Micrometer-thick, atomically random SiGeSn for silicon-integrated infrared optoelectronics

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A true monolithic infrared photonics platform is within the reach if strain and bandgap energy can be independently engineered in SiGeSn semiconductors. However, this Si-compatible family of group-IV semiconductors is typically strained and inherently metastable, making the epitaxial growth fraught with extended defects and compositional gradients. Herein, we control the growth kinetics to achieve epitaxial Si0.06Ge0.90Sn0.04 layers lattice-matched to a Ge on Si substrate, with a uniform content and a thickness up to 1.5 μm. Atomic-level studies demonstrate high crystalline quality and uniform composition and confirm the absence of short-range ordering and clusters. Room temperature spectroscopic ellipsometry and transmission measurements show direct bandgap absorption at 0.83 eV and a reduced indirect bandgap absorption at lower energies. Si0.06Ge0.90Sn0.04 photoconductive devices exhibit a dark current similar to that of Ge devices and a slightly higher room-temperature spectral responsivity reaching 1 A/W above 0.82 eV (i.e. below 1.5 μm wavelengths). These results underline the enhanced performance in lattice-matched devices and pave the way to introduce SiGeSn semiconductors as building blocks to implement the long-sought-after silicon-integrated infrared optoelectronics.

Keywords: SiGeSn semiconductors, epitaxy, infrared optoelectronics, monolithic silicon photonics, photodetectors.
I. Introduction

SiGeSn ternary semiconductors are silicon-compatible materials providing the capability to independently engineer the bandgap energy and lattice parameter in a similar fashion to the well-established III-V and II-VI semiconductors. [1] The availability of these Sn-containing group IV semiconductors (SiGeSn) would enable key building blocks for silicon-integrated monolithic photonic and optoelectronic devices. [2] With this perspective, major efforts have been recently expended to develop SiGeSn materials. However, the vast majority of studies have been focusing on GeSn binary semiconductors leading to the demonstration of a range of devices operating at the short-wave infrared (SWIR: 1.4-3 µm) and mid-wave IR (MWIR: 3-8 µm) wavelengths. [1,3–10] Direct bandgap absorption and emission are now at reach using GeSn grown on Si at Sn contents above ~10 at.%, which is more than 10 times higher than the ~1 at.% equilibrium solubility of Sn in Ge. [11] These achievements are clear evidence that the thermodynamic constraints inherent to GeSn can be surmounted yielding device quality material by controlling nonequilibrium growth kinetics in strain-engineered multi-layer heterostructures. By minimizing the epitaxial compressive strain and keeping the growth temperature well below 400 °C, phase separation and segregation of Sn are avoided and high-quality GeSn epilayers are obtained. [12–14]

In ternary SiGeSn semiconductors, the thermodynamic constraints are exacerbated as the equilibrium solubility of Sn in Si is about one order of magnitude lower than in Ge. [15] By increasing Si incorporation, the bandgap of the material increases and the optical properties can be tuned to shorter wavelengths in the near-IR (NIR: 0.75-1.4 µm). [1,2,16] At the same time, the possibility to control the lattice parameter by varying the Si/Sn ratio allows to decouple strain and composition effects, which is critical to implement lattice-matched SiGeSn/GeSn heterostructures.
Earlier reports demonstrated the growth of SiGeSn at thicknesses below 600 nm and bandgap energies in the 0.8-1.2 eV range. [16–23] Increasing the thickness of SiGeSn layers above 1 µm is crucial to fully exploit the attractive properties of these emerging semiconductors. [2] It is important to note that the growth of thicker layers must also preserve the composition uniformity and material quality. In fact, it has been shown that Sn incorporation is greatly affected by strain relaxation as the layers grow thicker, [13] leading to a compositional gradient. Circumventing these challenges and achieving thick and uniform layers is of paramount importance not only to enhance the IR absorption, but also to implement the hybrid III-V/SiGeSn multijunction solar cells [24,25] and improve the performance of GeSn-based light emitting devices. [9,10,26–32] For instance, in the recently demonstrated electrically-pumped Ge$_{0.89}$Sn$_{0.11}$ lasers, Si$_{0.03}$Ge$_{0.89}$Sn$_{0.08}$ barriers are limited to a thickness of 250 nm. [10] Thicker SiGeSn layers would reduce scattering of the lasing mode with upper interfaces, and with a higher Si content carrier confinement in the Ge$_{0.89}$Sn$_{0.11}$ active layer would be preserved at room-temperature, further enhancing radiative emission and device efficiency. [2] Moreover, despite SiGeSn being an indirect band gap material, it has a lower Γ- to L-valley energy separation as compared to Ge. [1] This is expected to improve direct bandgap absorption and thus enhance the performance of IR photodetectors, while providing low leakage current that could enable the operation under high bias voltages.

While significant advances in the epitaxy of GeSn alloys were achieved in the last few years, [12,13,33,34] the growth of micrometer-thick and uniform metastable SiGeSn is yet to be demonstrated. In general, the monolithic growth of Sn-containing group IV semiconductors is achieved using Ge virtual substrate on Si (Ge-VS/Si). Si is a smaller atom than Ge and Sn, and its incorporation in the lattice results in a higher compressive strain that could compromise the metastable state of the Sn-saturated alloys. [13,35] Moreover, a site-competition process between
Si and Sn atoms might occur during growth, where a higher temperature enhances Si incorporation at the same Si/Ge supply in the gas phase. [27] The addition of Si$_2$H$_6$ during growth could also reduce the catalytic effect of GeH$_4$. [36] This results in a higher H coverage of the surface that decreases growth rate and promotes the accumulation of Sn at the surface, eventually leading to Sn surface segregation, with a detrimental effect on material quality. [27] Herein, we demonstrate that these outstanding issues can be resolved leading to the growth of 1.5 µm-thick Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ that is lattice-matched to the Ge-VS/Si wafer. High crystalline quality, uniform composition, and the absence of Sn segregation and clustering are demonstrated at the-atomic level in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$, where a n-type carrier concentration of $-5\times10^{16}$ cm$^{-3}$ is estimated. Spectroscopic ellipsometry and transmission measurements at room temperature indicate direct bandgap absorption at 0.83 eV, with a reduced indirect bandgap absorption at lower energies. Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ photoconductive devices exhibit identical dark current to that measured for Ge devices, which is 10 times lower than similar devices made of lattice-mismatched Ge$_{1-x}$Sn$_x$ ($x\geq$10 at.%) heterostructures. The relatively low dark current in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ is relevant to high bias voltage applications with reduced noise and power dissipation and highlights the benefit of a lattice-matched growth on device performance. Lastly, a spectral responsivity of 1.0-1.1 A/W in the 1.0-1.5 µm wavelength range was recorded at room temperature in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$, slightly above the value obtained for similar Ge devices.
II. Experimental methods

Samples were grown on a 4-inch Si (100) wafers in a low-pressure chemical vapor deposition (CVD) reactor using ultra-pure H₂ carrier gas, and 10 % monogermene (GeH₄), 2 % disilane (Si₂H₆) and tin-tetrachloride (SnCl₄) precursors. First, a 1.9 μm-thick Ge-VS was grown with a two-temperature step process (450/600 °C) and using post-growth thermal cyclic annealing (>800 °C). Next, a ~10 nm-thick Ge₀.₉₉Sn₀.₀₁ nucleation layer was grown at 360 °C for 10 minutes using a Ge/Sn ratio (in gas phase) of ~2500. [13] Si₂H₆ was then introduced in the chamber (Si/Sn ratio in gas phase of ~15), without modifying the GeH₄ and SnCl₄ supply, for the 6 hours growth of the 1.5 μm-thick Si₀.₀₆Ge₀.₉₀Sn₀.₀₄ layer.

Atom Probe Tomography (APT) measurements were performed in a LEAP 4000X-HR from Cameca. APT analyses in Figure 2 were made in a LEAP 5000XS from Cameca. Both machines utilize a laser producing picosecond pulses at 355 nm at a variable repetition rate of a few 100 kHz for laser assisted atom probe tomography. The tip-shaped samples for APT were prepared using a FIB based procedure introduced in Ref. [37] in a FEI Helios FIB using a Gallium ion beam with energies between 30 and 5 kV.

Spectroscopic ellipsometry measurements were performed using a J. A. Woollam® RC2-XI ellipsometer with a dual rotating compensator. Data were acquired from 250 to 2500 nm with 1 nm step and at incident angles ranging from of 60° to 85° with a 5° step. Near-Brewster angle (between 70° and 80°) SE measurements were undertaken to build the optical model that is based on a three-layer system (Si₀.₀₆Ge₀.₉₀Sn₀.₀₄, Ge-VS, Si wafer) and includes a surface roughness layer. For each sample, a second set of measurements was taken at different orientation to verify the in-plane isotropy of the film. The samples were confirmed to be isotropic in x-y plane. Polarized
transmission and reflectance measurements (for s and p polarizations, at the incident angle of 75°) were also performed on bare substrates first, and then on substrates with as-grown Ge-VS using Cary 50 UV-VIS universal measurement spectrophotometer (UMS) at identical angle of incidence as the SE. A thorough description of the measurement and modelling strategy of the optical properties of the semiconductors is presented in the Supplemental Material.

Polarized Transmission Spectroscopy was performed using a double beam spectrophotometer equipped with rotating sample and detector stages (Cary 7000 UMS from Agilent Technologies). The reflectance (R) and transmittance (T) data were acquired at various angles of incidence without moving the sample (from 60° to 85° so that R and T matches the SE AOI). Polarization-dependent measurements were limited to the 250-2500 nm range, which matches with the SE spectral range. The unpolarized transmission data are fitted simultaneously with the SE parameters to validate the built optical model.

Back-to-back C-V devices were fabricated with electron-beam deposition of SiO₂/Ti/Au (20/10/70 nm) and characterized using a Keithley 4200a parameter analyzer connected to a RT probe station. The fabrication of metal-semiconductor-metal photoconductive devices consisted of a single photolithography layer to deposit Ti/ Au (10/70 nm) metal contacts using electron-beam evaporation tool. The I-V measurements were acquired using the aforementioned parameter analyzer. The photocurrent was measured at 1.55 μm wavelength showing a calibrated responsivity of 0.57, 0.66, 0.95 and 1.02 for as-grown Si₀.₀₆Ge₀.₉₀Sn₀.₀₄, Ge (1.₉ μm), Ge (3.₀ μm), and annealed Si₀.₀₆Ge₀.₉₀Sn₀.₀₄, respectively, at 25 V. The spectral responsivity was measured using Bruker Vertex 80 FTIR spectrometer, a calibrated NIR light source, and lock-in amplifier operating at 500 Hz (chopper along the NIR light optical path).
III. Results and Discussion

III.a) Growth and atomic-level properties.

The Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ layers were grown on 100 mm Ge-VS/Si (100) wafers in a low-pressure chemical vapor deposition (CVD) reactor using commercially available precursors (GeH$_4$, Si$_2$H$_6$, SnCl$_4$). Because of the higher growth temperature of 360 °C used for Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ compared to GeSn growth (≤320 °C), [3,38] a careful control over the Si supply is required to avoid phase separation and segregation of Sn during growth. At fixed Ge/Sn ratio in the gas phase (i.e. constant GeH$_4$ and SnCl$_4$ flows) of ~2500, the incorporation of Si increases with Si$_2$H$_6$ flow, but the material quality rapidly deteriorates when a Si/Sn ratio surpasses a critical value of ~15. In this regime, the growth evolves from planar to three-dimensional islands with a lateral dimension of a few microns (Supplemental Material S1). We found that the critical threshold for the Si$_2$H$_6$ supply can be increased by using a higher Ge/Sn ratio, however without enhancing Si incorporation or improving the crystalline quality of the SiGeSn epilayer. As a result, material degradation still occurs at a similar Si/Sn ratio. Analogous precursors’ flow parameter windows were obtained by increasing the growth temperature to 370 °C, with a reduction in the Si and Sn content by less than 0.5 at.% (Supplemental Material S1). Decreasing the temperature to 350 °C did not enable high quality growth of a metastable SiGeSn layer. These results indicate that the growth of thick and uniform SiGeSn can only be obtained in a narrow window of the growth parameter space.

Following the optimized process, a 1.5 μm-thick Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ layer was grown on a 1.9 μm-thick Ge-VS, as shown in the cross-sectional scanning transmission electron microscopy (STEM) image in Figure 1a. The parameters obtained from the structural analysis are listed in Table 1. We note that the simultaneous incorporation of Si and Sn yields a lattice-matched growth
on Ge, with a larger bandgap in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ than Ge, as discussed below. In low-resolution TEM (Figure 1b), few misfit dislocations are detected at the Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$-Ge interface, and no threading dislocations are observed in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ at the TEM imaging scale. The Ge-Si interface exhibits higher dislocation density (Figure 1c), which is expected for a lattice-mismatched growth. The high crystalline quality of the Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$/Ge heterostructure is demonstrated by X-ray diffraction spectroscopy (XRD). Figure 1d displays a typical 2θ-ω scan performed around the (004) XRD order. The Si and Ge peaks are visible at 69.10 ° and 66.06 °, respectively, while the Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ peak is recorded at 65.72 °. In a strain-free GeSn layer, a peak shift to lower angles corresponds to an increase in Sn content in the layer, and as Si is incorporated the diffraction peak shifts to larger angles. Considering that both Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ and Ge layers have a comparable thickness, the similar XRD peak intensities and full width at half maxima indicate that the crystalline quality of Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ is identical to that of Ge. To evaluate the residual strain in the as-grown layers, reciprocal space mapping (RSM) measurements around the asymmetrical (224) XRD peak were performed, as exhibited in Figure 1e. The small in-plane tensile strain $\varepsilon_{||} \leq 0.2 \%$ in Ge originates from the differences existing between the thermal expansion coefficients of Si and Ge. The Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ layer has an in-plane lattice constant of $a_{||} = 5.669$ Å and out-of-plane lattice constant of $a_{\perp} = 5.680$ Å, corresponding to a very low compressive strain $\varepsilon_{||} = -0.2 \%$. Considering the limited plastic relaxation (Figure 1b), the TEM and XRD results confirm that Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ is nearly lattice-matched to Ge-VS.

The atomic-level chemical composition of the grown layers was studied by atom probe tomography (APT). The 3D reconstruction of a typical APT tip is shown in Figure 2a, where different atoms are color-coded: Si (green), Ge (blue), and Sn (red). In the APT compositional profile (Figure 2b), the uniform incorporation of Si and Sn is confirmed at a measured composition
of 4 at.% and 6 at.% across the top ~1400 nm-thick layer, respectively. The measured content fluctuations are less than 0.3 at.%. Note, that the lower signal-to-noise ratio close to the sample surface originates from the reduced volume in the upper portion of the APT tip. A compositional gradient is visible in the 150 nm-thick region near the SiGeSn/Ge interface, resulting from strain-driven incorporation and diffusion (Supplemental Material S2). Based on the APT 3D maps, statistical analyses were performed on the entire Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ layer to investigate the relative positions of Si, Ge, and Sn atoms and assess whether a random alloy is formed as it is typically assumed in theoretical modeling of the optical and electronic properties. [1] First, the nearest-neighbor (NN) distributions are evaluated up to the 10$^{th}$ order (solid spheres) and compared with a randomly shuffled assignment of the element to the same underlying point cloud of atom positions reconstructed from the measured data (dashed black curves). [39] The results of the NN analysis are shown in Figure 2c for the Si-Si (top) and Sn-Sn (bottom) pair of atoms. The agreement between experimental data and randomized data proves the absence of Sn and Si clusters containing more than 10 atoms, [40,41] and the absence of precipitates as expected for a locally random alloy. The APT data show a compositional gradient lower than 0.2 at.%/$\mu$m for both Si and Sn atoms, thus confirming the absence of significant concentration gradients across a ~1400 nm-thick portion of the Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ layer. Frequency distribution analysis (FDA) and partial radial distribution function (p-RDF) analysis (see Supplemental Material S2), again comparing the measured distribution of atoms with a randomly shuffled arrangement, are also in agreement with a locally random alloy.
III.b) Analysis of residual free carrier density.

The demonstrated high structural quality of Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ paves the way to investigate the potential of this materials systems in optoelectronic devices. As a first step, a more detailed knowledge of the type of conductivity and free carrier concentration in the epilayer would provide valuable information for device processing and optimization. A low carrier concentration, eventually tunable to reach compensation, would reduce the dark current, enhance the response time in photodetector devices, and enable high-speed operation by reducing parasitic capacitance.

To estimate the residual free carrier density, capacitance-voltage (C-V) measurements were performed in a back-to-back geometry (Figure 3a), and the obtained results are shown in Figure 3b. P-type carrier concentration in the 2·10$^{16}$-2·10$^{17}$ cm$^{-3}$ range was measured for Ge epilayers grown at different thicknesses (7·10$^{16}$ cm$^{-3}$ from Ref. [38] at a thickness of 1.6 µm is shown in Figure 3b). No effect of the thickness on the carrier concentration in Ge was observed. Interestingly, n-type carrier concentration of -5±3·10$^{16}$ cm$^{-3}$ was measured in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$. This behavior is consistent and always observed in all SiGeSn samples regardless of their thickness (not shown). Moreover, frequency-dependence C-V measurements show switching characteristics that are similar to state-of-the-art n-type metal oxide semiconductor capacitors (MOSCaps), which further supports the n-type conductivity obtained in our SiGeSn sample (Supplemental Material S3). This behavior differs from the p-type conductivity recorded for SiGeSn layers at a Si (Sn) content up to 10 at.% (14 at.%) and a thickness up to 600 nm. [23] While only one experimental study is available for SiGeSn so far, it is also worth mentioning that GeSn layers show consistently a p-type carrier concentration in the 1-5·10$^{17}$ cm$^{-3}$ range. [23,38,42]

In a broad sense, due to the relatively low growth temperature of metastable Sn-containing group IV semiconductors, point defects, such as divacancies and vacancy-clusters, [43,44] can be
electrically active and their nature can impact the conductivity type and residual free carrier concentration. However, point defects in SiGeSn and their effects on the electronic behavior are yet to be investigated. Moreover, as intrinsic GeSn shows consistently a p-type behavior, the incorporation of Si should be examined as a potential factor that may influence the background doping. This can possibly occur by affecting the defect complexes and their charge states. It is, however, important to note that p-type residual doping is observed in epitaxial Ge and does not change in undoped SiGe semiconductors at Si contents in the 10-30 at.% range, where the carrier concentration lies below $5 \cdot 10^{15}$ cm$^3$. [45] Therefore, it is even more challenging to evaluate the role of Si in SiGeSn, where the lattice properties are very different. Background doping in the CVD reactor can also be a plausible element to investigate. Herein, we would like to stress that our undoped GeSn [3,38] layers and SiGeSn were grown in the same reactor and they were found to exhibit an opposite conductivity. Additionally, it is noteworthy that the SiGeSn samples are kept at 360 °C for a few hours during growth, hence at $\geq 50$ °C higher temperature compared to GeSn. [3,38] This extended thermal annealing process, combined with a low growth rate (~4 nm/min), could play a significant role in diffusion and annihilation of point defects in SiGeSn. In-depth studies are needed to provide the necessary theoretical framework to elucidate the origin of the residual free carriers and their type in SiGeSn. Experimental investigations of vacancies and vacancy-like defects using positron lifetime annihilation spectroscopy combined with electrical characterization would be a good start to shed new light on this phenomenon. [43,44]
III.c) Optical properties.

Spectroscopic ellipsometry (SE) and UV-VIS spectrophotometry measurements were combined to characterize the as-grown layers, as shown in Figure 4. Based on these two techniques, an independent and consistent evaluation of the direct bandgap is obtained (see Supplemental Material S4 for more details). The real and imaginary parts $\varepsilon_1$ and $\varepsilon_2$ of the complex dielectric function are displayed in Figure 4a. The $E_0$, $E_1$, and $E_1+\Delta_1$ critical points (CPs) in the joint density of states are identified in the curves and their values are listed in Table 1. Because of the higher surface roughness (RMS) in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ (up to 30 nm) compared to Ge-VS (<5 nm), a reduction in the $E_2$ peak is observed. The direct band gap of the samples is estimated from the $E_0$ CP transition by fitting the square of the absorption coefficient $\alpha$ using a Tauc plot procedure, as shown in Figure 4b. [46,47] Direct bandgap values of 0.836±0.002 eV, 0.779±0.008 eV, and 0.785±0.002 eV are obtained for Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$, 1.9 $\mu$m-thick Ge and 3.0 $\mu$m-thick Ge samples, respectively. The small tensile strain ($\varepsilon_{||} \leq 0.20\%$) in the Ge epilayer results in a direct bandgap energy being lower than that of bulk Ge (0.80 eV), where the energy difference with the latter decreases with increasing epilayer thickness (strain decreases from 0.20 % to 0.15 %). A steep cut-off at lower energies is visible in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$, with a reduced contribution from the Urbach tail compared to Ge. This indicates a suppression of the indirect bandgap absorption in favor of the direct one (inset in Figure 4b, logarithmic scale for $\alpha$). Following a similar approach to that described in Refs. [6,48], the Urbach tail, which is attributed to the transition between bandtail states, defined as electronic states right above the valence band and the conduction band, was quantified. To that end, the absorption coefficient was fitted, below the band gap, to the following relationship:

$$\alpha = A\sqrt{\Delta E/2} \exp\left(\frac{h\nu - E_g^r}{\Delta E}\right)$$

(Eq. 1)
where $A$ and $\Delta E$ (Urbach energy) are material-dependant parameters and $E_g^\Gamma$ is the direct bandgap. $\Delta E$ values of $5.7 \pm 0.3$ meV, $12.2 \pm 0.5$ meV, and $14.8 \pm 0.5$ meV were obtained for the Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$, 1.9 $\mu$m-thick Ge, and 3.0 $\mu$m-thick Ge layers, respectively. Our estimated Urbach energy for Ge is in excellent agreement with the work of Tran et al. [6] It is noteworthy that $\Delta E$ is reduced by half in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ compared to Ge, thus confirming the high crystalline quality of the ternary alloy. This observation is similar to what previously reported in GeSn with compositions up to 17 at.% [5,6] and combined with the reduced indirect bandgap absorption it highlights the excellent optical quality of Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ enabled by the lattice-matched epitaxy.

The SE-estimated band gaps are compared (vertical dashed line in Figure 4c) with those from transmission spectra, as displayed in Figure 4c. While absorption in Ge takes place at 0.77 eV, the Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ contributes to additional absorption above 0.83 eV. The bandgap is quantified through fitting the transmission spectra. The dashed red lines in Figure 4c highlight the result of the fitting process, confirming the accuracy of the optical model (Figure 4a). A transfer matrix method (TMM) was undertaken to theoretically quantify the transmission. [49] The obtained values agree with the peaks observed in the first derivative of the transmission ($dT/dE$), as displayed in Figure 4d. The two distinct peaks at $0.775 \pm 0.005$ and $0.788 \pm 0.005$ eV in the 3.0 $\mu$m-thick Ge-VS (less resolved in the thinner sample) correspond to the $\Gamma$-transitions associated with light-holes (LH) and heavy-holes (HH), respectively. Because of the residual tensile strain, the LH-HH degeneracy is lifted and the bandgap energy is slightly reduced relative to bulk Ge. [50] We note that the presence of Fabry-Perot interference fringes in the transmission measurements, with spacing dependent on the thickness, does not affect the estimation of the 0.83 eV direct bandgap of Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$, which closely matches the value obtained from the SE analysis.
III.d) Room-temperature spectral photoresponsivity.

To investigate the electrical properties of Si<sub>0.06</sub>Ge<sub>0.90</sub>Sn<sub>0.04</sub>, current-voltage (I-V) curves are acquired on photoconductive devices (PD) in Figure 5a. The optical micrograph of the Si<sub>0.06</sub>Ge<sub>0.90</sub>Sn<sub>0.04</sub> PD and related dark current as a function of the applied bias are displayed in Figure 5a. A Schottky behavior is recorded in the as-grown device (blue curve) with a knee voltage of ~6 V. By performing rapid thermal annealing (RTA) at 380 °C for 30 s an Ohmic behavior is obtained (green curve), which is most likely due to Fermi level unpinning as a result of metal diffusion into Si<sub>0.06</sub>Ge<sub>0.90</sub>Sn<sub>0.04</sub>. Figure 5b compares the I-V curves of the annealed Si<sub>0.06</sub>Ge<sub>0.90</sub>Sn<sub>0.04</sub> PD with the 1.9 μm-thick (dotted dark red curve) and 3.0 μm-thick (dashed red curve) Ge PDs. Similar dark current is measured in these three sets of devices. At first, this finding indicates that the lattice-matched Si<sub>0.06</sub>Ge<sub>0.90</sub>Sn<sub>0.04</sub> growth on Ge-VS (Figure 1) limits growth defects in the heterostructure, thereby preventing any additional defect-related leakage current. It is worth noting that growth defects have already been demonstrated to increase dark and leakage currents in Ge devices, [51] while no similar studies are available for SiGeSn to date. Nevertheless, the similarities between SiGeSn and Ge devices was not expected. Indeed, considering that Ge layers were grown at a higher temperature of 600 °C (vs. 360 °C for Si<sub>0.06</sub>Ge<sub>0.90</sub>Sn<sub>0.04</sub>) and were subjected to thermal annealing above 800 °C, a lower amount of point defects is expected in Ge compared to SiGeSn. However, similar experimental values (but opposite sign) for the intrinsic carrier concentration \( n_i \) are obtained for both materials (Figure 3). This seems to indicate that a possible difference in concentration of point defects in these materials does not dramatically affect the absolute value of \( n_i \). When compared to lattice-mismatched GeSn PDs at Sn contents above 10 at.% grown in the same CVD reactor, [38] the dark current and intrinsic carrier concentration in Ge and Si<sub>0.06</sub>Ge<sub>0.90</sub>Sn<sub>0.04</sub> devices are one order of magnitude lower. Multiple factors can lead to
a higher intrinsic carrier concentration $n_i$ in GeSn, such as the smaller bandgap (<0.5 eV), a change in the density of states, and possibly a higher density of point defects. All these factors, combined with a higher density of dislocations in the lattice-matched multi-layer heterostructure, result in a higher leakage current in GeSn.

Room-temperature spectral responsivity curves of Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ and Ge PDs are shown in Figure 6. A bias voltage of 25 V (effective electric field 15 kV/cm$^{-1}$) was selected for the photocurrent measurements to show the potential for applications at high voltages based on Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$, such as single-photon avalanche photodetectors. [52] However, operation at lower voltages is also possible in annealed devices. We first focus on the Ge PDs, where a steep increase in responsivity above 0.75 eV and a rather flat curve in the 0.82-1.15 eV range are observed, followed by a small decrease at higher energies (Figure 6a). Above bandgap carrier thermalization [53] could reduce PD efficiency at the highest detection energies. By increasing the Ge thickness from 1.9 to 3.0 μm, the responsivity increases across the whole measurement range, with a peak responsivity of ~0.96 A/W at 0.83 eV (i.e. 1.5 μm wavelength) in the 3.0 μm-thick Ge PD. The increase in responsivity with layer thickness indicates that the larger amount of photogenerated carriers in a thicker Ge epilayer can be efficiently collected by the PD on top, thus showing limited carrier trapping at misfit, threading dislocations in the heterostructure. The higher responsivity at larger thickness is also in agreement with the reduction in threading dislocation density as Ge thickness increases. [54] The derivative of the responsivity as a function of the energy is shown in Figure 6b (bottom panel). In Ge PD, a single peak at 0.78 eV is obtained, hence at the same energy of the LH-HH doublet peak in Figure 4d. In the as-grown Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ PD device, a peak responsivity of 0.57 A/W is measured at 0.84 eV. Interestingly, this value almost doubles up to 1.04 A/W after RTA, thus with a similar enhancement ratio to what is observed in
the I-V curves (Figure 5a). As expected, an additional Si\(_{0.06}\)Ge\(_{0.90}\)Sn\(_{0.04}\) absorption edge is visible at 0.82 eV, which is \(~40\) meV above the Ge-related peak. This energy shift is in perfect agreement with SE and transmission measurements (Figure 3) and it is unaffected by post-growth RTA. Increasing the Si content would increase the energy shift toward higher energy bandgap, which offers high potential for photovoltaic applications. [24,55] The fact that the spectral responsivity of annealed Si\(_{0.06}\)Ge\(_{0.90}\)Sn\(_{0.04}\) PDs slightly outperforms that of Ge-based ones is rather surprising given the thermal budget applied to each set of these devices. Indeed, as mentioned above, Ge layers were subjected to post-growth thermal cyclic annealing in H\(_2\) above 800 °C to reduce threading dislocation density and improve crystallinity, which should increase PD performance. In Si\(_{0.06}\)Ge\(_{0.90}\)Sn\(_{0.04}\), the rapid thermal annealing was limited to 380 °C (30 s) to maintain the crystalline quality of these metastable layers. [56] Nevertheless, optimized thermal annealing protocols for SiGeSn could further increase device efficiency.

The results above demonstrate that high quality, micrometer-thick SiGeSn semiconductors can be grown with optoelectronic properties that can deliver similar (if not higher) performance as Ge/Si devices. This, combined with the possibility to independently engineer the lattice parameter and bandgap energy, paves the way for SiGeSn as a suitable material for IR detection. Unlike conventional II-VI and III-V semiconductors used in IR applications, SiGeSn can be tuned from indirect to direct bandgap material by controlling the Sn/Si composition ratio, thus enabling advanced carrier lifetime engineering at a tunable (or fixed) energy of the optical absorption. [57] Moreover, the SiGeSn directness (\( \Delta = E_r - E_L \)) increases with Sn content leading to higher absorption, while preserving the long carrier lifetime of an indirect bandgap semiconductor. This would lead to electrons to scatter from direct to indirect valleys in the conduction band, thus suppressing radiative and Auger recombination and potentially resulting in a quasi-direct
semiconductor regime with $k$-space charge separation. [2] High carrier collection efficiency is required for the development and integration of a 1.0 eV SiGeSn junction in hybrid Ge/InGaAs/InGaP multijunction solar cells as an alternative approach to conventional III-V/Ge devices. [24,55] In lattice-matched Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$/Ge heterostructures, optically-generated carriers in Ge can diffuse through the SiGeSn heterostructure due to the low dislocation density, and be collected on the sample surface. This is a promising feature that can be beneficial for the integration in scalable solar cells.

IV. Conclusion

In this work, we demonstrated the lattice-matched growth of a 1.5 μm-thick Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ layer on a Ge-VS/Si wafer. Structural and atomistic characterization reveal the high crystalline quality, uniform composition, and the absence of short-range ordering effects and clusters in the Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ epilayer. Room temperature direct bandgap absorption at 0.83 eV in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ was investigated by combining spectroscopic ellipsometry, transmission, and photocurrent measurements. The optical analysis shows a reduction of the indirect bandgap absorption at lower energies and of the Urbach energy. Similar dark current was estimated in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ and Ge photoconductive devices and found to be one order of magnitude lower than that of binary GeSn multi-layer devices. The low dark current in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ further highlights the benefit of a lattice-matched growth on device performance, thus paving the way for high bias voltage applications with reduced noise and power dissipation. Lastly, spectral responsivity of 1.0-1.1 A/W in the 0.82-1.15 eV range (i.e., 1.5-1.0 μm wavelength range) was recorded at room temperature in Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$, hence comparable to similar devices made of
Ge. These results cement the relevance of SiGeSn as versatile building blocks for silicon-integrated infrared optoelectronics.

**Supplemental Material**

Supplemental Material is available online or from the author.

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Notes

The authors declare no competing financial interest.

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**Conflict of Interest**

The authors declare no conflict of interest.
Data Availability
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Figures and table captions

Figure 1. (a) STEM image of the 1.5/1.9 μm-thick Si_{0.06}Ge_{0.90}Sn_{0.04}/Ge-VS heterostructure grown on a Si wafer. (b-c) Low-resolution TEM images acquired across the heterostructure showing the Si_{0.06}Ge_{0.90}Sn_{0.04}/Ge-VS (b) and Ge-VS/Si (c) interfaces. (d) 2θ-ω scan around the (004) X-ray diffraction order. (e) RSM around the asymmetrical (224) reflection.

Figure 2. (a-b) APT 3D reconstruction (a) and compositional profiles for the Si, Sn atoms (b). (e) Enlarged view of (d) showing the interface region between Si_{0.06}Ge_{0.90}Sn_{0.04} and Ge-VS. (f) NN distributions evaluated up to the 10th order (solid spheres) for the Si-Si (top curves) and Sn-Sn (bottom curves) pairs. The theoretical curves for a perfect random alloy are shown as dashed black curves.

Figure 3. (a) Optical micrograph and schematics of the back-to-back metal-oxide-semiconductor device. (b) C-V curves for Si_{0.06}Ge_{0.90}Sn_{0.04} and Ge-VS acquired at a frequency of 1 MHz. The latter curve was adapted from Ref. [38].

Figure 4. (a) Complex dielectric function (ε_1 (dashed line) and ε_2 (solid line)) of 1.5/1.9 μm-thick Si_{0.06}Ge_{0.90}Sn_{0.04}/Ge-VS (blue curves), 1.9 μm-thick Ge-VS (red curves), and 3.0 μm-thick Ge-VS (dark red curves) samples. (b) Tauc plot (αhν)^2 and linear fit for the bandgap (dashed lines). Inset: Urbach tail fit (dotted lines) for α. (c) Transmission measurements (solid curves) and simulated curves calculated from the SE built optical model (dotted curves). (d) Derivative of the T as a
function of energy showing independent HH and LH bands. The vertical dashed lines in (c-d) are the estimated $E_0$ values from SE.

**Figure 5.** (a) Optical micrographs and I-V curves for as-grown (blue) and annealed (green) Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ PD devices. (c) I-V curves for annealed (green) Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$, 1.9 µm-thick (dashed red) and 3.0 µm-thick (dotted dark red) Ge-VS PDs. The curves for Ge$_{1-x}$Sn$_x$ (x=10.5-13-17 at.%, pink-orange-purple curves) PDs from Ref. [38] are shown as a comparison.

**Figure 6.** (a) Responsivity curves for all samples acquired at a bias voltage of 25 V. (b) Enlarged view of (a) and corresponding derivative as a function of the energy. Vertical dashed lines indicate the $E_g$ values estimated from the optical measurements in Figure 4.

**Table 1.** List of the structural and optoelectronic parameters obtained from TEM, APT, SE, transmission (T), and photodetector (PD) responsivity measurements.

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Figure 1
Figure 2

(a) Si, Ge, Sn
(b) Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$

1550 nm

Position (nm)

APT composition (at. %)

Si
Sn

(c) Si-Si distance (nm)

Counts/events (arb. units)

Sn-Sn distance (nm)

2nd 3rd 4th 5th 10th

1st 2nd 3rd 4th 5th 10th
Figure 3
Figure 5

(a) 

(b) 

[Graph showing dark current vs. bias for Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ and Si$_{0.06}$Ge$_{0.94}$Sn$_{0.04}$ samples before and after annealing.] 

[Graph showing dark current vs. bias for Ge$_{1-x}$Sn$_x$ with different Sn concentrations and Ge-VS with different film thicknesses.]
Figure 6
|                  | Thickness (nm) | Strain (%) | \(a_0\) (Å) | \(E_0\) [SE] (eV) | \(E_1\) [SE] (eV) | \(E_1 + \Delta_1\) [SE] (eV) | \(\Delta E\) [SE] (meV) | \(E_\Gamma\) [T] (eV) | \(E_\Gamma\) [PD] (eV) |
|------------------|----------------|------------|----------------|-----------------|----------------|-------------------------------|------------------------|-------------------|-------------------|
| Si_{0.06}Ge_{0.90}Sn_{0.04} | 1550 (±20)     | -0.21      | 5.669 (l)     | 0.836           | 2.099          | 2.301                         | 5.7                    | 0.829             | 0.823             |
|                  |                |            | 5.680 (l)     | (±0.002)        | (±0.03)        | (±0.03)                       | (±0.3)                 | (±0.02)           | (±0.04)           |
|                  |                |            | (±0.001)      | (±0.001)        | (±0.001)       | (±0.001)                      | (±0.001)               | (±0.001)          | (±0.001)          |
| Ge-VS            | 3000 (±20)     | 0.15       | 5.666 (l)     | 0.785           | 2.121          | 2.305                         | 14.8                   | 0.775             | 0.784             |
|                  |                |            | 5.651 (l)     | (±0.002)        | (±0.01)        | (±0.01)                       | (±0.5)                 | 0.788             | (±0.04)           |
|                  |                |            | (±0.001)      | (±0.001)        | (±0.001)       | (±0.001)                      | (±0.01)               | (±0.01)           | (±0.01)           |
| Ge-VS            | 1900 (±20)     | 0.20       | 5.669 (l)     | 0.779           | 2.115          | 2.298                         | 12.2                   | 0.775             | 0.777             |
|                  |                |            | 5.650 (l)     | (±0.008)        | (±0.01)        | (±0.02)                       | (±0.5)                 | 0.788             | (±0.04)           |
|                  |                |            | (±0.001)      | (±0.001)        | (±0.001)       | (±0.001)                      | (±0.01)               | (±0.01)           | (±0.01)           |

**Table 1**
Supplemental Material:

Micrometer-thick, atomically random SiGeSn for silicon-integrated infrared optoelectronics

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S1. Fine tuning of the composition during SiGeSn epitaxy

The effect of the \( \text{Si}_2\text{H}_6 \) precursor flow on the SiGeSn epitaxy was investigated using on a 500 nm-thick \( \text{Si}_{0.06}\text{Ge}_{0.90}\text{Sn}_{0.04} \) layer grown at 360 °C on a 250 nm-thick \( \text{Ge}_{0.975}\text{Sn}_{0.025} \) layer, as shown in Figure S1 and S2. A fixed Ge/Sn ratio in gas phase (i.e. constant GeH\(_4\) and SnCl\(_4\) flows) was kept constant across the SiGeSn/GeSn heterostructure, while the Si\(_2\)H\(_6\) supply was varied during growth. Two different set of samples were grown using Ge/Sn=2041 and Ge/Sn=2381. The \( 2\theta-\omega \) scans performed around the (004) XRD order acquired on multiple samples grown with a variable Si/Sn ratio in gas phase are shown in Figure S1a-b, while the angle of the SiGeSn peak is plotted in Figure S1c. This peak shifts to larger angles (i.e. higher Si content in a strain-free material) with increasing Si\(_2\)H\(_6\) flow, until a critical Si/Sn threshold is surpassed and the peak disappears. In this regime, a shoulder peak on the lower side of the Ge-VS peak develops, which resembles the situation that is commonly associated with phase separation and segregation of Sn at the surface. [1] Indeed, by comparing 20x20 μm\(^2\) atomic force microscopy (AFM) scans acquired for Ge/Sn=2041 with Si/Sn<15 (Figure S1d) and Si/Sn>15 (Figure S1e) the growth evolves from planar into three-dimensional islands with a lateral dimension of a few microns when the critical threshold is surpassed. We note that when the GeH\(_4\) flow was increased (Ge/Sn=2381) a similar trend was observed, however with an increased critical Si/Sn threshold Si/Sn=21. This behavior suggests that a complex interplay in the decomposition kinetics of GeH\(_4\)-SnCl\(_4\)-Si\(_2\)H\(_6\) precursors most likely occurs during growth.

The effect the growth temperature on the SiGeSn epitaxy is shown in Figure S3. By increasing the temperature to 370 °C a reduction in the Si and Sn content by less than 0.5 at.% is observed, without compromising the structural quality of the material. A decrease in growth temperature to 350 °C did result, however, in three-dimensional islands growth, as discussed above in Figure S1.
Figure S1. (a-b) $2\theta$-$\omega$ scan around the (004) X-ray diffraction order for samples grown with a variable Si$_2$H$_6$ flow grown with a fixed Ge/Sn=2041 (a) and Ge/Sn=2381 (b). (c) Plot of the SiGeSn peak position as a function of the Si/Sn ratio in gas phase. Two different datasets are shown for Ge/Sn=2041 (red dots) and Ge/Sn=2381 (blue dots). (d-e) 20x20 $\mu$m$^2$ AFM images acquired Si/Sn<15 (d) and Si/Sn>15 (e) using Ge/Sn=2041.

Figure S2. (a-c) TEM image (a), APT compositional profile (b), and RSM around the asymmetrical (224) reflection (c) for the Si$_{0.08}$Ge$_{0.88}$Sn$_{0.04}$ sample grown at 360 °C using Ge/Sn=2041 and Si/Sn<15.
Figure S3. (a) 2θ-ω scan around the (004) X-ray diffraction order showing the effect of the growth temperature on the SiGeSn epitaxy. (b-d) TEM image (a), APT compositional profile (b), and RSM around the asymmetrical (224) reflection (c) for the Si$_{0.070}$Ge$_{0.895}$Sn$_{0.035}$ sample grown at 370 °C using Ge/Sn=2041 and Si/Sn<15.
S2. APT analysis of Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$

The enlarged view of Figure 2b in the proximity of the Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$-Ge interface is shown in Figure S4a-b. An increase in the Sn content from 1 at.% to 3.5 at.% is visible when moving ~150 nm away from the interface with Ge. This behavior could be related to the strain-driven incorporation during growth. A small compressive strain in the early stages of the SiGeSn growth would lower the amount of Sn that can be incorporated in the lattice. [2] Only by promoting plastic strain relaxation during growth, the incorporation of Sn would be progressively enhanced with layer thickness, which could explain the early compositional gradient. In the same thickness range, an increase of Si content is observed, which would suggest that Si incorporation is enhanced by the compressive strain, hence exhibiting the opposite behavior as compared to Sn. Moreover, temperature, dislocation, strain, and point defects play a critical role in the diffusion process of Si, Ge, and Sn atoms growth of lattice-mismatched heterostructures. In a coherent heterostructure, hence similar to Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$/Ge-VS in Figure 1, even when intermixing is thermally suppressed at low temperatures, the presence of point defects in the lattice (mono-and divacancies and vacancy clusters) could still enhance the diffusion of the atomic species through the crystal. [3,4] Additionally, metastability, hence the gradient in chemical potential, enhances diffusion in Sn-rich alloys at temperatures below 600 °C. [5] The Sn diffusion from Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ to Ge-VS (Figure S4b) could indeed be a vacancy-assisted process promoted by the metastable state of the alloy. Additionally, self-diffusion of Si, Ge, Sn atoms during growth could also take place during growth. However, the absence of clusters and short-range ordering in SiGeSn indicates that self-diffusion, if present, has a negligible effect on the quality of the epilayer.

In the frequency distribution analysis (FDA) shown in Figure S4c, a binning of 250 neighboring atoms was considered and then compared with the binomial distribution that is expected for a random alloy (dashed curves). Excellent agreement between measurements and simulated behavior is obtained. In the partial radial distribution function (p-RDF) analysis for the Si (Figure S4d) and Sn (Figure S4e) atoms the curves reach the measured stoichiometry of the sample, thus in further agreement with the expected random alloy nature of the material.
Figure S4. (a-b) Enlarged views of the APT compositional profiles from Figure 2b. The dotted horizontal lines indicate the noise level. (c) FDA analysis for 250 atoms. The binomial distributions are shown using dashed curves. (d-e) p-RDF for the Si (d) and Sn atoms (e).
S3. Frequency-dependent C-V measurements.

At a fixed frequency of 1 MHz (Fig. 3b) the active carrier concentration in the samples was estimated according to the following equation:

$$N_{\text{sub}} = \frac{2}{q \varepsilon_s A^2 \left( \frac{\Delta 1}{\Delta V_g} \right)^2}, \quad (\text{Eq. 1})$$

where $\varepsilon_s$ is the relative permittivity of the semiconductor, $A$ is the area of the gate, and $\left( \frac{\Delta 1}{\Delta V_g} \right)^2$ is the averaged slope of the linear part in transition region of the C-V curves. The relative permittivity of GeSn was assumed to be similar to pure Ge with a value of $\varepsilon_s = 16$. We note that a correction factor of 0.8 was used for the area in the B2B devices based on the dimensions of the ring geometry of the capacitor.

The representative multifrequency measurement on SiGeSn (back-to-back, B2B) metal oxide semiconductor capacitors (MOSCaps) in Figure S5 reveal well-formed, steep C-V characteristics without noticeable overall frequency dispersion and gate leakage. By varying the frequency over three orders of magnitude, a single minimum is observed at -0.9 V, which indicates that only the device of interest (with smaller area) is dominant in the SiGeSn B2B MOSCap device. Although a slight frequency dispersion in accumulation region can be observed, which might be attributed to series resistance, the device shows switching characteristics that are similar to the state-of-the-art n-type MOSCaps. This further supports the estimation of the n-type doping in the material. The MOSCaps from low bandgap semiconductors typically depict bumps in their response curves which are attributed to the presence of defect states in the vicinity of the semiconductor/oxide interface ($D_{it}$). The SiGeSn MOSCaps not only show U-shaped low frequency behavior at low to moderate frequencies (>1 kHz) at room temperature (ascribed to enhanced minority carrier generation, originating from the small bandgap at dark condition), but its response is also free from any weak inversion bump (related to moderate $D_n$) or bump in the depletion region (related to significantly higher $D_n$).
S4. Spectroscopic ellipsometry measurements protocol.

In spectroscopic ellipsometry (SE) measurements, a beam of linearly polarized light is emitted onto the surface of a solid sample at an oblique angle of incidence (AOI). SE measure the amplitude ratio and the phase difference between $p$- and $s$-polarizations, from which the optical constants can be deduced. The ellipsometric angle $(\Psi, \Delta)$ were acquired from 250 to 2500 nm with 1 nm step at 6 AOI (between 60° and 85° with a 5° step), on a J.A. Woollam© RC2-XI spectroscopic ellipsometer, with a dual rotating compensator. The dielectric functions of the SiGeSn samples on Ge were obtained by modeling the ellipsometry data and doing a multi-sample analysis (MSA). The dielectric functions for the GeO$_2$ [6] and SnO$_2$ [7] were used in tabulated form from published data whereas the dielectric function of Ge was measured independently with SE and modelled from two as-grown CVD-samples with 1.9 µm and 3 µm layers thicknesses. Tensile strain in both Ge layers was estimated with HRXRD around 0.20 % and 0.14 %, respectively.

Direct and reverse SE and spectrophotometry were combined to measure the band gap of the two semiconductors (Ge-VS, Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$). Figure S6 details the measurement strategy as well as a schematic representation of the SE multilayer model composing each sample. The red and blue
arrows refer, respectively, to a direct (from the top of the sample) or reverse (from the bottom of the sample) SE measurement whereas the blue arrow is either a measurement of reflectance ($R$) when the substrate is single side polished (ISP) or both transmittance ($T$) and $R$ if the substrate is double side polished (DSP). Next, to extract the band gap from these semiconductors, Multi-sample analysis (MSA) was used, and an SE model was built and fitted the $R$, $T$, and SE measurement simultaneously whenever possible, as shown in panel (a) and (b) of Figure S6.

![Figure S6: Measurement strategy for the (a) Ge-VS, and (b) Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ semiconductors. The red arrows indicate the direct (from the top of the sample) or reverse (from the bottom of the sample) SE measurement, whereas the blue arrows are the $R$ and $T$ measurement. For ISP Si-substrate, only $R$ was measured from the top surface. The shown numbers (x2) indicate the number of grown samples that were characterized with multi-sample analysis.](image)

For reliable fitting of the ellipsometry data of group-IV semiconductor thin films, the following steps were followed:

1. The multi-sample analysis (MSA) approach was used to model the reverse and direct SE measurement as well as $R$ and $T$ of the 1.5µm thick Si$_{0.06}$Ge$_{0.90}$Sn$_{0.04}$ layer grown on a Ge-VS/DSP-Si.

2. Independent thickness measurement was performed with STEM and APT (Figure 1a-c and Figure 2b), surface characterization with AFM (Figure S1d) to quantify the surface roughness layer (RMS), and strain with XRD and RSM maps (Figure 1e).

3. Adequate optical description of Si-substrate is important. To build an accurate optical model to extract the band gap of the SiGeSn layer, modelling the s- and p-polarized transmission and reflectance spectra at different AOI as well as the direct and reverse ellipsometric data was
considered as highlighted previously. However, some difficulties were encountered that hindered the analysis. The issue encountered while fitting the SE parameters was that the agreement of the model with the transmission data was significantly worse than the agreement with the ellipsometry data. This can partly occur due to higher sensitivity of the MSE value to the agreement between experimental and calculated ($\Psi$, $\Delta$) as compared to $T$, and/or due to inadequate description of the optical properties of the substrate. Therefore, we have examined the optical functions of the Si substrate more closely and have performed simultaneous fitting of the transmission and ellipsometry data for the Si substrate. We found that the commonly used Johs-Herzinger model [8] does not adequately describe the substrate transmission and reflection, while good fit can be obtained using a generalized oscillator model to account for the fact that there is a very small absorption in the substrate, induced by the p-type doping of the wafer (B-doped with resistivity of 1-10 $\Omega$.cm), resulting in a significant fit improvement (MSE < 2) (see Figure S7). The blue line in Figure S7 indicates the fitted transmittance calculated with the newly built generalized oscillator optical model.

![Figure S7](image)

**Figure S7:** Modeled transmittance near Brewster angle 75° of DSP (Virginia Semiconductor and MTI Corp. wafer suppliers) Si substrate with the JH model [8] (dashed red) and the new optical model (blue).

(4) The thickness of the layers in the optical models (Figure S6) is fixed, and the optical properties ($n$ and $k$) are fitted to the PSEMI model in the entire spectral range. For direct or indirect semiconductors, one of the most sophisticated dispersion models is the parametric semiconductor
model (PSEMI) developed by Johs-Herzinger, [9,10] which is based upon the mathematical formalism developed by Garland and Kim. [11] Recently, it has been established that for group-IV tetrahedral semiconductors, the PSEMI model can accurately evaluate the critical points for relaxed and/or strained group-IV alloys [12,13] or thin-film semiconductors. The primary purpose of the PSEMI model is to accurately reproduce the dielectric function of semiconductors with complicated critical point structures (E0, E1, E1+Δ1, etc.) in a Kramers-Kronig consistent manner. The result of the built optical model is shown in Figure S8 for the 4 semiconductors where the SE parameter (tan Ψ) is shown at all the spectral range for only 3 AOI (for clarity reasons). The inset in Figure S7 indicate the accuracy of the model (the small MSE also corroborate the quality of the fit) to extract the band gap of the 2 semiconductors as the fitted and experimental data are shown in a small energy range (from 0.5 eV to 1 eV).

Repeat step 4 with and without EMA layer to account for the surface roughness (if roughness is small, improvement with EMA is also small, and parameter uncertainties may be large).

**Figure S8.** Raw (full circles) and fitted (red lines) ellipsometric parameter (tan Ψ) for the different studied semiconductors at three different angles of incidence (70°, 75° and 80°) near the Brewster angle of Si and Ge. From top panel to bottom: Si0.06Ge0.9Sn0.04, and 1.9 µm-thick Ge-VS. The 2 insets correspond to a zoom in the spectral region between 0.5 and 1 eV, as the direct band gap of the 2 semiconductors is hidden within the observed interference fringes.
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