Strain-free GeSn nanomembranes enabled by transfer-printing techniques for advanced optoelectronic applications

Tai, Yeh-Chen; Yeh, Po-Lun; An, Shu; Cheng, Hung-Hsiang; Kim, Munho; Chang, Guo-En

2020

Tai, Y., Yeh, P., An, S., Cheng, H., Kim, M. & Chang, G. (2020). Strain-free GeSn nanomembranes enabled by transfer-printing techniques for advanced optoelectronic applications. *Nanotechnology*, 31(44), 445301-.
<https://dx.doi.org/10.1088/1361-6528/aba6b1>

<https://hdl.handle.net/10356/153651>

<https://doi.org/10.1088/1361-6528/aba6b1>

© 2020 IOP Publishing Ltd. All rights reserved. This is an author-created, un-copyedited version of an article accepted for publication in *Nanotechnology*. IOP Publishing Ltd is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The definitive publisher authenticated version is available online at <https://doi.org/10.1088/1361-6528/aba6b1>.

Downloaded on 26 Apr 2023 18:20:12 SGT

Strain-free GeSn nanomembranes enabled by transfer-printing techniques for advanced optoelectronic applications

Yeh-Chen Tai¹, Po-Lun Yeh¹, Shu An², H. H. Cheng³, Munho Kim^{2*}, and Guo-En Chang^{1*}

¹. Department of Mechanical Engineering, and Advanced Institute of Manufacturing with High-Tech Innovations (AIM-HI), National Chung Cheng University, Chiayi 62102, Taiwan

²School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798 Singapore, Singapore

³Center for Condensed Matter Sciences, and Graduate Institute of Electronics Engineering, National Taiwan University, Taipei 10617, Taiwan

* Address correspondence to: imegec@ccu.edu.tw (Guo-En Chang)

munho.kim@ntu.edu.sg (Munho Kim).

Abstract

GeSn alloys have emerged as promising materials for silicon-based optoelectronic devices. However, the epitaxy of pseudomorphic GeSn layers on a Ge buffer is susceptible to a significant compressive strain that significantly hinders the performance of GeSn-based photonic devices. Herein, we report on a new strategy to produce strain-free GeSn nanomembranes for advanced optoelectronic applications. The GeSn alloys were grown on a silicon-on-insulator substrate using a Ge buffer, and it has a residual compressive strain. By transfer-printing the GeSn/Ge/Si multi-layers, followed by etching the Si template and the Ge buffer layers, respectively, the residual compressive strain was completely removed to achieve strain-free GeSn layers. A bandgap reduction was also observed as a result of strain relaxation. Furthermore, theoretical analysis was performed to evaluate the effect of strain relaxation on the GeSn-based optoelectronic devices. The proposed approach offers a practical and viable method for preparing strain-free GeSn alloys for advanced optoelectronic applications.

Main text

Group-IV germanium-tin (GeSn) material systems have recently gained increasing attention for optoelectronic applications [1, 2]. Pure Ge is a fairly abundant and less toxic semiconductor compared with III–V semiconductor compounds, and has been widely used in the current Si semiconductor electronics industry. However, the indirect bandgap of pure Ge prevents its applicability in high-performance optoelectronic applications. However, the energy difference between the direct conduction band and the lowest L-valley conduction band edge ($\Delta E_{\Gamma L}$) is only 136 meV at room temperature [3], thus suggesting the possibility of engineering the band gap from indirect to direct to facilitate the use of the material in advanced optoelectronic applications. Extensive efforts have been made to enable indirect-to-

direct bandgap transition. This indirect-to-direct bandgap transition can be achieved by alloying Ge with its group-IV neighbor, Sn [4]. The introduction of Sn into Ge significantly decreases both the direct and indirect bandgaps, resulting in reduced $\Delta E_{\Gamma L}$. With a Sn content of ~6% [5], bulk GeSn can be transformed into a direct bandgap material, thereby making it suitable for efficient photonic devices. In addition, the bandgap energy of GeSn can be widely tuned by adjusting the Sn composition, thus offering a widely tunable range in the mid-infrared applications [6–8]. Although the solid solubility of Sn in Ge is less than 2% in equilibrium, recent advances in low-temperature growth techniques have enabled the growth of high-quality GeSn layers with a Sn composition up to 30% [6–13]. Based on this development, GeSn-based LEDs/lasers [9, 14–16], modulators [17], and photodetectors (PDs) [18–28] have also been recently demonstrated.

Although the GeSn material system exhibits great potential for optoelectronic applications, the epitaxial growth of GeSn experiences many challenges. The lattice constant of GeSn is more than 4.2% larger than that of Si, thus making it very challenging to directly grow high-quality GeSn layers on Si substrates. Instead, the Ge buffer technology was introduced to reduce the lattice mismatch between GeSn and the substrate [20, 21]. However, the disadvantage of the epitaxial growth of GeSn on the virtual Ge substrate is the introduction of a crucial compressive strain (~0.143% per 1% Sn), which significantly reduces the effect of Sn-alloying on the band structures, and thus, the performance of GeSn-based optoelectronic devices. The compressive strain can significantly increase both the direct and indirect bandgap energies. The direct bandgap energy shifts approximately five times faster than the indirect bandgap energy, thereby significantly increasing $\Delta E_{\Gamma L}$ [3]. As a result, the Sn content required to achieve indirect-to-direct bandgap transition is considerably increased from ~6% for the bulk GeSn to ~17% for the pseudomorphic GeSn on Ge [29]. This could significantly increase the level of challenge to achieve direct-bandgap GeSn alloys. In

addition, the increased direct bandgap due to the compressive strain will induce a blue shift in the direct-gap absorption edge [30], thereby counteracting the bandgap reduction by Sn-alloying and weakening the bandgap energy tunability for photonic devices. Furthermore, a higher Sn composition also degrades the thermal budget of GeSn alloys. Therefore, it is crucial to relax the compressive strain in the GeSn films to enhance the performance of GeSn-based photonic devices.

To address this challenge, several approaches have been developed to reduce the residual compressive strain in GeSn, such as the use of III–V lattice-matched buffer layers [5], graded GeSn virtual substrates [9], and suspending structures by selectively removing the Ge buffer layer [32]. In this paper, we present a new strategy to achieve strain-free GeSn alloys via a transfer-printing of nanomembranes (NMs). Single-crystalline semiconductor NMs are transferrable free-standing thin films with unique advantages such as excellent mechanical flexibility and material quality (e.g., high mobility and light absorption) [33–38]. By transfer-printing the GeSn NMs and removing the Ge buffer layer, the compressive strain that was initially stored in the GeSn was successfully removed. The structural properties of transfer-printed GeSn NMs were systematically investigated using X-ray diffraction (XRD) and Raman spectroscopy. Furthermore, the bandgap variation due to the strain relaxation was confirmed based on transmission experiments. The impact of strain relaxation on the bandgap energy of GeSn was theoretically analyzed. These results demonstrate a practical method for achieving strain-free GeSn layers for advanced optoelectronic applications.

Figure 1. (a) SIMS depth profile along the growth direction and (b) (224) X-ray reciprocal space mapping of the grown GeSn sample.

The sample used in this study was grown using solid-source molecular beam epitaxy (MBE) on a (001) silicon-on-insulator substrate (SOI) substrate with a 2.5- μm -thick top Si layer and a 1 μm -thick buried oxide (BOX) layer. Here, the BOX layer functions as the sacrificing layer for the undercut process. A 120-nm-thick Ge virtual substrate (VS) was initially grown using a two-step growth technique, consisting of a 60-nm Ge buffer layer grown at a low temperature (LT) of 350 $^{\circ}\text{C}$, followed by an in-situ annealing at 800 $^{\circ}\text{C}$ for 5 min. A 60-nm Ge buffer layer was further grown at a high temperature (HT) of 550 $^{\circ}\text{C}$. Subsequently, the growth temperature was decreased to 150 $^{\circ}\text{C}$ to facilitate the growth of the 370-nm-thick GeSn layer. Finally, a 3-nm-thick Si cap layer was deposited. The structural properties and Sn composition of the grown GeSn sample were systematically investigated using secondary ion mass spectroscopy (SIMS) and XRD. Figure 1 shows the SIMS atomic distributions of the Ge and Sn atoms along the growth direction, from which the thickness of the GeSn layer is determined to be 370 nm. A uniform Sn distribution was confirmed in the GeSn layer. Figure

1(b) shows the XRD (224) reciprocal space mapping (XRDRSM) results for the grown GeSn sample. Several peaks were observed, which are associated with the low-temperature (LT) Ge buffer, high-temperature (HT) Ge buffer and GeSn layers, respectively. The GeSn peak and HT Ge peaks were aligned at the Q_x , as indicated by the pseudomorphic line, thereby suggesting that the GeSn layer was pseudomorphic with respect to the Ge buffer layer. From the Q_x value, the in-plane lattice constant was obtained as $a^{\parallel} = 5.6616 \text{ \AA}$, which is slightly larger than that of bulk Ge ($a_0 = 5.6573 \text{ \AA}$ [39]), and suggests an in-plane strain of 0.077% in the HT Ge buffer. On the other hand, from the Q_y value of the GeSn peak, the out-of-plane lattice constant of GeSn was obtained as $a^{\perp} = 5.6989 \text{ \AA}$. With the in-plane and out-of-plane lattice constants, the bulk lattice constant of the GeSn layer can be obtained using:

$$a_0 = \frac{a^{\perp} + 2a^{\parallel}\mu}{1 + 2\mu} \quad (1)$$

where, $\mu = C_{12} / C_{11}$ is the ratio of the elastic constants and the value for $\text{Ge}_{1-x}\text{Sn}_x$ is $\mu = 0.3738 + 0.1676x - 0.0296x^2$ [7, 40]. On the other hand, the composition-dependent lattice constant of bulk $\text{Ge}_{1-x}\text{Sn}_x$ is:

$$a_0(\text{Ge}_{1-x}\text{Sn}_x) = (1-x)a_0(\text{Ge}) + xa_0(\text{Sn}) - bx(1-x) \quad (2)$$

where, $a_0(\text{Ge}) = 5.6573 \text{ \AA}$ and $a_0(\text{Sn}) = 6.4892 \text{ \AA}$ are the bulk lattice constants of Ge and α -Sn, respectively, and $b = -0.066 \text{ \AA}$ is the bowing parameter [40]. Substituting the extracted lattice constant of GeSn from the XRDRSM experiments into Eq. (2) yields $x = 3.3\%$ for the grown GeSn sample. The corresponding in-plane biaxial strain in the GeSn layer is $\varepsilon_{\parallel} = -0.41\%$.

Figure 2. (a) The schematic representation of the fabrication of strain-free GeSn NMs; (a-i) Growth of a 370-nm-thick GeSn alloy on SOIs by MBE, (a-ii) Patterning NMs with an array of etching holes followed by an HF undercut process, (a-iii) Flip-transferring of $3 \times 3 \text{ mm}^2$ -sized GeSn NMs on SU-8 2002 coated PET substrates, with the Si template layer facing the top, (a-iv) Preparation of strain-free GeSn NMs via etching down to the GeSn layer by removing the top Si template and Ge buffer layers. (b and c) Corresponding cross-sectional view and AFM images for each step. (d) An optical image of strain-free GeSn NMs on PET and its magnified microscopic image.

Figure 2 depicts a schematic representation of the process used to obtain strain-free GeSn NMs. In short, the strain-free GeSn NMs were fabricated using a transfer-printing technique, followed by the removal of the Ge buffer layer. The process began with the epitaxial growth of the 370-nm GeSn alloy using MBE (Figure 1(a-i)). Standard photolithography and dry etching were used to pattern the NMs with an array of etching holes, followed by a hydrofluoric (HF) undercut process (Figure 2(a-ii)) [33]. Then, the released NMs (i.e., GeSn/Ge/Si) were flip transfer-printed on an adhesive layer (SU-8 2002) with a thickness of $\sim 2 \text{ μm}$, then coated on the 120- μm polyethylene terephthalate (PET) (Figure 2(a-iii)). Figure

2(b) depicts the corresponding cross-sectional structure of NMs in the respective steps. The printed NMs had a Si template layer facing the top (Figure 2(b-iii)). Finally, the strain-free GeSn NMs with a final thickness of ~ 200 nm were obtained by a precise CF_4 gas-based etching of the top Si template and Ge buffer layers, respectively (Figure 2(a-iv)). In addition, the change in surface roughness was measured by atomic force microscopy (AFM). As shown in Figure 2(c), the root mean square (RMS) roughness of GeSn on the SOI is 6.24 nm. The flip-transferred GeSn NMs had an RMS roughness of 1.46 nm with the Si template layer positioned face up. It is widely known that a smooth interface exists between the Si template and the BOX layers of the SOIs fabricated using a Smart-Cut technique [41]. A final RMS roughness of 3.6 nm was measured from the strain-free GeSn NMs. The result indicates that the surface roughness of the GeSn was reduced, which enables further device fabrication.

Figure 3. 2θ scans for the as grown GeSn sample, transfer-printed GeSn sample, and bulk Ge.

To examine the strain relaxation of the transfer-printed GeSn layer, XRD and μ -Raman spectroscopy were conducted. Figure 3 shows the X-ray 2θ scans for the as-grown GeSn sample, the transfer-printed GeSn NMs, and a bulk Ge wafer. From the Bragg angle (θ), the out-of-plane lattice constant can be determined via $a^\perp = 2\lambda / \sin \theta$, where $\lambda = 0.15406 \text{ nm}$ is the wavelength of the X-ray. The Bragg angle of the as-grown GeSn sample was noticeably smaller than that of bulk Ge because of the larger lattice constant of GeSn and the out-of-plane tensile strain. In addition, the Bragg angle of the transfer-printed GeSn NMs is significantly larger than that of as-grown GeSn sample, thus highlighting the significant strain relaxation. From the Bragg angle, the out-of-plane lattice constant of the transfer-printed GeSn is extracted as $a^\perp = 5.686 \text{ \AA}$. This value is almost identical to the bulk lattice constant of the GeSn layer ($a_0 = 5.685 \text{ \AA}$), thereby suggesting that the transfer-printed GeSn layer is strain free. These results demonstrate that the compressive strain stored in the GeSn layer can be removed using the transfer-printing techniques.

Figure 4. Raman spectra of bulk Ge, as-grown GeSn sample, and transfer-printed strain-free GeSn NMs.

The μ -Raman experiments were conducted under a backscattering scheme with an unpolarized 633 nm laser focused onto the sample surface via a 20 $\times$ objective with a spot size of ~ 10 μ m, in which the LO phonon mode was obtained. The intensity of the laser was intentionally kept low to hinder the thermal heating effect. Figure 4 shows the Raman shifts for bulk Ge, as-grown GeSn, and transfer-printed GeSn measured at room temperature. A peak was observed at 300 cm⁻¹ for bulk Ge, which is associated with the Ge-Ge LO phonon mode. For the as-grown GeSn sample, the Raman peak shifted to a lower wavenumber compared with the bulk Ge reference because of the introduction of Sn. The main peak associated with a shoulder at a higher wavenumber was observed. The former and latter peaks are attributed to Ge-Ge LO phonon mode from the GeSn and the Ge buffer layers,

respectively. The peak values were obtained by fitting the data using Gaussian functions, and the results were displayed as the solid lines in Fig. 4(b), yielding $\omega = 298.842 \pm 0.183 \text{ cm}^{-1}$ for the GeSn layer. For transfer-printed GeSn NMs, as shown in Fig. 4(c), it is evident that the Raman peak shifted further to a lower wavenumber of $\omega = 296.486 \pm 0.103 \text{ cm}^{-1}$, which again supports the strain relaxation in GeSn NMs. For biaxially stressed $\text{Ge}_{1-x}\text{Sn}_x$ layers, the Raman shifts of the Ge-Ge LO mode can be linked to the Sn composition and the in-plane strain by:

$$\Delta\omega(x, \varepsilon_{\parallel}) = ax + b\varepsilon_{\parallel} \quad (3)$$

From the Sn composition and strain values obtained from the X-ray experiments and the Raman shifts, we obtained $a = -106.48 \pm 3.21 \text{ cm}^{-1}$ and $b = 573.90 \pm 19.76 \text{ cm}^{-1}$, which are in good agreement with recent works [32].

Figure 5. (a) Measured absorbance spectra of the as-grown GeSn on SOI and transfer-printed GeSn nanomembrane at room-temperature. The signal distortions near 1200 and 1400 nm are attributed to the absorption by the SU8 layer. (b) Tauc plots of the as-grown GeSn on SOI and transfer-printed GeSn nanomembrane for the determination of direct bandgap. The dashed line represents the linear fit near the band edge.

To confirm the bandgap variation caused by strain relaxation, transmission experiments at room temperature were performed using micro-Fourier transform infrared (μ -FTIR) microscopy in a normal incidence transmission configuration with a spot size of ~ 10 μm . Figure 5(a) depicts the measured absorbance spectra of the as-grown GeSn on SOI and transfer-printed GeSn NMs. For the as-grown GeSn on SOI, the absorbance spectrum exhibits significant ripple structures because of the vertical cavity created by the top GeSn/air interface and the bottom BOX/Si interface that cause significant interference in the layers [15]. The absorbance reduces at a photo energy of ~ 700 meV, corresponding to the direct-gap absorption edge of the pseudomorphic GeSn layer. On the other hand, for the transfer-printed GeSn NMs, less significant ripple structures in the spectral region were observed. The comparison of the absorbance spectra reveals the differences in the layer structures. To extract the direct bandgap, the Tauc equation was employed [7]:

$$\alpha \hbar\omega = A(\hbar\omega - E_g^\Gamma)^{1/2} \quad (4)$$

where α is the absorption coefficient, A is an energy-independent constant, and $\hbar\omega$ is the photon energy. Figure 5(b) depicts the Tauc plot that was converted from the absorbance spectra for the as-grown GeSn on the SOI and the transfer-printed GeSn NMs. Fitting the Tauc plot near the band edge using Eq. (4) yields a direct bandgap $E_g^\Gamma = 714$ meV and $E_g^\Gamma = 698$ meV for the as-grown GeSn on SOI transfer-printed GeSn NMs, respectively. The observed reduction in the direct bandgap is attributed to the strain relaxation in the GeSn NMs. To further confirm the bandgap reduction by the strain relaxation effect, we analyzed the strained bandgap energy using deformation potential theory [33, 34] (see Supporting Information). The direct bandgap of pseudomorphic $\text{Ge}_{0.0967}\text{Sn}_{0.033}$ on the Ge buffer and the strain-free $\text{Ge}_{0.0967}\text{Sn}_{0.033}$ NMs are calculated to be 708 and 683 meV, respectively, which is in good agreement with the experimental results.

Having demonstrated the achievement of strain relaxation using transfer-printing techniques, we theoretically discuss the impact of strain relaxation on the bandgap energies for advanced optoelectronic applications. Figure 6(a) and 6(b) illuminate the strain effect on the band structure of the GeSn alloys. When Sn is utilized, both the direct and indirect bandgaps decreased and their energy difference was reduced. In the case of the GeSn layers pseudomorphically grown on Ge buffer layers, the layers are subjected to an in-plane biaxial compressive stress, which significantly impacts the band structure. First, the compressive strain pushes both the Γ - and L-conduction band edges up. In addition, it splits the degeneracy of the valence band and brings the heavy hole (HH) band above the light hole (LH) band. As a result, the top valence band is HH-like, and the lowest direct (indirect) bandgap is defined as the energy difference between the Γ -valley (L-valley) conduction band and the HH band, $E_g^{\Gamma\text{-HH}}$ ($E_g^{\text{L-HH}}$). Figure 6(c) shows the calculated $E_g^{\Gamma\text{-HH}}$ for the biaxially-stressed $\text{Ge}_{1-x}\text{Sn}_x$ alloys in terms of the Sn composition and the strain, using deformation potential theory (see Supporting Information), in which the pseudomorphic $\text{Ge}_{1-x}\text{Sn}_x$ on Ge is indicated by the white dashed line. As the Sn content increases, the resultant compressive strain also increases, thereby significantly increasing the $E_g^{\Gamma\text{-HH}}$ and redshifting the absorption edge. This property is crucial for the photodetector applications when the GeSn is used as the active layer. Figure 6(d) depicts the comparison of the calculated absorption coefficient spectra for the pseudomorphic $\text{Ge}_{1-x}\text{Sn}_x$ on Ge and the strain-free $\text{Ge}_{1-x}\text{Sn}_x$ (the theoretical models are given in Supporting Information). The pseudomorphic $\text{Ge}_{1-x}\text{Sn}_x$ on Ge exhibits a larger $E_g^{\Gamma\text{-HH}}$ and thus, a shorter cutoff wavelength and smaller absorption coefficient than the strain-free $\text{Ge}_{1-x}\text{Sn}_x$. As a result, PDs with a pseudomorphic $\text{Ge}_{1-x}\text{Sn}_x$ on Ge as the active layer exhibit a weaker quantum efficiency and narrower photodetection range than the counterparts with strain-free $\text{Ge}_{1-x}\text{Sn}_x$ active layer. Thus, it is critically important to relax the compressive strain to enhance the performance of GeSn-based photodetectors. Second, the compressive strain

also significantly impacts the light-emitting efficiency of GeSn. Figure 6(e) shows the calculated $\Delta E_{\Gamma L}$ for the biaxially-stressed $\text{Ge}_{1-x}\text{Sn}_x$ alloys as a function of Sn composition and in-plane strain, where the pseudomorphic $\text{Ge}_{1-x}\text{Sn}_x$ on Ge is represented by the white dashed line. The introduction of Sn significantly reduces the $\Delta E_{\Gamma L}$ to achieve an indirect-to-direct bandgap transition. For the strain-free GeSn alloys, our calculations demonstrate that a Sn content of 6.6% is sufficient to achieve the direct bandgap. As a result, the GeSn alloys can be used as efficient light emitters. However, the compressive strain hinders the reduction of $\Delta E_{\Gamma L}$ by Sn-alloying. As a result, a much higher Sn content of 16.01% is required to achieve the indirect-to-direct bandgap transition. Hence, fewer electrons will be injected into the direct conduction band for efficient electron-hole recombination in the case of the pseudomorphic $\text{Ge}_{1-x}\text{Sn}_x$ on Ge, compared with that of the strain-free $\text{Ge}_{1-x}\text{Sn}_x$. To highlight the effect of the compressive strain, Figure 6(f) shows the comparison of the calculated spontaneous emission rate (r_{sp}) for the pseudomorphic $\text{Ge}_{1-x}\text{Sn}_x$ on Ge and that of the strain-free $\text{Ge}_{1-x}\text{Sn}_x$. As the Sn content increases, the R_{sp} significantly increases due to the reduced $\Delta E_{\Gamma L}$. However, the pseudomorphic $\text{Ge}_{1-x}\text{Sn}_x$ on Ge exhibits a much weaker r_{sp} than the strain-free $\text{Ge}_{1-x}\text{Sn}_x$ due to the larger $\Delta E_{\Gamma L}$. The presence of compressive strain can significantly reduce the light-emitting efficiency of the GeSn light emitters, thereby increasing the threshold of GeSn lasers. This analysis highlights the importance of relaxing the compressive strain stored in the GeSn layers for optoelectronic applications. Therefore, our proposed transfer-printing technique can provide a viable approach for achieving high-performance GeSn optoelectronic devices.

Figure 6. Schematic representation of the band structure of (a) strain-free and (b) compressively-strained GeSn alloys. (c) Calculated lowest direct bandgap energy ($E_g^{\Gamma-HH}$) of $\text{Ge}_{1-x}\text{Sn}_x$ alloys as a function of in-plane compressive strain and Sn composition. (d) Calculated absorption coefficient spectra of pseudomorphic $\text{Ge}_{1-x}\text{Sn}_x$ on Ge and strain-free $\text{Ge}_{1-x}\text{Sn}_x$ with different Sn compositions. (e) Calculated energy difference between the direct and indirect conduction bands ($\Delta E_{\Gamma L}$) of $\text{Ge}_{1-x}\text{Sn}_x$ alloys as a function of in-plane

compressive strain and Sn composition. (f) Calculated spontaneous emission rate per unit volume per unit energy interval for pseudomorphic $\text{Ge}_{1-x}\text{Sn}_x$ on Ge and strain-free $\text{Ge}_{1-x}\text{Sn}_x$ with different Sn compositions.

In conclusion, we have developed a novel approach to achieve strain-free GeSn NMs for advanced optoelectronic applications. Pseudomorphic GeSn alloys with a Sn composition of 3.3% were first grown on SOI substrates via a Ge buffer using MBE. A significant amount of compressive strain was induced in the GeSn alloys due to the Ge buffer layer. The inherent compressive strain was completely removed by the transfer-printing of GeSn/Ge/Si multilayers followed by the removal of the Si template and the Ge buffer layer. Strain analysis was conducted on the GeSn NMs using XRD, Raman, and FTIR. The compressive strain was completely relaxed. The reduction of the direct bandgap energy of GeSn from 714 to 698 meV was experimentally confirmed by transmission experiments. The effect of compressive strain on the bandgap energies, absorption coefficient, and light emitting efficiency was theoretically studied, highlighting that the relaxation of compressive strain can significantly enhance the performance of GeSn photodetectors and light emitters. Overall, our novel approach for fabricating the strain-free GeSn NMs provides a great potential for high-performance GeSn optoelectronic device applications.

This work at CCU was supported by the Ministry of Science and Technology of Taiwan (MOST) under the grant Nos. MOST 108-2221-E-194-055 and MOST 109-2636-E-194-002, and the Advanced Institute of Manufacturing with High-tech Innovations (AIM-HI) from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan. The work at NTU was supported by NTU start-up grant (M4082289.040) and Singapore MOE AcRF Tier 1 grant (M4012124.040). The authors would like to thank Dr. Hui Li at National Taiwan University,

Taiwan, for providing assistance in the material growth, and Dr. I-Fang Cheng at Taiwan Semiconductor Research Institute, Taiwan, for providing assistance in the Raman experiments.

Availability of data

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

- [1] R. Soref, The Past, Present, and Future of Silicon Photonics, IEEE J. Sel. Topics Quantum Electron. 12, 1678 (2006).
- [2] R. Soref, Silicon-based silicon–germanium–tin heterostructure photonics, Phil. Trans. R. Soc. A 372 (2014).
- [3] G. E. Chang, S. W. Chang, and S L Chuang, Theory for n-type doped, tensile-strained Ge-Si_xGe_ySn_{1-x-y} quantum-well lasers at telecom wavelength, Opt. Express 17 (14), 11246–11258 (2009).
- [4] R. A. Soref and L. Friedman, Direct-gap Ge/GeSn/Si and GeSn/Ge/Si heterostructure, Superlattices Microstruct. 14, 189–193 (1993).
- [5] R. Chen, H. Lin, Y. Huo, C. Hitzman, K. I. Kamins, and J. S. Harris, Increased photoluminescence of strain-reduced, high-Sn composition Ge_{1-x}Sn_x alloys grown by molecular beam epitaxy. Appl. Phys. Lett. 99, 181125 (2011).
- [6] G. He and H. A. Atwater, Interband transitions in Sn_xGe_{1-x} alloys, Phys. Rev. Lett., 79(10), 1937–1940 (1997).
- [7] J. Z. Chen, H. Li, H. H. Cheng, and G. E. Chang, Structural and optical characteristics of Ge_{1-x}Sn_x/Ge superlattices grown on Ge-buffered Si(001) wafers, Optical Materials Express 4(6), 1178–1185 (2014).
- [8] H. Tran, W. Du, S. A. Ghetmiri, A. Mosleh, G. Sun, R. A. Soref, J. Margetis, J. Tolle, B. Li, H. A. Naseem, and S.-Q. Yu, Systematic study of Ge_{1-x}Sn_x absorption coefficient and

- refractive index for the device applications of Si-based optoelectronics, *J. Appl. Phys.* **119**(10), 103106 (2016).
- [9] J. Margetis, S. Al-Kabi, W. Du, W. Dou, Z. Yiyin, T. Pham, P. Grant, S. A. Ghetmiri, M. Aboozar, B. Li, J. Liu, G. Sun, R. A. Soref, J. Tolle, M. Mortazavi, and S.-Q. Yu, Si-Based GeSn Lasers with Wavelength Coverage of 2–3 μm and Operating Temperatures up to 180 K, *ACS Photonics* **5**(3), 827–833 (2018).
- [10] M. Oehme, K. Kostecky, M. Schmid, F. Oliveira, E. Kasper, and J. Schulze, Epitaxial growth of strained and unstrained GeSn alloys up to 25% Sn, *Thin Solid Films* **557**, 169-172 (2014).
- [11] I. S. Yu, T. H. Wu, K. Y. Wu, H. H. Cheng, V. I. Mashanov, A. I. Nikiforov, O. P. Pchelyakov, and X. S. Wu, Investigation of $\text{Ge}_{1-x}\text{Sn}_x/\text{Ge}$ with high Sn composition grown at low-temperature, *AIP Adv.* **1**, 042118 (2011).
- [12] S. A. Ghetmiri, W. Du, J. Margetis, A. Mosleh, L. Cousar, B. R. Conley, L. Domulevicz, A. Nazzal, G. Sun, R. A. Soref, J. Tolle, B. Li, H. A. Naseem, and S.-Q. Yu, Direct-bandgap GeSn grown on silicon with 2230 nm photoluminescence, *Appl. Phys. Lett.* **105**, 151109 (2014).
- [13] C. Xu, P. M. Wallace, D. A. Ringwala, S. L. Y. Chang, C. D. Poweleit, J. Kouvetakis, and J. Menendez, Mid-infrared (3–8 μm) $\text{Ge}_{1-y}\text{Sn}_y$ alloys ($0.15 < y < 0.30$): Synthesis, structural, and optical properties, *Appl. Phys. Lett.* **114**, 212104 (2019).
- [14] S. Wirths, R. Geiger, N. von den Driesch, G. Mussler, T. Stoica, S. Mantl, Z. Ikonik, M. Luysberg, S. Chiussi, J. M. Hartmann, H. Sigg, J. Faist, D. Buca, and D. Grutzmacher, Lasing in direct-bandgap GeSn alloy grown on Si, *Nat. Photonics* **9**(2), 88–92 (2015).
- [15] B. J. Huang, C. Y. Chang, Y. D. Hsieh, R. A. Soref, G. Sun, H. H. Cheng, and G. E. Chang, Electrically injected GeSn vertical-cavity surface emitters on silicon-on-insulator platforms, *ACS Photonics* **6**(8), 1931–1938 (2019).

- [16] J. Chrétien, N. Pauc, F. A. Pilon, M. Bertrand, Q. M. Thai, L. Casiez, N. Bernier, H. Dansas, P. Gergaud, E. Delamadeleine, R. Khazaka, H. Sigg, J. Faist, A. Chelnokov, V. Reboud, J.-M. Hartmann, V. Calvo, GeSn lasers covering a wide wavelength range thanks to uniaxial tensile strain. *ACS Photonics* 6, 2462–2469 (2019).
- [17] J. H. Lin, Y. D. Hsieh, B. J. Huang, H. H. Cheng, and G. E. Chang, Mid-infrared GeSn electro-absorption optical modulators on silicon, <https://arxiv.org/abs/1809.07150>.
- [18] R. Roucka, J. Mathews, C. Weng, R. Beeler, J. Tolle, J. Menendez, and J. Kouvetakis, High-Performance Near- IR Photodiodes: A Novel Chemistry-Based Approach to Ge and Ge–Sn Devices Integrated on Silicon, *IEEE J. Quantum Electron.* 47(2), 213 (2011).
- [19] S. Su, B. Cheng, C. Xue, W. Wang, Q. Cao, H. Xue, W. Hu, G. Zhang, Y. Zuo, and Q. Wang, GeSn p-i-n photodetector for all telecommunication bands detection, *Opt. Express* 19(7), 6400–6405 (2011).
- [20] M. Oehme, M. Schmid, M. Kaschel, M. Gollhofer, D. Widmann, E. Kasper, and J. Schulze, GeSn p-i-n detectors integrated on Si with up to 4% Sn, *Appl. Phys. Lett.* 101, 141110 (2012).
- [21] H. H. Tseng, H. Li, V. Mashanov, Y. J. Yang, H. H. Cheng, G. E. Chang, R. A. Soref, and G. Sun, GeSn-based p-i-n photodiodes with strained active layer on a Si wafer, *Appl. Phys. Lett.* 103, 231907 (2013).
- [22] Y. H. Peng, H. H. Cheng, V. I. Mashanov, and G. E. Chang, GeSn p-i-n waveguide photodetectors on silicon substrates, *Appl. Phys. Lett.* 105, 231109 (2014).
- [23] Y. H. Huang, G. E. Chang, H. Li, and H. H. Cheng, Sn-based waveguide p-i-n photodetector with strained GeSn/Ge multiple-quantum-well active layer, *Opt. Lett.* 42, 1652–1655 (2017).
- [24] Y. Dong, W. Wang, S. Xu, D. Lei, X. Gong, X. Guo, H. Wang, S. Y. Lee, W. K. Loke, S. F. Yoon, and Y. C. Yeo, Two-micron-wavelength germanium-tin photodiodes with low dark current and gigahertz bandwidth," *Opt. Express* 25, 15818-15827 (2017)

- [25] H. Tran, T. Pham, W. Du, Y. Zhang, P. Grant, J. Grant, G. Sun, R. Soref, J. Margetis, J. Tolle, B. Li, M. Mortazavi, and S. Q. Yu, High performance $\text{Ge}_{0.89}\text{Sn}_{0.11}$ photodiodes for low-cost shortwave infrared imaging, *J. Appl. Phys.* 124, 013101 (2018).
- [26] B. J. Huang, J. H. Lin, H. H. Cheng, and G. E. Chang, GeSn resonant-cavity-enhanced photodetectors on silicon-on-insulator platforms, *Optics Letters* 43(6), 1215–1218 (2018).
- [27] C. H. Tsai, B. J. Huang, R. A. Soref, G. Sun, H. H. Cheng, and G. E. Chang, GeSn resonant-cavity-enhanced photodetectors for efficient photodetection at the 2 μm wavelength band, *Opt. Lett.* 45, 1463-1466 (2020).
- [28] W. T. Hung, D. Barshilia, R. Basu, H. H. Cheng, and G. E. Chang, Silicon-based high-responsivity GeSn short-wave infrared heterojunction phototransistors with a floating base, *Opt. Lett.* 45, 1088-1091 (2020).
- [29] A. A. Tonkikh, C. Eisenschmidt, V. G. Talalaev, N. D. Zakharov, J. Schilling, G. Schmidt, P. Werner, Pseudomorphic GeSn/Ge(001) quantum wells: Examining indirect band gap bowing, *Appl Phys Lett* 103, 032106 (2013).
- [30] G. E. Chang, R. Basu, B. Mukhopadhyay, and P. K. Basu, Design and Modeling of GeSn-based heterojunction phototransistors for communication applications, *IEEE J. Sel. Top. Quant. Electron.* 22, 425 (2016).
- [31] H. Li, Y. X. Cui, K. Y. Wu, W. K. Tseng, H. H. Cheng, and H. Chen, Strain relaxation and Sn segregation in GeSn epilayers under thermal treatment, *Appl. Phys. Lett.* 102, 251907 (2013).
- [32] A. Gassenq, L. Milord, J. Aubin, N. Pauc, K. Guillo, J. Rothman, D. Rouchon, A. Chelnokov, J. M. Hartmann, V. Reboud, and V. Calvo, Raman spectral shift versus strain and composition in GeSn layers with 6%–15% Sn content, *Appl. Phys. Lett.* 110, 112101 (2017).

- [33] M. Kim, S.-C. Liu, T. J. Kim, J. Lee, J.-H. Seo, W. Zhou and Z. Ma, Light absorption enhancement in Ge nanomembranes and its optoelectronic application, *Opt. Express*, 24(15), 16894 (2016).
- [34] M. Kim, H. Mi, M. Cho, J.-H. Seo, W. Zhou, S. Gong, and Z. Ma, Tunable biaxial in-plane compressive strain in a Si nanomembranes transferred on a polyimide film, *Appl. Phys. Lett.* 106, 212107 (2015).
- [35] J.-H. Seo, E. Swinnich, Y.-Y. Zhang, and M. Kim, Low dimensional freestanding semiconductors for flexible optoelectronics: materials, synthesis, process, and applications, *Mater. Res. Lett.* 8(4), 123 (2020).
- [36] M. Kim, J.-H. Seo, U. Singiseti, and Z. Ma, Recent advances in free-standing single crystalline wide band-gap semiconductors and their applications: GaN, SiC, ZnO, β -Ga₂O₃, and diamond, *J. Mater. Chem* 5(33), 8338 (2017).
- [37] Y. H. Jung, T.-H. Chang, H. Zhang, C. Yao, Q. Zheng, V. W. Yang, H. Mi, M. Kim, S. J. Cho, D.-W. Park, H. Jiang, J. Lee, Y. Qiu, W. Zhou, Z. Cai, S. Gong, and Z. Ma, High-performance green flexible electronics based on biodegradable cellulose nanofibril paper, *Nat. Commun.* 6, 7170 (2015).
- [38] J.-H. Seo, K. Zhang, M. Kim, D. Zhao, H. Yang, W. Zhou, and Z. Ma, Flexible phototransistors based on single-crystalline silicon nanomembranes, *Adv. Opt. Mater.* 4(1), 120 (2016).
- [39] G. E. Chang, S. W. Chang, and S L Chuang, Strain-balanced Ge_zSn_{1-z}/Si_xGe_ySn_{1-x-y} multiple-quantum-well lasers, *IEEE Journal of Quantum Electronics* 46(12), 1813-1820 (2010).
- [40] R. Beeler, R. Roucka, A. V. G. Chizmeshya, J. Kouvetakis, and J. Menendez, Nonlinear structure-composition relationships in the Ge_{1-y}Sn_y/Si(100) ($y < 0.15$) system, *Phys. Rev. B* 84, 035204 (2011).

- [41] M. Cho, J.-H. Seo, J. Lee, D. Zhao, H. Mi, X. Yin, M. Kim, X. Wang, W. Zhou, and Z. Ma, Ultra-thin distributed Bragg reflectors via stacked single-crystalline silicon nanomembranes, *Appl. Phys. Lett.* 106, 181107 (2015).