and bulk-like SRH processes. Moreover, a thin $\text{Ge}_{1-x}\text{Sn}_x$ layer in a photodetector is plausible, providing an efficient charge separation length. Additional surface passivation can diminish the effect of strong surface recombination, increasing the overall performance of the device by decreasing a dark current density.

Also, the fast surface recombination is vital for electrically-driven light-emitting devices since the carrier losses upon injection increase the threshold current density. In this case, equally important is the SRH recombination. Omitting the discussion on the nature of lasing states in the $\text{Ge}_{1-x}\text{Sn}_x$ epilayers, we can extrapolate our results on typically used thick $\text{Ge}_{1-x}\text{Sn}_x$ layers in laser devices. We believe that increasing a thickness of a $\text{Ge}_{1-x}\text{Sn}_x$ epilayer, above the critical thickness, results in a strain relaxation. This process introduces defects at the interface between strained relaxed $\text{Ge}_{1-x}\text{Sn}_x$ and relaxed Ge epilayers and within the $\text{Ge}_{1-x}\text{Sn}_x$ epilayer.

These defects act as efficient non-radiative recombination centers. Thus, in thick $\text{Ge}_{1-x}\text{Sn}_x$ epilayers, the SRH processes are expected to play a more significant role than reported in our work. However, the lasing is still possible at the cost of high injection current density, which is a major disadvantage.

Finally, we can speculate on a possible origin of the density of states, taking part in a lasing process. We have already underlined an essential role of electronic states located within the $\text{Ge}_{1-x}\text{Sn}_x$ bandgap, acting as efficient radiative recombination centers, despite the indirect-band character of researched $\text{Ge}_{1-x}\text{Sn}_x$ epilayers. These states can play a major role in the lasing process. However, there is another scenario that could be realized in $\text{Ge}_{1-x}\text{Sn}_x$ epilayers. Because the electron lifetime on the trap states and defects-on-dislocations remains quite long, under a high carrier injection regime, which is typical for laser operation, then the carrier relaxation to these states is appearing to be inefficient. Thus, remained high density of photo-injected carriers in the mobility edge of $\text{Ge}_{1-x}\text{Sn}_x$ could be responsible for the lasing process.

Methods

GeSn Sample Growth. Epitaxial materials for this research were grown with a help of chemical vapor deposition at reduced pressure in an industrial type ASM Epsilon 2000 system and on 200 mm diameter Si(001) wafers. The epitaxial structure consists of a ~ 700 nm thick relaxed Ge buffer followed by compressively strained $\text{Ge}_{1-x}\text{Sn}_x$ epilayer on the surface. Commercial and purified GeH_4 and SnCl_4 precursors were used to grow $\text{Ge}_{1-x}\text{Sn}_x$ epilayers. The epitaxial process was carried out in a hydrogen atmosphere at a reduced pressure. The epitaxial materials are intentionally undoped. Five structures with Sn content of 6%, 8.5%, 9.5%, 11%, and 12% in the $\text{Ge}_{1-x}\text{Sn}_x$ epilayers were used in this research. In addition, the relaxed Ge buffer on Si was grown and used as a reference. A chemical composition and thickness of each $\text{Ge}_{1-x}\text{Sn}_x$ epilayer are summarized in Tab. 1. State of strain in each epilayer and Sn content in $\text{Ge}_{1-x}\text{Sn}_x$ epilayer were measured by HR-XRD. Epilayers' thicknesses were obtained with the help of XTEM. More details about the samples growth and structural data can be found elsewhere.

Information on the studied here $\text{Ge}_{1-x}\text{Sn}_x$ epilayers. Chemical content is obtained from a high-resolution X-ray diffraction experiment and the thickness is evaluated from cross-sectional transmission electron microscopy pictures of the structures. Strain values are obtained from the analysis of Raman spectroscopy data (see Supporting information, S1).

Sn content (%)	thickness (nm)	strain (%)
6.0	44	-0.62
8.5	63	-0.95
9.5	54	-1.08
11.0	48	-1.30
12.0	36	-1.48

Steady-state spectroscopic measurements. Structures were enclosed in the helium-flow optical cryostat allowing for the sample temperature control in the range of $10\text{--}300\text{ K}$. In the absorption-like $\Delta R/R$ experiment, a halogen lamp was used as a broadband probe beam source. The 630 nm line from a semiconductor diode laser was employed for photo-modulation purposes. The 0.3 m-focal-length monochromator dispersed the white light reflected off the sample and measured via the lock-in technique at the reference modulation frequency of 280 Hz, using a thermoelectrically cooled PbS photodiode. The same experimental configuration with the switched-off halogen lamp was used for measuring the steady-state PL spectra.

Time-resolved differential reflectivity experiment. The experiment is set-up in the reflection mode. A Ti:Sapphire ultra-fast oscillator was used as an excitation source. The oscillator generates trains of $\sim 140\text{ fs}$ -long pump pulses at a repetition frequency of 76 MHz with the $E_{\text{pump}} = 1.49\text{ eV}$ photon energy in the pulse. The pulse train synchronously feeds the optical parametric oscillator (OPO), in which the non-linear photon energy conversion allowed for the tuning of the probe pulse photon energy in the range of $\sim 0.54\text{ eV}$ to $\sim 0.67\text{ eV}$. The length of a probe pulse was $\sim 230\text{ fs}$ with the corresponding pulse broadening of $\sim 8\text{ meV}$. The time delay between probe and pump pulses arriving at the sample surface was set by varying a mechanical delay line providing a resolution of $\sim 0.3\text{ ps}$.

Time-resolved photoluminescence. TRPL was measured with a standard PL setup by a time-correlated single photon counting method. In this case, a structure was excited at $E_{\text{exc}} = 1.49\text{ eV}$ by a train of $\sim 140\text{ fs}$ -long pulses from the Ti:Sapphire oscillator. The TRPL signal was filtered by a 0.5 m -long monochromator, and photons were collected by a NbN superconducting detector. The overall temporal resolution of the TRPL setup was $\sim 80\text{ ps}$.

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The following file is available free of charge.

- Rogowicz et al. supporting information: Raman spectroscopy of the v-Ge substrate and $\text{Ge}_{1-x}\text{Sn}_x$ epilayers; fitting parameters of $\Delta R/R$ features for the $\text{Ge}_{1-x}\text{Sn}_x$ epilayers; theoretical estimations of the $\text{Ge}_{1-x}\text{Sn}_x$ band structure evolution with the Sn mole fraction; examples of Time-Resolved Differential Reflectivity (TRDR) and Time-Resolved Photoluminescence (TRPL) traces; an example of XRD trace for the high-Sn content GeSn epilayer.