Mid-infrared emission and absorption in strained and relaxed GeSn semiconductors

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By independently engineering strain and composition, this work demonstrates and investigates direct band gap emission in the mid-infrared range from GeSn layers grown on silicon. We extend the room-temperature emission wavelength above ~4.0 μm upon post-growth strain relaxation in layers with uniform Sn content of 17 at.%. The fundamental mechanisms governing the optical emission are discussed based on temperature-dependent photoluminescence, transmission measurements, and theoretical simulations. Regardless of strain and composition, these analyses confirm that single-peak emission is always observed in the probed temperature range of 4-300 K, ruling out defect- and impurity-related emission. Moreover, carrier losses into thermally-activated non-radiative recombination channels are found to be greatly minimized as a result of strain relaxation. Transmission measurements validate the direct band absorption in strained and relaxed samples at energies closely matching photoluminescence data. These results highlight the strong potential of GeSn semiconductors as versatile building blocks for scalable, compact, and silicon-compatible mid-infrared photonics and quantum opto-electronics.
I. INTRODUCTION

Free-space communications, infrared harvesting, biological and chemical sensing, and imaging technologies would strongly benefit from the availability of scalable, cost-effective, and silicon-(Si-) compatible mid-infrared (MIR) opto-electronic devices. With this perspective, Sn-containing group IV semiconductors (Si)GeSn grown on Si wafers have recently been the subject of extensive investigations. [1–5] At the core of these expended efforts is the ability to harness the efficient direct bandgap emission from these emerging semiconductors, which can be achieved at a Sn content around 10 at.% in fully relaxed layers. It is, however, noteworthy that this critical composition is significantly above the ~1 at.% equilibrium solubility of Sn in Ge, which calls for a precise control of the growth kinetics to prevent phase separation and avoid Sn segregation and material degradation. Moreover, the epitaxial growth of GeSn is typically achieved on Si wafers using a Ge interlayer, commonly known as Ge virtual substrate (Ge-VS), resulting in inherently compressively strained GeSn. [6,7] This residual compressive strain increases Sn content threshold for the indirect-to-direct bandgap crossover and the associated optical emission is shifted to higher energies relative to that of a relaxed material. [8–10] Moreover, the accumulated strain in GeSn epitaxial layers was found to affect the incorporation of Sn throughout the growth, which can lead to graded composition as layers grow thicker. [6,7]

Among the strategies to circumvent GeSn growth hurdles, lattice parameter engineering using multi-layer and step-graded growth has been shown to be effective in controlling the Sn content and its uniformity. This process was exploited in recent studies demonstrating room temperature optical emission down to 0.36 eV (~3.4 μm wavelength), [4] as well as optically-pumped lasing operating between 3.1-3.4 μm at temperatures in the 180-270 K range. [11–13] Post-growth control and manipulation of strain have also been utilized to extend the emission range
as longer emission wavelengths can be achieved through relaxation and tensile strain engineering. [2–4,11,14] [15]

Notwithstanding contributions from the aforementioned studies, in-depth investigations of GeSn optical emission are, however, still in their infancy. Besides the ability to engineer innovative optoelectronic devices, the availability of high-quality GeSn layers also provides a rich playground to explore and uncover their fundamental properties and probe their behavior as a function of key parameters, namely temperature, strain, and composition. As mentioned above, strain and composition are always interrelated in epitaxial GeSn layers. Here, we decouple and elucidate their individual effects on the optical emission of GeSn by performing systematic studies on the optical emission of strained and relaxed GeSn in the 4-300 K range. The emission spectra are then discussed in the light of 8×8 $\mathbf{k} \cdot \mathbf{p}$ band structure calculations and transmission measurements. We found that the optical emission wavelength at room temperature (RT) can be extended above 4 µm upon significant post-growth relaxation of the compressive strain in under-etched Ge$_{0.83}$Sn$_{0.17}$. By cooling down to 4 K, the single emission peak is preserved in both strained and relaxed layers, indicative of the direct band gap emission across the entire temperature range. Thermally activated non-radiative recombination channels were found to have a negligible effect on the emission of Ge$_{0.83}$Sn$_{0.17}$ and no additional impurity-related emission were observed upon relaxation. Interestingly, in relaxed Ge$_{0.83}$Sn$_{0.17}$, the reduction in PL intensity at 300 K is relatively limited and the measured intensity is ~10 % of that recorded at 4 K. Similar behavior was found in lower Sn content layers Ge$_{0.863}$Sn$_{0.137}$, with an initial in-plane compressive strain of -0.4 %. By performing transmission measurements, the contribution of layers with different composition can be precisely decoupled. These measurements confirm the recorded behavior of PL emission energy
upon lattice relaxation, thus providing an additional demonstration of the band gap directness in both strained and relaxed $\text{Ge}_{0.83}\text{Sn}_{0.17}$ samples, as well in the relaxed $\text{Ge}_{0.863}\text{Sn}_{0.137}$.

II. METHODS

The layers investigated in this work were grown on a 4-inch Si (100) wafers in a low-pressure chemical vapor deposition (CVD) reactor using ultra-pure $\text{H}_2$ carrier gas, and 10 % monogermane ($\text{GeH}_4$) and tin-tetrachloride ($\text{SnCl}_4$) precursors, following a recently developed growth protocol. [4,7,16,17] First, a 600-700 nm-thick Ge-VS was grown at 450 °C, followed by thermal cyclic annealing (>800 °C) and additional Ge deposition. The $\text{Ge}_{0.83}\text{Sn}_{0.17}$ sample with a uniform composition was grown using a GeSn multi-layer heterostructure, where the incorporation of Sn was controlled by the growth temperature. [16] The 17 at.% top layer (TL), 12-10 at.% middle layer (ML), and 8 at.% bottom layer (BL) were grown at 280 °C, 300 °C, and 320 °C, respectively, with a TL/ML/BL thickness of 160/155/65 nm. [4] In the compositionally graded $\text{Ge}_{0.863}\text{Sn}_{0.137}$ sample, a 8 at.% buffer layer (320 °C) with a thickness of ~60 nm was used for the subsequent growth of the (graded-uniform) 10.5/12.9-13.7 at.% layer at 300 °C on top. [17] To relax the epitaxial strain, the grown layers were released from the substrates by patterning and underteaching micro-disks. First, 7 μm-wide disks were defined in ma-N 2410 resist with electron beam lithography. Micro-disks were patterned with a 10 μm pitch over 2.5×2.5 mm$^2$ arrays. This was followed by two successive reactive ion etching (RIE) steps. First, a $\text{Cl}_2$-based plasma was used to vertically etch the GeSn layer and transfer the resist pattern to the Ge-VS. Second, Ge was selectively etched in a $\text{CF}_4$-based plasma, resulting in released GeSn micro-disks.
The luminescence properties of the samples were measured using a Fourier transform infrared spectrometry (FTIR) based photoluminescence setup, described in Supplemental Material S1. The investigated samples were mounted in a vertically oriented helium flow cryostat with accurate temperature control. The samples were then illuminated using a 35 kHz modulated CW 976 nm laser to allow for lock-in technique. The laser was focused using a 20.3 mm focal length, off-axis parabolic mirror which also collected the PL signal and coupled it through the FTIR system which was equipped with a HgCdTe detector and a Potassium Bromide beam splitter. The full path of the PL emission was nitrogen purged to prevent water absorption lines in the measured spectra. To filter out the laser from the PL signal a germanium window was used as a long-pass filter. All measurement presented in this paper have been performed at an excitation density of ~1kW/cm², with the exception of the PL measured on the micro disks, which were measured at 4 kW/cm². To derive the Arrhenius parameters in a comparable way, all samples have been measured at 4 kW/cm². The absorption spectra were measured by coupling a light source through a Thermo Scientific Nicolet IS50R FTIR system, focusing it through a sample into a gold-coated integrating sphere and collected at a baffled port using a liquid nitrogen cooled HgCdTe detector. As a light source a LEUKOS ELECTRO MIR 4.1 supercontinuum laser has been used for the as-grown Ge₀.₈₃Sn₀.₁₇ and Ge₀.₈₆₃Sn₀.₁₃₇ samples and a glowbar for the micro-disk etched Ge₀.₈₃Sn₀.₁₇ sample because the absorption edge shifted out of the spectrum of the supercontinuum. The full optical path could not be purged with N₂ therefore background spectra have been measured directly before every transmission measurement. A schematic of the used setup for this experiment is shown in Supplemental Material S1.
III. RESULTS AND DISCUSSION

A. Fabrication and band structure of highly relaxed Ge$_{0.83}$Sn$_{0.17}$

Fig. 1a exhibits a cross-sectional scanning transmission electron microscopy (STEM) image of the GeSn 17/12/8 at.% (TL/ML/BL) multi-layer stacking, with thicknesses of 160/155/65 nm, [4] grown on Ge-VS/Si substrate. The composition of each layer is estimated from Reciprocal Space Mapping (RSM) around the asymmetrical (224) X-ray diffraction (XRD) peak (Fig. 1b). We note that the Sn content values obtained from the RSM map can be underestimated by 0.5-1.0 at.% as compared to values obtained using atom probe tomography measurements. [4] This difference may come from the difference in the volumes analyzed by each technique. For consistency, compositions extracted from RSM will be employed as they are averaged over a volume comparable to that probed in PL studies. The RSM data indicate that the TL is under an in-plane biaxial compressive strain $\varepsilon_{\parallel} = -1.3 \%$. As mentioned in the previous section, to significantly relax this residual strain, it suffices to release the GeSn layers by etching away the underlying Ge VS, as illustrated in Fig. 1c. The scanning electron microscope (SEM) image in Fig. 1d shows a typical array of micro-disks having a diameter of 7 μm and a pitch of 10 μm. The CF$_4$ etching time was selected to completely release the GeSn micro-disks which collapse onto the Si wafer. We note that a small residual thickness of the Ge-VS layer is visible on the Si substrate under the micro-disk after the fabrication process (Supplemental Material S2), which does not affect the strain in the micro-disks because they are detached from the substrate.

Raman measurements were performed on the micro-disk arrays to evaluate the residual strain in the GeSn TL. Note that Raman spectra are recorded from the TL without any contribution from the underlaying layers as the penetration depth of the 633 nm excitation laser (<30 nm) is
significantly smaller than the TL thickness (160 nm). Fig. 1e displays Raman spectra acquired at the center of a single micro-disk (red curve). As a reference, the Raman spectrum of the as-grown Ge$_{0.83}$Sn$_{0.17}$ layer is also shown (blue curve). The Ge-Ge LO mode of the as-grown layer is centered at ~292 cm$^{-1}$, whereas the same mode shifts down to ~287 cm$^{-1}$ in the under-etched micro-disks. The observed ~5 cm$^{-1}$ shift corresponds to a strain relaxation from the as-grown value of -1.3 % down to -0.2 % in the micro-disks. Note that Raman spectra associated to the area between micro-disks only show the Si-Si LO mode at 520 cm$^{-1}$ from the substrate (Supplemental Material S2), indicating that the Ge-VS was completely etched leading to the observed strain relaxation. The measured residual strain (-0.2 %) in the TL even after the complete release of the micro-disks is expected because the GeSn stack includes three layers with a variable composition. This post-etching strain analysis is consistent with systematic studies decoupling Sn content and strain effects on GeSn Raman vibrational modes. [16]

To elucidate the effects of composition and strain on the optical properties of the investigated GeSn stacking, an accurate theoretical framework to evaluate the band structure of these multilayers is highly coveted. For instance, to be able to quantitatively interpret any spectroscopic related transitions, the band gap in each layer of the TL/ML/BL stacking needs to be estimated as a function of strain and Sn content. To that end, we employed the 8-band $k\cdot p$ model together with the envelope function approximation (EFA). [18] The strain implementation is based on the Bir-Pikus formalism. [19] Additionally, the model solid theory was adopted to estimate the conduction and valence band offset profiles of various high symmetry bands. [20,21] Note that Vegards’s law is inaccurate to estimate the bandgaps of GeSn compounds due to significant bowing effects of the $L$ and $\Gamma$ high symmetry points. To circumvent this limitation, the bowing parameters (at 0 K) $b_\Gamma = 1.94$ and $b_L = 1.23$ were used. [22] The obtained band lineup
diagrams for the Ge\textsubscript{0.92}Sn\textsubscript{0.08}/Ge\textsubscript{0.88}Sn\textsubscript{0.12}/Ge\textsubscript{0.83}Sn\textsubscript{0.17} stack are shown in Fig. 2 for the as-grown and relaxed layers. From these diagrams, the electron and holes are predicted to diffuse into the upmost 17 at.% layer, as a result of the band offset with the 12 at.% ML being higher than 30 meV for both electrons and heavy holes (HH). Besides, the strain relaxation (from -1.3% to -0.2%) in the TL layer induces an increase in the energy difference between $L$ and $\Gamma$ minima in the conduction band $E_g^{L-\Gamma} (= E_g^L - E_g^\Gamma)$ of 83 meV, which should enhance band-to-band recombination. Furthermore, the LH-HH splitting is reduced by 80 meV in the TL layer. The valence (conduction) band offset between the ML and TL is reduced (increased) by 14 meV (56 meV) due to strain relaxation. Note that Low et al. [23] have shown using empirical pseudopotential methods that the band gaps for the unstrained Ge\textsubscript{0.83}Sn\textsubscript{0.17} at $\Gamma$ and $L$ Brillouin directions to be equal to 0.42 eV and 0.45 eV. This compares well with our $k\cdot p$ parametrization which gives 0.421 eV and 0.525 eV, respectively. Additionally, based on Gupta et al., [8] the as-grown ML layer (12% at. Sn, -0.54% compressive strain) is expected to have a direct band gap of 0.54 eV, which is in perfect agreement with our $k\cdot p$ model indicating that the ML direct gap transition equals 0.574 eV. Our calculations predict a type-I band alignment in the GeSn multi-layer heterostructure, where the radiative recombination should occur in the 17 at.% TL. These calculated results are discussed further below in the light of the optical measurements.

B. Room temperature PL and transmission measurements for Ge\textsubscript{0.83}Sn\textsubscript{0.17}

To experimentally investigate the effect of strain relaxation on the optical properties of GeSn, room-temperature PL and transmission measurements were performed on both as-grown layers and etched micro-disk arrays. We first focus on the PL spectra displayed in Fig. 3. In the as-grown
Ge$_{0.83}$Sn$_{0.17}$, a main emission peak centered at 0.362±0.005 eV (i.e. 3.4 μm wavelength) is recorded with a full-width at half maximum (FWHM) of 40-50 meV. A low intensity emission peak at ~0.43 eV is also visible, which could be related either to the optical recombination in the underlying 12 at. % ML or to optical transitions involving LH instead of HH, as it will be discussed later in the context of data displayed in Fig. 4. Note that the optical emission in this sample mainly originates from the 17 at. % TL. [4] In the micro-disks, the optical emission is redshifted to 0.315±0.005 eV (FWHM~60-70 meV) compared to the as-grown sample, thus covering a broader range in the MIR up to 4.0-4.5 μm (Fig. 3b). The measured ~45 meV shift (i.e., ~0.5 μm in wavelength) in the optical emission is induced by the strain relaxation from the as-grown value of -1.3 % to -0.2 % in the micro-disks. The observed increase in the FWHM of the emission peak in the micro-disks could be related to small fluctuations in strain between different micro-disks, or due to strain-induced HH-LH band splitting decreasing from ~100 meV to ~20 meV in micro-disks, which could make the LH also contribute to the width of main emission peak and therefore broaden it. A comparison with published data must take in consideration both composition and strain values to reach an accurate assessment. Von Driesch et al. showed PL emission down to 0.39 eV in partially-relaxed Ge$_{0.86}$Sn$_{0.14}$ ($\varepsilon_{||}$=−0.6 %), [14] and Calvo et al. demonstrated PL emission at ~0.37 eV in Ge$_{0.84}$Sn$_{0.16}$ ($\varepsilon_{||}$=−0.8 %). [3] These results are consistent with the lower emission energies observed for our strained and relaxed Ge$_{0.83}$Sn$_{0.17}$ layers, as displayed in Fig. 3. However, the reported optical emission at 0.385 eV in significantly relaxed Ge$_{0.825}$Sn$_{0.175}$ ($\varepsilon_{||}$=−0.3 %) [2] deviates from this trend and seems to be higher than what it should be. In fact, at nearly the same composition and strain in Ge$_{0.83}$Sn$_{0.17}$ micro-disks the emission energy is 0.31 eV (Fig. 3), which is practically identical to the case of strain-free Ge$_{0.81}$Sn$_{0.19}$ nanowires, where the PL emission is observed at 0.30 eV at room-temperature. [24]
The optical emission from Ge$_{0.83}$Sn$_{0.17}$ layers is then correlated with the transmission measurements performed at 300 K, as shown in Supplementary information S3-4. To provide a precise evaluation of the transmission data and to be able to determine the band gaps of individual layers we define the absorbance as:

$$A = \sum \alpha_i \cdot d_i , \ (1)$$

where $\alpha_i$ and $d_i$ are the absorption coefficient and thickness of layer $i$ in the stack, respectively. Surface reflections between different layers were taken into account and the corresponding spectra have been baseline-corrected to compensate for free-carrier absorption, [25,26] as elaborated in the Supplemental Material S3-4. The obtained $A^2$ curves are plotted in Fig. 3 together with their respective PL spectra. In a direct band gap semiconductor, the absorption coefficient $\alpha$ scales as the square root of the energy and linearly with $A$. Therefore, $A^2$ shows a linear behavior with energy where the bandgap is given by the energy-axis crossing. The $A^2$ spectrum shows a bandgap for the as-grown 17 at.% ($\varepsilon_{||} = -1.3\%$) of 0.345±0.005 eV, which lies on the rising edge of the corresponding PL signal centered at 0.362 eV as expected. Limited contribution from the Urbach tail to $A^2$ is visible, in agreement with previous report on GeSn with composition up to 10 at.% Sn. [27] A band gap of 0.36 eV was estimated at 4 K using the 8-band $k \cdot p$ method (Fig. 2). Considering the temperature dependence of PL emission (i.e. direct band gap), as discussed later in Figs. 4-5, a band gap of ~0.31 eV is predicted at 300 K (see Supplemental Material S5). The 30-40 meV difference between the PL and $k \cdot p$ value arises from the use of a non-optimized deformation potential constant, due to the scarcity of accurate experimental studies available in literature. In this work, the deformation potential constants were based on the work of Chang et al. [28] Similarly, the bandgap of the 12 at.% Sn ($\varepsilon_{||} = -0.5\%$) ML is found to be 0.46±0.02 eV.
The extrapolated 8-band $k \cdot p$ band gap value at 300 K is in the 0.34-0.36 eV range, depending on the strain value considered (see Supplemental Material S5). The 0.46 eV edge is in very good agreement with the ~0.45 eV estimated for $\text{Ge}_{0.875}\text{Sn}_{0.125}$ ($\varepsilon \parallel = -0.3 \%$) using reflection measurements by Driesch et al.. [14] The band gaps found for the MLs suffer from a small red-shift because their energy-axis crossing is also partially hindered by the absorption in the TL which is accounted for with a larger error margin. Nonetheless, the values for both samples agree closely and show the robustness of the method. The third onset above 0.6 eV is a result from both the 8 at.% BL as well as the thick Ge-VS layer where transitions to the indirect L-minimum dominate.

Interestingly, in $\text{Ge}_{0.83}\text{Sn}_{0.17}$ micro-disks only one absorption onset at is visible 0.311±0.005 eV. The identified band gap energy in this case lies at the center of the PL instead of being on the rising slope. This very small discrepancy is probably a result of tiny fluctuations in the strain relaxation, where PL is more likely to probe the lowest band gap material and the absorption measurement averages all contributions. It is, however, worth noting that the measured 35±7 meV shift with respect to the as-grown (strained) $\text{Ge}_{0.83}\text{Sn}_{0.17}$ is in good agreement with the ~45 meV shift estimated from PL measurements. This confirms the band gap shift induced by strain relaxation from the as-grown value of -1.3 % to -0.2 % in micro-disks. Surprisingly, a rather flat $A^2$ curve is observed above 0.45 eV, without any additional absorption edges at higher energy associated with the 12-8 at.% Sn layers. The absence of additional absorption peaks can plausibly be attributed to the significantly lower signal-to-noise ratio in the transmission measurements obtained for micro-disks (because of a reduced absorption volume and a fraction of transmitted light not interacting with the disks).
C. Temperature-dependent PL measurements in Ge$_{0.83}$Sn$_{0.17}$

To investigate the evolution of the direct band gap with temperature and strain and to identify any possible optically active defect levels, temperature-dependent PL spectra were acquired in the 4-300 K temperature range for both the as-grown and the micro-disk sample. These results are displayed in Fig. 4a-d. For the as-grown Ge$_{0.83}$Sn$_{0.17}$ layer at 4 K (Fig. 4a), a single emission peak at 0.413±0.001 eV is observed (FWHM=19.0±0.5 meV). The symmetric shape of the peak is attributed to limited band-filling, indicating a low-carrier injection regime, as shown in the power-dependent PL measurements at 4 K in the Supplemental Material S6. Free- and bound-exciton recombination is observed at very low power (constant energy), [29–31] while band-to-band emission dominates at higher power with a Burstein-Moss shift of 2-6 meV/decade. [32] Note that no power-dependent energy shift, using similar excitation power densities, was measured at 300 K, [4] which further confirms that the direct band gap is maintained at room-temperature. In addition, we notice the absence of quenching of the PL intensity at high excitation densities, indicating that Auger non-radiative recombination does not play a role (see Supplemental Material S6), which is rather surprising for a narrow band gap semiconductor. When the temperature is increased to ~50 K, a small blueshift (1.0-1.5 meV) is observed, followed by a progressive redshift as the temperature increases to 300 K, as displayed in Fig. 4c. No additional peaks are detected in the whole temperature range. The temperature-dependent PL spectra for the Ge$_{0.83}$Sn$_{0.17}$ micro-disk arrays are shown in Fig. 4b. A main emission peak centered at 0.365±0.001 eV (FWHM=42±3 meV) is detected at 4 K. The emission energy remains constant up to 50 K, followed by a progressive redshift at higher temperatures, reaching 0.315 eV at 300 K. We note that the absence of a small blueshift (<2 meV) below 50 K might simply result from the higher FWHM in micro-disks compared to as-grown layers. We highlight that the ~50 meV energy difference recorded at
50 K between the as-grown layer and the micro-disks is close to the 45 meV observed at 300 K. Thus, the strain in the multilayer structure changes only by a negligible amount with temperature without affecting the band gap directness across the probed temperature range. The absence of additional PL peaks indicates that the optical recombination dominates in the Ge$_{0.83}$Sn$_{0.17}$ layer regardless of temperature. The fit of emission energy as a function of temperature is performed using the Vina’s equation: [33]

$$E_g = a - b \left( 1 + \frac{2}{\exp\left(\frac{\theta_D}{T}\right)-1} \right),$$

(2)

where $a$ is a constant, $b$ is the strength of the electron-phonon interaction, and $\theta_D$ is the mean temperature of the phonons contributing to the scattering process. The values obtained using Eq. (2) are listed in Table 1. When compared to the widely used Varshi’s equation, [34] the Vina’s equation provides higher fit accuracy in the high temperature regime for materials with lower $\theta_D$ materials like Ge (374 K) and $\alpha$-Sn (270 K) as compared to Si (640 K). [33,35]

The integrated PL intensities, as a function of the inverse of temperature, for as-grown Ge$_{0.83}$Sn$_{0.17}$ layers and micro-disk array are displayed in Fig. 4d. The data are normalized to the intensity measured at 4 K for each set of samples. Overall, the PL emission exhibits the same qualitative behavior for both samples, viz., a monotonous decrease as temperature increases, which becomes more pronounced above 100 K. Overall, at 300 K, a decrease in the PL intensity to ~2 % compared to the 4 K intensity is measured for the as-grown layer, whereas in micro-disk array this decrease is rather limited to ~10 % suggesting an increase in the quantum efficiency in strain relaxed micro-disks. In the micro-disk array, a small stagnation in the reduction of intensity is measured around 240 K. Since no change in PL emission energy is observed (Fig. 4c), which would have been an indication of impurities ionization, [36] this behavior indicates that non-
Radiative channels become inactive at high temperature leaving direct band gap radiative recombination as the dominating mechanism. [37,38]

To shed more light on the non-radiative processes in these samples, the integrated PL intensities are fitted with Arrhenius functions (dashed lines in Fig. 4d) considering two active non-radiative recombination channels, according to:

\[
I = \frac{1}{\left[ 1 + c_1 \cdot \exp\left( -\frac{E_{a1}^1}{kT} \right) + c_2 \cdot \exp\left( -\frac{E_{a2}^2}{kT} \right) \right]},
\]

where \( c_1 \) and \( c_2 \) are constants, \( E_{a1}^1 \) and \( E_{a2}^2 \) are the activation energies, and \( k \) is the Boltzmann constant. [39] This set of parameters contains rich information on physical recombination processes. [38] The results obtained from the fit using Eq. (3) are listed in Table 2. The first activation energy \( E_{a1}^1 \) is \( \sim 5 \) meV in as-grown layers and micro-disks suggesting a common loss mechanism for the two materials. This loss could be facilitated by a shallow impurity level ionizing at low temperatures, perhaps related to the observed 1-2 meV blueshift in as-grown layer at low temperatures. Thus, in Ge\(_{0.83}\)Sn\(_{0.17}\) the recorded PL below 50 K is most likely due to a 1-4 meV shallow level, whereas band-to-band recombination is observed at higher temperatures. [31,36]

The second activation energy \( E_{a2}^2 \) indicates the presence of a 20-40 meV higher energy non-radiative recombination channel, which could originate from inter-valley tunneling of electrons into the L-minimum or from a deeper impurity level within the band gap. The calculated band diagram of Ge\(_{0.83}\)Sn\(_{0.17}\) (Fig. 2) indicates that the L-minimum is \( \sim 150 \) meV and \( \sim 233 \) meV higher compared to the \( \Gamma \)-minimum in as-grown (strained) and micro-disks (relaxed) samples, respectively. Thus, inter-valley tunneling is an unlikely carrier diffusion process in Ge\(_{0.83}\)Sn\(_{0.17}\) across the entire 4-300 K temperature range. Other possible loss mechanisms are surface traps or
defects within the layer (i.e., impurities and point defects), which are both thermally activated sources of non-radiative recombination. Herein, it is important to mention that no impurities are observed in atom-probe tomography (APT) measurements (detection limit $\sim 1 \times 10^{17} \text{ cm}^{-3}$) [40] of Ge$_{0.83}$Sn$_{0.17}$ layer (Supplemental Material S7) [4]. However, point defects in a semiconductor, such as vacancies and vacancy complexes, can also affect the optical properties due to carrier trapping. [41–43] The presence of divacancies and, to a limited extent, of vacancy-clusters at room-temperature has been recently confirmed in as-grown GeSn layers [17] and they might contribute to the activation energy $E_a^2$ as an additional non-radiative recombination channel. Another plausible interpretation for $E_a^2$ would be the loss of carriers due to diffusion from 17 at.% TL to 12 at.% ML, where they (partially) recombine non-radiatively. In the as-grown layer, the calculated valance and conduction band offsets between TL and ML, $\Delta E_c=33 \text{ meV}$, $\Delta E_v=51 \text{ meV}$ (Fig. 2), are both close to the activation energy $E_a^2$ (41±1 meV) as provided by the fit. This means that both electrons and holes can diffuse to the ML, where an overall quench in PL will already be observed when only one of the two charge carriers leaks away. With this mechanism in mind, one might argue that the observed $\sim 0.45 \text{ eV}$ PL peak in the as-grown Ge$_{0.83}$Sn$_{0.17}$ above 180 K (Fig. 4a) sample could be associated with emission from the 12 at.% ML instead of a contribution of LH-HH splitting in the strained 17 at.% TL. In a relaxed layer, the offset of conduction and valence bands ($\Delta E_c=89 \text{ meV}$, $\Delta E_v=37 \text{ meV}$) changes such that only holes can be thermally excited into the ML.
D. Effect of composition on the optical properties.

In addition to the post-growth relaxation described above and for the sake of comparison, we examine in the following strain relaxation achieved during epitaxial growth using a compositionally graded GeSn layer. In this configuration, the lattice parameter gradually increases throughout the layer thickness and additional Sn atoms are incorporated in the growing layer, which results in a graded profile. [7] To put the effect of strain relaxation and composition in perspective, we compare the results in Figs. 3&4 with a lower Sn-content graded Ge_{0.863}Sn_{0.137} sample that is relatively highly relaxed (\(\varepsilon || = -0.4\%\)) and shows PL emission at a similar energy to that of as-grown Ge_{0.83}Sn_{0.17} sample. The high relaxation on the other hand makes a direct comparison with the previously discussed micro-disk possible while considering the difference in composition. The compositionally graded growth starts with a \(~60\) nm-thick nucleation layer with 8 at.% Sn, followed by a \(~700\) nm-thick GeSn layer (Fig. 5a). In this layer, a graded composition (60-400 nm) from 10.5 to 12.9 at.% is observed, followed by a uniform composition (400-700 nm) of 13.7 at.%.

The graded and uniform layers are also visible in the RSM map in Fig. 5b, as described in references [7,17]. The residual in-plane strain across the GeSn layers is lower than \(-0.4\%\), thus indicating a high degree of strain relaxation. Room-temperature PL spectra measured for this sample are plotted in Fig. 5c. A main emission peak centered at 0.380±0.010 eV is observed, however, with a relatively large FWHM of \(~100\) meV that most likely results from the gradual change in the band gap energy across the graded layer (i.e. emission from the lower Sn content layers). Note that in the as-grown Ge_{0.83}Sn_{0.17} sample with a uniform composition, the FWHM is half of the value obtained in the compositionally graded Ge_{0.863}Sn_{0.137}. Additionally, the 0.38 eV emission in Ge_{0.863}Sn_{0.137} is in line with the emission at \(~0.39\) eV reported for partially relaxed Ge_{0.86}Sn_{0.14} (\(\varepsilon || = -0.6\%\)). [14] In the transmission data and corresponding absorbance
curve (Fig. 5c), the direct band gap absorption edge for the layer with a composition of 13.7 at.% is visible at 0.380±0.005 eV, while the edge at 0.45±0.01 eV corresponds to the compositionally-graded 12.9-10.5 at.% layer. The very good agreement between the PL and absorption data demonstrates that the radiative recombination takes place in the upmost Ge$_{0.863}$Sn$_{0.137}$ layer. Furthermore, in Ge/Ge$_{0.87}$Sn$_{0.13}$ core/shell nanowires ($\varepsilon_{\text{shell}} \sim -0.4 \%$), the PL emission and absorption edge of 0.46-0.47 eV were estimated, [36] which is in excellent agreement with the optical data of the compositionally-graded 12.9-10.5 at.% layer discussed above. In temperature-dependent PL measurements (Fig. 5d-f), a single emission peak is observed throughout the 4-300 K range. At 4 K, the emission peak is centered at 0.416±0.001 eV (FWHM=42.0±0.5 meV) and its width is 2× larger than that of the Ge$_{0.83}$Sn$_{0.17}$ layer. This difference in FWHM remains similar to that observed at room-temperature. When the temperature is increased the emission energy in Ge$_{0.863}$Sn$_{0.137}$ remains unaffected up to 80 K, followed by a progressive decrease at higher temperature, reaching 0.381 eV at 300 K. When the temperature rises from 4 K to 300 K, the integrated PL intensity drops to ~15 % of its initial value, which is very similar to what observed in relaxed Ge$_{0.83}$Sn$_{0.17}$ micro-disks (Fig. 4d). The values estimated from the Vina’s fit (eq. 1, Table 1) and activation energies $E_a^1$ and $E_a^2$ values from the Arrhenius plot (eq. 2, Table 2) are in the same range as those obtained for Ge$_{0.83}$Sn$_{0.17}$. Therefore, the graded composition in the as-grown Ge$_{0.863}$Sn$_{0.137}$ has a negligible effect on the energy of shallow levels, while it increases the emission linewidth by a factor 2 at all temperatures when compared to Ge$_{0.83}$Sn$_{0.17}$. Despite the broader PL peak, the strain relaxation resulting from the graded composition promotes optical recombination and minimizes non-radiative recombination channels, in analogy to the Ge$_{0.83}$Sn$_{0.17}$ micro-disk arrays discussed above. Thus, the optical properties of GeSn are enhanced regardless of the method used to achieve strain relaxation.
Curiously enough, the negligible role of defect- and impurity-related emission seen in the data exhibited in Fig. 4-5 remains one of the striking observations when the current work is compared to literature despite the higher Sn content in the investigated layers. In fact, the few available studies highlighted clear contributions from dislocations and impurities on the temperature-dependent PL emission in GeSn at Sn content close or above 10 at.%. [36,37,44] For instance, Pezzoli et al. discussed the trapping of carriers in dislocations observed at low temperature in indirect band gap Ge$_{0.91}$Sn$_{0.09}$, indicating that subsequent thermal de-trapping seems to result in an enhanced PL intensity due to increased radiative band-to-band recombination. [37] Defect-related deep levels (~150 meV) were also observed in pseudomorphic (<50 nm-thick) Ge$_{0.875}$Sn$_{0.125}$ layers, which are possibly associated to the presence of dislocations in GeSn/Ge-VS heterostructure. [44] For thicker layers (>500 nm-thick), the emission from deep-levels was absent, however, a ~8 meV blue-shift of the PL emission energy was clearly observed when temperature increases from 4 K to 100 K ($E_a$ ~32 meV), followed by a rapid quenching of the emission at higher temperatures. This behavior indicates the presence of shallow impurity levels within the band gap that are ionized above 100 K (shallow level). Impurity ionization (20-30 meV) into the band gap emission with increasing temperature was also observed in Ge/Ge$_{0.87}$Sn$_{0.13}$ core/shell nanowires [36] and in Ge$_{0.81}$Sn$_{0.19}$ nanowires. [24] Obviously, any explanation of these differences would be challenging at this stage. However, it is sensible to consider the influence of growth conditions on the possible incorporation of point defects and impurities. In this regards, one can invoke the growth rate as an obvious difference as the layers investigated in this work are grown at a rate of ~1.5 nm/min, which is ~10 times lower than comparable samples from other research groups. [7] Nonetheless, the growth of GeSn shells around Ge nanowires was performed at a lower growth rate (<1 nm/min) [36] for which PL emission associated with deep levels was
observed, thus hinting to other possible critical factors. As a matter of fact, further in-depth investigations are needed to decipher the key parameters affecting the impurity and vacancy incorporation, their complexes, and their role in shaping the optical properties of GeSn semiconductors.

IV. CONCLUSIONS

In this work, we demonstrated that room-temperature optical emission in GeSn can be extended to longer wavelengths in the mid-infrared range by independently controlling strain and composition. The observed single-peak PL emission at 300 K in the as-grown Ge$_{0.83}$Sn$_{0.17}$ shifts from 0.362 eV to 0.315 eV (i.e. $\sim$3.4 $\mu$m to $\sim$4.0 $\mu$m wavelength) by releasing most of the -1.3 % compressive strain in under-etched micro-disks, in qualitative agreement with 8×8 $k\cdot p$ band structure calculations. No additional PL peaks are visible when cooling down as-grown and micro-disk samples to 4 K, suggesting the absence of defect- and impurity-related emission and that direct band gap emission is preserved. By increasing temperature from 4 K to 300 K, the PL intensity is reduced to 3 % and 10 % of the initial value in as-grown and relaxed Ge$_{0.83}$Sn$_{0.17}$, respectively. Therefore, as a consequence of strain relaxation carrier losses into thermally-activated non-radiative recombination channels are minimized. These observations are confirmed in Ge$_{0.863}$Sn$_{0.137}$, where a significant strain relaxation is obtained as a result of graded composition. However, a broader 300 K PL emission peak at 0.380 eV is obtained as compared to Ge$_{0.83}$Sn$_{0.17}$ with uniform composition. Regardless of strain and composition, impurities and other non-radiative recombination channels seem to have no detrimental effect on PL emission. Transmission measurements performed at 300 K give a deep insight into the absorption process in GeSn multi-layer structures and confirm the effect of strain relaxation in inducing a redshift of the absorption
edge. Additionally, these analyses also demonstrate the band gap directness in strained and relaxed $\text{Ge}_{0.83}\text{Sn}_{0.17}$ layers as well as in the compositionally-graded $\text{Ge}_{0.863}\text{Sn}_{0.137}$. Thus, the control of both strain and composition uniformity is of paramount importance to engineer the emission operational range and linewidth in GeSn opto-electronic devices. Applications requiring a narrower spectral range would benefit from the use of uniform, GeSn layers, where a large amount of Sn can be incorporated while avoiding phase segregation. [45] Whereas, a graded composition would enhance the absorption at a larger layer thickness and cover a broader spectral range.

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Notes:
The authors declare no competing financial interest.
FIGURES CAPTIONS

Figure 1. (a) Cross-sectional TEM image along the [110] zone axis of the GeSn 17/12/8 at.% (TL/ML/BL) multi-layer stacking grown on the Ge-VS/Si substrate. Adapted from Ref. [4]. (b) XRD-RSM around the asymmetrical (224) reflection for the as-grown Ge\textsubscript{0.83}Sn\textsubscript{0.17} sample. Adapted from Ref. [4]. (c) Schematics of the micro-disks fabrication process. (d) SEM image of the Ge\textsubscript{0.83}Sn\textsubscript{0.17} micro-disks (45° tilting angle). (e) Normalized Raman spectra for Ge\textsubscript{0.83}Sn\textsubscript{0.17} acquired on the as-grown (blue curve) and on the central portion of the micro-disk (red curve).

Figure 2. (a-b) Calculated 8×8 $k$-$p$ band lineup for the Ge\textsubscript{0.83}Sn\textsubscript{0.17} with an in-plane biaxial strain $\varepsilon_{||} = -1.3 \%$ (as-grown) (a) and $\varepsilon_{||} = -0.2 \%$ (micro-disks) (b).

Figure 3. (a-b) PL spectra and absorption coefficient squared ($A^2$) at 300 K for the Ge\textsubscript{0.83}Sn\textsubscript{0.17} as-grown (a) and micro-disk (b) samples. In the $A^2$ curves, the intercept of the straight dashed line extrapolates the energy of the optical transition(s).

Figure 4. (a-b) Temperature-dependent PL measurements in the 4-300 K range for the Ge\textsubscript{0.83}Sn\textsubscript{0.17} as-grown (a) and micro-disks (b). Spectra are normalized to their own maximum. (c-d) Emission energy as a function of the temperature (c) and integrated PL intensity, normalized to their respective intensity at 4 K, as a function of the inverse of the temperature (d) extracted from the (a,b). The fit of the curves in (c) was performed using Eq. (2), while the data in (d) were fitted using Eq. (3) (dashed curves).

Figure 5. (a) Cross-sectional TEM image along the [110] zone axis of the Ge\textsubscript{0.863}Sn\textsubscript{0.137} sample grown on the Ge-VS/Si substrate. Adapted from Ref. [17]. (b) XRD-RSM around the asymmetrical (224) reflection. Adapted from Ref. [17]. (c) PL spectra and absorption coefficient squared ($A^2$) at 300 K, (d) Temperature-dependent PL measurements in the 4-300 K range. (e-f)
Emission energy as a function of the temperature (e) and integrated PL intensity as a function of the inverse of the temperature (f) extracted from the (d).

**Table 1.** List of the parameters \((a, b, \theta_0)\) extracted from the Vina’s fit (Eq. 2) of Fig. 4c and Fig. 5e.

**Table 2.** List of the parameters \((E_a^1, E_a^2, c_1, c_2)\) extracted from the fit considering two non-radiative recombination channels (Eq. 3) of Fig. 4d and Fig. 5f.
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Figure 1
Figure 4
Figure 5
|                | a (eV)     | b (eV)     | $\theta_D$ (K) |
|----------------|------------|------------|----------------|
| **As-grown**   |            |            |                |
| 17.0 at.%      | 0.479 ±0.015 | 0.066 ±0.015 | 380±40         |
| **Micros-disks** |           |            |                |
| 17.0 at.%      | 0.396 ±0.004 | 0.031 ±0.004 | 247±17         |
| **As-grown**   |            |            |                |
| 13.7 at.%      | 0.456 ±0.005 | 0.039 ±0.005 | 330±17         |

**Table 1**
|                | $E_a^1$ (meV) | $c_1$     | $E_a^2$ (meV) | $c_2$     |
|----------------|--------------|-----------|--------------|-----------|
| **As-grown**   |              |           |              |           |
| 17 at.%        | 6.0 ±0.4     | 1.8 ±0.2  | 41 ±1        | 129 ±9    |
| Micro-disks    |              |           |              |           |
| 17 at.%        | 5 ±1         | 0.6 ±0.3  | 24 ±1        | 21 ±2     |
| **As-grown**   |              |           |              |           |
| 13.7 at.%      | 4.7 ±0.2     | 0.42 ±0.02| 25.6 ±0.2    | 13.5 ±0.1 |

*Table 2*
Supplemental Material:

Mid-infrared emission and absorption in strained and relaxed GeSn semiconductors

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S1. Description of transmission setup.

Figure S1. Schematics of the optical setup used for transmission measurements. A supercontinuum laser has been used as a white light source with emission up to 4.1 µm, or has been replaced by the internal glowbar of the FTIR system for measurements further in the infrared. The emission of the source was then coupled through the interferometer and focused onto the sample which was placed at the entrance of a gold-coated integrating sphere. The light was collected from the integrating sphere through a baffled port and focused onto an HgCdTe-detector. Background measurements have been performed directly before each transmission measurement and the total transmission was determined as $T_{tot} = T_{meas}/T_{background}$. The further analysis of the data is described in Supplemental Material S3.
S2. Structural characterization of the $\text{Ge}_{0.83}\text{Sn}_{0.17}$ micro-disks.

**Figure S2.** (a-b) SEM images the $\text{Ge}_{0.83}\text{Sn}_{0.17}$ micro-disk arrays ($45^\circ$ tilting angle) showing few micro-disks that are detached from the Ge-VS and redeposited in a different location. (c-d) Raman maps indicating the complete GeSn and Ge-VS removal in between the micro-disks (c) and the peak position across the individual micro-disks (d).

S3. Determination of the absorbance from transmission measurements

To interpret how the absorption coefficients follow from the measured transmission $T$, the propagation of a ray of light through a sample is considered as shown in schematic Fig. S3. The two processes that are taken into account are absorption when the ray of light travels through a layer and reflection at every refractive-index-changing interface. The transmission through a layer $i$ is given by $t_i = \exp(-\alpha_i \cdot d_i)$ where $\alpha_i$ is the absorption coefficient of the respective layer and $d_i$ the thickness. The reflections $R_{i,j}$ at the interfaces are determined using the Fresnel equations for
perpendicular incidence give in equation S1 when the light ray travels from medium $i$ to $j$. Here $n_i$ and $n_j$ are the refractive indices of the respective media.

$$R_{i,j} = \frac{(n_i - n_j)^2}{n_i + n_j} \quad \text{(eq. S1)}$$

Modelling the ray of light through the full sample can be done in two different approaches. Firstly, we can assume that the only significant reflections occur at the air-sample interfaces (Fig. 3a) and that the refractive indices inside the sample are comparable. Additionally, the refractive index changes gradually throughout the sample from high, on the Sn-rich GeSn side to low on the silicon side. This means that the light expands adiabatically into the material and that reflections are suppressed. The lack of reflections between the layers in the sample means that the transmission through the layers can simply be multiplied resulting in an effective transmission $t_{tot}$ given by equation S2.

$$t_{tot} = \prod_i t_i = \exp\left(\sum_i -\alpha_i \cdot d_i\right) = \exp(-A) \quad \text{(eq. S2)}$$

In equation S2 also the absorbance $A$ is introduced, defined as in equation S3. The absorbance is a variable that linearly scales with the absorption coefficient $\alpha_i$ but is experimentally more easily accessible yet can be interpreted similarly.

$$A = \sum_i A_i = \sum_i \alpha_i \cdot d_i \quad \text{(eq. S3)}$$
Figure S3. Schematics of all reflections taken into account for the determination of the total transmission $T_{tot}$. Where in (a) only the reflections at the outside of the samples are taken into account (equation S4) and in (b) the additional reflection on the germanium-silicon interface (equation S5). In this figure $t_x$ is a transmission through a respective medium, $R_x$ is a reflection between two media and $R_x^*$ and $T_x^*$ are the effective reflection and transmission through a layer taking into account multiple reflections.

When taking into account multiple reflections on both sides of the sample the general equation S4 is found [1,2] in which $T_{tot}$ is the net transmission measured through the sample.

$$T_{tot} = \frac{(1 - R_L) \cdot (1 - R_R) \cdot \frac{t_{tot}}{1 - t_{tot}^2 \cdot R_L \cdot R_R}}{1 - t_{tot}^2 \cdot R_L \cdot R_R}$$  \hspace{1cm} (eq. S4)

A second, more exact approach is to also consider the reflections at the germanium-silicon interface inside the sample as depicted in Fig. S3. The reason that only this interface is relevant is because the refractive index of Ge ($n_{Ge}=4.2$) is barely different from the indices of GeSn alloys, [3] whereas Si ($n_{Si}=3.4$) does make a contrast. Calculating the net transmission $T_{tot}$ through a multilayer sample requires a more thorough approach [1,4] given in equation S5.
Here the total transmission $T_{tot}$ through the sample depends on the net transmission $T_R^*$ (given in eq. S6) and the net reflection $R_R^*$ (given in eq. S7) of the Si substrate while taking into account multiple reflections in the substrate. Note that both expression S4 and S5 neglect interference effects, however the backsides of the measured samples are unpolished and therefore no interference is observed in the measurements, justifying this analysis. Equation S4-S7 depend on $t_{top}$ and $t_{sub}$ which are the net transmission through the top layers and through the silicon substrate respectively. However in this work no absorption in the relevant wavelength regime is expected from the silicon substrate which allows us to choose $t_{sub} = 1$ and $t_{top} = t_{tot}$.

$$R_R^* = R_M + \frac{(1 - R_M)^2 \cdot R_R \cdot t_{sub}^2}{1 - R_M \cdot R_R \cdot t_{sub}^2}$$  \hspace{1cm} (eq. S6)

$$T_R^* = \frac{(1 - R_M) \cdot (1 - R_R) \cdot t_{sub}}{1 - R_M \cdot R_R \cdot t_{sub}^2}$$  \hspace{1cm} (eq. S7)

Using the above mentioned simplification both equation S4 and S5 can be solved for $t_{tot}$ and can be plotted as a function of the measured transmission $T_{tot}$, as depicted in Fig. S4a. For the making of this plot the reflections $R_L, R_M$ and $R_R$ are determined using equation S1 where refractive indices of $n_{Si}=3.4$ and $n_{Ge}=4.2$ have been chosen.
Figure S4. Relation between the measured transmission $T_{tot}$ and the transmission due to non-absorbed light $t_{tot}$ (a) and the relation between $T_{tot}$ and the absorbance (equation S3) (b) of the measured GeSn samples. In these graphs no reflections at interfaces are taken into account (black line), only reflections at the air-sample interfaces are taken into account (solid blue line, equation S4) and air-sample interfaces and the Ge-Si interface inside the sample are taken into account (orange dashed line, equation S5). All graphs are calculated using refractive indices of $n_{Si}=3.4$ and $n_{Ge}=4.2$.

It becomes apparent from Fig. S4a that equation 4 and equation 5 produce almost identical results and that the additional reflection between the germanium and silicon layer can safely be neglected. This result does also show that it is unnecessary to further complicate the model by including reflections between different GeSn layers, which would require the precise estimation of the refractive indices of each layer.

Using equation S2 in combination with equation S4, the absorbance $A$ of the full sample can be found from the measured transmission $T_{tot}$ as also shown in Fig. S4b. Considering the layers that are relevant in the measured system the absorbance $A$ is given by $A = \alpha_{TL} d_{TL} + \alpha_{ML} d_{ML} + \alpha_{BL} d_{BL} + \alpha_{GeVS} d_{GeVS}$, as previously mentioned the silicon substrate has no relevant absorption in the probed wavelength regime and is neglected. For energies that are smaller than the bandgap of the GeSn middle layer, light is only absorbed in the top layer and $A = \alpha_{TL} d_{TL}$, thus by dividing this part of the data by $d_{TL}$ the absorption coefficient of the top-layer can be estimated. However
for energies higher that the bandgap of the middle layer always more than one layer contribute to
the absorption and the interpretation becomes non-trivial.

So far only the absorption due to transitions over the band gap have been considered which are
characterised by a wavelength dependent absorption coefficient. However, free-carrier absorption
(intra-band absorption) can also have a significant contribution to the total absorption especially
in a small bandgap material where carriers can be thermally excited and towards the infrared. To
compensate for this additional contribution all the found absorption spectra have been baseline
corrected such that the absorption coefficient goes to zero for small energies.

S4. Transmittance and absorbance spectra.

Figure S5. (a) The transmittance and absorbance of the as-grown Ge$_{0.83}$Sn$_{0.17}$ sample, measured
using a supercontinuum source. (b) The transmittance and absorbance of the Ge$_{0.83}$Sn$_{0.17}$ micro-
disks, measured using a glow bar. (c) The transmittance and absorbance of the as-grown
Ge$_{0.863}$Sn$_{0.137}$ sample, measured using a supercontinuum source. The $A$ curve is a derived function
from transmission data according to the procedure described in Supplemental Material S3.
**S5. Extrapolated \( k \cdot p \) band gap at 300 K**

![Graph showing extrapolated band gap values](image)

**Figure S6.** (a-b) Extrapolated 8-band \( k \cdot p \) band gap value at 300 K based on the temperature dependence of the PL emission (Figures 4-5) for strained and relaxed Ge\(_{0.83}\)Sn\(_{0.17}\) (a) and Ge\(_{0.88}\)Sn\(_{0.12}\) (b).

**S6. Power-dependent PL measurements on as-grown Ge\(_{0.83}\)Sn\(_{0.17}\) at 4K.**

The power-dependent PL spectra acquired in the 6.9 W/cm\(^2\) to 5.4 kW/cm\(^2\) range are plotted in Fig. S3a, while the integrated PL intensity \((I_{PL})\) and emission energy are plotted as function of the excitation power density \((P_{EXC})\). Free- and bound-exciton recombination [5–7] is observed at low power with a slope \(m \sim 1\), which is extracted from fitting the data with the power law \(I_{PL} \propto P_{EXC}^m\), and a constant emission energy. At higher excitation power band to band emission is visible, where a Burstein-Moss effect [8] with blue-shift of 2–6 meV/decade is estimated.
Figure S7. (a) PL spectra, normalized to their own maximum, acquired using excitation power densities from 6.9 W/cm² to 5.4 kW/cm². (b-c) Plot of the integrated PL intensity, normalized to its integrated intensity at the highest excitation density (b) and emission energy (c) as a function of the excitation power density.

S7. Absence of impurities in atom probe tomography (APT) measurement.

Figure S8. Mass spectrum extracted from the APT measurements of Ge₀.₈₃Sn₀.₁₇ from Ref. [9].
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