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Si-based Germanium-Tin (GeSn) Emitters for Short-Wave Infrared Optoelectronics

Seyed Amir Ghetmiri

University of Arkansas, Fayetteville

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Si-based Germanium-Tin (GeSn) Emitters for Short-Wave Infrared Optoelectronics

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in Microelectronics-Photonics

by

Seyed Amir Ghetmiri
University of Shiraz
Bachelor of Science in Physics, 2004
Shahid Bahonar University of Kerman
Master of Science in Photonics, 2009

December 2016
University of Arkansas

This dissertation is approved for recommendation to the Graduate Council.

Dr. Shui-Qing (Fisher) Yu
Dissertation Director

Dr. Gregory Salamo
Dissertation Co-Director

Dr. Hameed A. Naseem
Committee Member

Dr. Simon Ang
Committee Member

Dr. Zhong Chen
Committee Member

Dr. Rick Wise
Ex-Officio Member
The following signatories attest that all software used in this dissertation was legally licensed for use by Seyed Amir Ghetmiri for research purposes and publication.

__________________________________    __________________________________

Seyed Amir Ghetmiri, Student    Dr. Shui-Qing (Fisher) Yu, Dissertation Director

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__________________________________    __________________________________

Dr. Rick Wise, Program Director    Dr. Shui-Qing (Fisher) Yu, Dissertation Director
Abstract

Conventional integrated electronics have reached a physical limit, and their efficiency has been influenced by the generated heat in the high-density electronic packages. Integrated photonic circuits based on the highly developed Si complementary-metal-oxide-semiconductor (CMOS) infrastructure was proposed as a viable solution; however, Si-based emitters are the most challenging component for the monolithic integrated photonic circuits. The indirect bandgap of silicon and germanium is a bottleneck for the further development of photonic and optoelectronic integrated circuits.

The Ge$_{1-x}$Sn$_x$ alloy, a group IV material system compatible with Si CMOS technology, was suggested as a desirable material that theoretically exhibits a direct bandgap when Sn composition increases. Last decade, efforts were made to develop high quality Ge$_{1-x}$Sn$_x$ films on Si substrate using commercial reactors. Moreover, the effect of Sn composition on the bandgap energy of Ge$_{1-x}$Sn$_x$ alloys was theoretically investigated.

In this work, the development of Si-based Ge$_{1-x}$Sn$_x$ emitters was pursued with study the temperature-dependent bandgap emission of Ge$_{1-x}$Sn$_x$ structures for the short-wave infrared (SWIR) wavelength range (between 1.5 to 3 μm). The photoluminescence (PL) emissions from the bandgap of Ge$_{1-x}$Sn$_x$ films were investigated and a direct bandgap Ge$_{1-x}$Sn$_x$ was demonstrated for the first time based on the careful analysis of the PL spectra line-width and also the strain-dependent bandgap concept. In addition, the Ge$_{1-x}$Sn$_x$ advanced structure including SiGeSn/GeSn/SiGeSn single quantum well (QW) and Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge double heterostructures (DHS) were studied. The GeSn QW PL emission was scrutinized from 10 to 300 K and the carrier confinement was analyzed through band offset calculations in the QW structure. Moreover, the electrical and optical characteristics of n-i-p Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge light emitting diodes (LEDs) with surface emitting and edge emitting configurations were examined.
at different temperatures. Additionally, the lasing performance from the DHS
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direct bandgap Ge$_{0.9}$Sn$_{0.1}$ QW with Type-I band alignment favorable for the high carrier
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Dedication

To my family
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Chapter 1. Introduction

1.1 Motivation

Ever increasing demand for data transmission as well as decreasing the size of microelectronic chips has become a challenge for researchers in the field of microelectronics. The current technology, including electrical connections with nanometer scale transistors, experiences a bottleneck in the speed of data transmission and reception [1]–[3]. Moore’s law approaches its limit, and the traditional transistor-based electronic circuits are not able to provide the demanded data communication speed due to the power dissipation and heat generation within electrical interconnects [4], [5]. An innovative approach to solve those issues is to exploit massless photons instead of electrons in the integrated circuits and establish photonic integrated circuits (PICs) [6], [7]. The idea of implementing photons in the integrated circuits and using photon data transmission instead of electrons dates back to 70s after the invention of the laser. Since then, researchers’ efforts to achieve PICs resulted in presenting different components of the PICs, including laser sources, optical waveguides, optical modulators, optical interconnects, and photodetectors. To establish a platform for fabrication of all optoelectronic components on a single chip, the Si complementary metal-oxide semiconductor (CMOS) technology was considered as the most feasible and cost-effective solution to deliver CMOS compatible photonic chips [7]–[9]. The advanced Si photonic devices could take advantage of the mature Si electronics industry.

During the last decades, monolithically fabricated Si photonic devices based on the Si CMOS technology were developed. Low-loss waveguides based on Si on insulator (SiO$_2$) [10]–[16], high-speed germanium (Ge) on Si detectors [17]–[21], and high-speed modulators based on Si/SiGe quantum well [22]–[24] have already been presented. A highly efficient Si-based light
source, compatible with a CMOS process, has been a challenge for decades [8], [25], [26]–[28]. The indirect bandgap of Si hinders the possibility of producing emitters based on Si. The current technology to produce the on-chip light source is based on III-V emitters on Si either through growing heterogeneous III-V material on Si [25]–[28] or via a chip bonding process to attach III-V emitting devices on a Si substrate [29], [30]. Technologies implementing group III-V materials were pursued and the results of those achievements have been applied by several companies such as Intel, Kotura, Luxtera, Cisco and others; however, the following drawbacks preclude the implementation of group III-V materials and the other hybrid integration on Si microelectronics. Either the direct integration of III-V heterostructures on Si or chip bonding has disadvantages that limit the application of group III-V materials in Si CMOS integration. The required high temperature (> 450 °C) growth of group III-V devices is not compatible with Si CMOS integration process due to different thermal expansion coefficient of Si components and III-V elements [31]–[34]. On the other hand, chip bonding of group III-V optoelectronic devices to Si microelectronic circuits brings about misalignment issues, introduction of inevitable defects, and higher costs. Moreover, mass production of costly group III-V materials would not be economic in the multi-billion-dollar VLSI industry [35]. Therefore, technology of III-V photonic devices on Si does not provide a CMOS compatible scheme and cost-effective solution for the future of PICs.

1.2 Germanium-based optoelectronic emitters

The idea of monolithic device integration of group IV materials on Si was first presented by R. A. Soref in 1992 [8]. Afterward, investigation on the third semiconductor element of group IV periodic table, germanium (Ge), accelerated unprecedentedly [36], [37]. Although Ge is an
indirect bandgap semiconductor, the small energy difference ($\Delta E_{\Gamma-L}=136$ meV) between the direct and indirect bandgap in Ge exhibits an extraordinary feature in this material. That small energy difference could be overcome by heavily n-type doping of Ge and/or applying tensile strain on Ge. Both techniques reduce the difference between direct and indirect bandgap energies and eventually change the Ge to a direct bandgap semiconductor. As shown in Figure 1.1, by applying tensile strain on the Ge, the energy gap between $\Gamma$ and $L$ valleys reduces, and carriers start to penetrate to the $\Gamma$ valley. Further carrier injection to the $\Gamma$ valley occurs with heavily n-doping of Ge [38]–[40].

![Diagram showing the effect of tensile strain and heavily n-doping on the bandgap structure of Ge.](image)

Figure 1.1. The effect of tensile strain and heavily n-doping on the bandgap structure of Ge is presented in a schematic diagram. [41].

Based on Figure 1.1, the reduction of the difference between the $\Gamma$ and $L$ valleys of the Ge conduction band increases the carrier populations in the $\Gamma$ valley. Theoretically, in order to completely compensate the difference between the $\Gamma$ and $L$ valleys and change the $\Delta E_{\Gamma-L}$ from 136 meV to zero, the minimum doping concentration of $n = 8 \times 10^{18}$ cm$^{-3}$ is required. Figure 1.2
indicates the fraction of carriers in the Γ valley versus the reduction of $\Delta E_{\Gamma-L}$ from 136 meV to zero. This graph indicates that once the difference between the direct and indirect bandgaps reduces, more carriers populate the Γ valley resulting more direct bandgap behavior in Ge

![Graph showing the fraction of carriers in the Γ valley versus the bandgap energy difference between the Γ and L valley ($\Delta E_{\Gamma-L}$) in Ge.](image)

Figure 1.2. The fraction of carriers occupying the Γ valley versus the bandgap energy difference between the Γ and L valley ($\Delta E_{\Gamma-L}$) in Ge [42], [43].

Utilizing heavily n-doped Ge with doping concentration of $3 \times 10^{19}$ cm$^{-2}$ led to the first demonstration of room temperature optically- and electrically-pumped Ge lasers with emission at ~ 1.6 µm [40], [44], [45]. Moreover, 1.5% biaxial tensile strained Ge microdisks exhibited stimulated emission at wavelength between 1.55 µm to 2 µm [46]–[50]. Those achievements were the most promising presentation of group IV-based light emitters compatible with Si CMOS process. However, difficulties in the fabrication of tensile strain Ge and low efficiency of heavily n-doped Ge lasers precluded those techniques from being the final solution of group IV-based emitters for Si photonics.

1.3 Germanium Tin-based optoelectronic emitters; A new approach

The idea of alloying gray tin (α-Sn) to Ge to achieve a group IV direct bandgap material was first proposed by Goodman in 1982 based on the analytical studies of the Ge bandgap
evolution with Sn incorporation [51]. In the 1990s, in-depth theoretical studies on the direct bandgap GeSn and SiGeSn materials was initiated showing that the SiGeSn/GeSn technology with unique optical properties is capable of providing the viable solution for the group IV-based optoelectronic emitters compatible with Si CMOS platform [52]–[56]. The expansion of the SiGeSn/GeSn research was held back due to the undesired material quality; however, developments in chemical vapor deposition (CVD) techniques established a framework for commercial synthesis of the SiGeSn and GeSn alloys [57]–[61]. In 2002, after the investigation of the bandgap and lattice structure of GeSn and SiGeSn materials, researchers started to create GeSn alloys with different growth techniques [53], [62]–[66]. The thorough growth study of GeSn was led by J. Kouvetakis at Arizona State University [67]–[73] and later pursued by other researchers, including the GeSn research group at the University of Arkansas (U of A) led by S. Q. Yu [74]–[76].

Through in-depth study on the properties of SiGeSn and GeSn materials, the following unique capabilities were perceived for the SiGeSn/GeSn system as a foundation of group IV photonics and optoelectronics applications. 1) The material growth temperature (< 400 °C) is totally compatible with Si CMOS process. 2) The bandgap of SiGeSn/GeSn could be tuned based on variation of Si and Sn compositions. 3) A highly desired Type-I band alignment for group IV emitters is possible through bandgap engineering of GeSn/GeSn and SiGeSn/GeSn structures. 4) Wavelength coverage from 1 µm to 12 µm is attainable in the band-to-band transition of SiGeSn/GeSn materials, and longer wavelength can be achieved through inter-subband transitions. 5) Relaxed GeSn layers are able to serve a Si-based compliant layer for the growth of Ge and also III-V materials based on the lattice constant tunability [7], [73], [77]–[85].
Based on the above figures-of-merit, a variety of studies were performed on the material and device performance of GeSn and SiGeSn systems. The growth of Ge/GeSn and SiGeSn/GeSn was investigated using different growth mechanisms and the material characteristics were in agreement with the theoretical predictions. Moreover, GeSn- and SiGeSn-based devices for the short-wave infrared (between 1.5 to 3 µm) application were fabricated and scrutinized [86]–[90]. Significant results of the double heterostructure GeSn photodetectors [91], presented by U of A, and optically-pumped GeSn laser [92], demonstrated by the PGI-9 group in Germany are presented in Figure 1.3a and 1.3b, respectively.

Figure 1.3. (a) The comparison between the spectral detectivity (D*) of the GeSn photodiodes, fabricated and characterized in the U of A, and the commercialized detectors available in the market [91]. (b) The first results of optically-pumped GeSn lasers demonstrated by the PGI-9 group and their collaborators [92].

The GeSn photodetector reported by U of A has a broader detection coverage with longer wavelength cut-off at 2.4 µm compared to that of the extended InGaAs photodetector. The GeSn based photodetector produced in U of A is totally CMOS compatible useful for inexpensive military and civil applications.
1.3.1 Band structure of GeSn alloy

The semimetal diamond cubic Sn has a conduction band minimum of -0.41 eV at the Γ valley. The minimum of Γ valley in Ge is 0.79 eV higher than the minimum of the valence band; however, for α-Sn, the Γ valley minimum is lower than the valence band minimum by -0.41 eV. Once Sn and Ge are mixed together as a GeSn alloy, both L (indirect bandgap) and Γ (direct bandgap) valleys of Ge shrinks with rapid decrease of Γ compare to L valley.

Figure 1.4 shows the band structure of Ge and α-Sn. The changes of GeSn bandgap depends on the percentage of the Sn composition. Bandgap tunability by variation of Sn percentage is an advantageous capability of GeSn based optoelectronic devices.

![Figure 1.4. Band structure of Ge and α-Sn [93].](image)

Changes in the direct and indirect bandgap energies of GeSn alloys based on the variation of Sn composition are described based on the “bowed” Vegard’s law [94]:

\[
E_{\Gamma}^{\text{Ge}}(Ge_{1-x}Sn_x) = E_{\Gamma}^{Sn}(x) + E_{\Gamma}^{Ge}(1-x) - b_{\Gamma}^{GeSn}x(1-x) \quad \text{Direct bandgap} \quad (\text{Equation 1.1})
\]
\[ E^L_{gGe}(1-xSn_x) = E^L_{gSn}(x) + E^L_{gGe}(1-x) - b^L_{GeSn}x(1-x) \] Indirect bandgap (Equation 1.2)

where \( E^L_{gSn} \) and \( E^L_{gGe} \) are direct bandgap energies of Sn and Ge and \( E^L_{gSn} \) and \( E^L_{gGe} \) are indirect bandgap energies of Sn and Ge, respectively. The \( b^\Gamma_{GeSn} \) and \( b^L_{GeSn} \) are GeSn bowing parameters of the direct and indirect bandgaps. The values of the above parameters are shown in Table 1.1.

<table>
<thead>
<tr>
<th>( E^\Gamma_{gGe} ) (eV)</th>
<th>( E^\Gamma_{gSn} ) (eV)</th>
<th>( E^L_{gGe} ) (eV)</th>
<th>( E^L_{gSn} ) (eV)</th>
<th>( b^\Gamma_{GeSn} ) (eV)</th>
<th>( b^L_{GeSn} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.79</td>
<td>-0.41</td>
<td>0.66</td>
<td>0.09</td>
<td>2.92</td>
<td>0.68</td>
</tr>
</tbody>
</table>

As shown in Figure 1.5, plotting the direct and indirect bandgap energy peaks versus the Sn composition of GeSn alloy indicates that at a certain point, the \( \Gamma \) valley and L valley become equivalent (crossover point); thus, the GeSn changes to a direct bandgap material. In Figure 1.5, the crossover point of a strain-relaxed GeSn film is compared to the crossover point of a compressive-strained GeSn film with 1.1% strain in the lattice structure. As indicated in the figure, ~6% Sn is required to provide direct bandgap relaxed GeSn, but ~10% Sn could change the compressive-strained GeSn film with 1.1% strain in the lattice structure. It clearly indicated that lower compressive strain in the lattice requires less Sn composition to provide a direct bandgap GeSn alloy. The discrepancy reported on the Sn composition of the crossover point in different publications caused by considering different bowing parameters for the \( \Gamma \) valley and L valley of the conduction band. Also, some publications focused on numerical techniques to predict the crossover point. Techniques including virtual crystal approximation, density functional theory, empirical pseudopotential method, local density approximation, and generalized gradient approximation which were discussed by Gupta et al. [95]. However, there is no systematic study to establish a solid value for the crossover point of relaxed and strained...
GeSn alloy. Nevertheless, this point will be one of the critical aspects of the design of GeSn optoelectronic devices.

Figure 1.5. Changes in the bandgap energies of \( \Gamma \) and L valleys versus the Sn percentage in GeSn alloy for strained-relaxed (solid lines) and also a typical compressive-strained (dashed lines) GeSn films [96].

Figure 1.6 illustrates the change in the GeSn bandgap before and after the crossover point. As indicated, carriers mainly occupy the L valley when Sn composition is lower than the crossover value and GeSn is still an indirect bandgap material.

Figure 1.6. Schematic diagram of the bandgap of GeSn alloy (a) before and (b) after the crossover point for a strain-relaxed GeSn film. [97].
Once Sn composition exceeds the crossover value, the GeSn becomes a direct bandgap material, and carriers reside in the Γ valley leading to higher efficient recombination. As noticed, no heavily n-doping or tensile strain is required to achieve a direct bandgap GeSn alloy. Only an increase in the Sn composition leads to that turning point. As shown in Figure 1.6, after the crossover point the population of carriers increases in the Γ valley. The benefit of this phenomenon is the effective carrier recombination through the direct bandgap which leads to a highly efficient photon generation from the GeSn material. This advantage could be implemented in the design of GeSn-based emitters that can compete with the current expensive III-V emitter technology (a GaAs wafer costs at least 100 times more than Si wafer [98]).

In this work, the GeSn epitaxial films with different Sn compositions were investigated as the most reliable candidate for the group-IV based optoelectronic emitters compatible with Si CMOS process. The bandgap emission of GeSn alloys was explored for Sn compositions of 0% to 12%, and experimental results of the indirect and direct bandgap GeSn materials were presented. Emission from advanced GeSn device structures including quantum well, a double heterostructure, and laser cavity waveguides were studied. The results provided in this work is an inclusive baseline for the GeSn-based optoelectronic emitters compatible with Si photonic platform.

1.4 Organization

The theoretical and experimental study on the emission of GeSn materials and devices has been divided into six chapters. In Chapter 2, the GeSn growth technique and material characterization results are described and the optical characterization testing setups, designed and constructed for this research, are presented. Chapter 3 covers the detailed investigation on the PL
measurements on the thin and thick GeSn epitaxial films. The evidence of direct bandgap GeSn has been discussed and TRUE direct bandgap GeSn is demonstrated. In Chapter 4, the SiGeSn/GeSn quantum well band structures and carrier confinements in the quantum well region are studied and the temperature-dependent PL emissions are explored using different excitation lasers. The GeSn double heterostructures light emitting diodes are inspected in Chapter 5, and their temperature-dependent electrical, and optical properties are investigated. Chapter 6 describes the initial results of lasing from an optically pumped Ge/GeSn/Ge waveguide structure. The laser power density threshold and spectrum are presented and methods to further reduce the threshold power density and achieve higher efficient GeSn lasers are discussed. In Chapter 7, a summary and conclusion of this work is presented along with the future work suggested to improve the emission performance of GeSn emitters.
Chapter 2. Growth technique and characterization testing setups

2.1 (Si)GeSn film growth

The growth of GeSn alloys has been pursued by different researchers using a variety of mechanisms including molecular beam epitaxy (MBE) [62], [99], solid phase epitaxy and recrystallization [100], chemical vapor deposition (CVD) [67], [101], [102], and sputtering technique [103]. Among the listed techniques, only MBE and CVD presented high-quality GeSn films with device quality suitable for optoelectronic applications. The flexibility of the CVD technique for different growth conditions and also its compatibility with a complementary metal-oxide-semiconductor (CMOS) fabrication process has made CVD the most favorable approach among all GeSn and SiGeSn growth methods. Producing high-quality films as well as providing a cost-effective and repeatable growth technique with inexpensive commercially available precursors is desired to establish an industry standard CVD method. The ASM Epsilon® 2000-Plus reduced-pressure CVD (RPCVD) is a commercial CVD system that meets the above criteria to grow high-quality GeSn and SiGeSn films. Precursors used in ASM reactor, including SiH₄, GeH₄, and SnCl₄, are commercially available gases utilized in the growth of (Si)GeSn films [75].

2.1.1 Growth of GeSn films

The GeSn epitaxial films were grown inside the ASM Epsilon® 2000-Plus RPCVD system with a single run deposition process. The Epsilon reactor is a horizontal flow system with a graphite susceptor coated with silicon carbide located in a cold wall quartz chamber. Prior to the growth of GeSn films, a strain-relaxed Ge buffer layer with ~700 nm thickness was deposited on top of Si (100). The lattice mismatch between Si and GeSn films was compensated with the Ge buffer layer. The growth of Ge includes two steps; a low temperature growth to form a thin
Ge layer and subsequently, a high temperature growth to provide thick Ge layer. The high temperature process lowers the threading dislocation defects and increases the growth rate. After Ge buffer growth, the intrinsic GeSn films were grown in-situ on a Ge layer at a temperature lower than 400 °C under specific pressure and growth rate to control the Sn incorporation. Insolubility of Sn in Ge (<1%) requires the growth temperature to be less than 400 °C. A well-defined recipe from ASM [75] was followed to grow GeSn films with Sn compositions of 1% to 12%. Moreover, the n-type and p-type Ge and GeSn films were grown using PH₃ and B₂H₆, respectively, for device perspective.

Incorporation of Sn inside the GeSn films was measured using Rutherford backscattering (RBS) and Secondary Ion Mass Spectrometry (SIMS) and further examined with X-ray diffraction (XRD) technique. The RBS spectra of a Ge₀.₉₃Sn₀.₀₇/Ge/Si is shown in Figure 2.1a and the XRD measurements on the GeSn samples are presented in Figure 2.1b. Occupation of Sn in the substantial lattice sites is indicated based on the yield observed for Sn.

![Figure 2.1](image.png)

**Figure 2.1.** (a) Random and aligned spectra of a GeSn sample with 7% Sn composition. [75]. (b) The XRD 2theta-omega (2θ-ω) scans for GeSn films grown on Ge-buffered Si with different Sn incorporation from 1% to 12%. [104].
The Philips X’pert PRO XRD system [105] was employed to precisely characterize the lattice constants and Sn incorporation in GeSn. The 2 theta-omega (2θ-ω) scans from (004) plane of the GeSn samples with Sn compositions from 1% to 12% is presented in Figure 2.1b. The sharp peak around 69.2° is related to Si while peaks from Ge and GeSn films occurs between 66.5° to 64° due to their larger out-of-plane lattice constants. Less broadening in the peaks indicates the higher crystalline quality of the films.

The precise in-plane (a∥) and out-of-plane (a⊥) lattice constant of GeSn layers could be achieved from asymmetric reciprocal space mapping (RSM) of (2̅24) planes. The RSM plot of GeSn films with 6% and 7% Sn compositions with thicknesses of 85 nm and 240 nm are shown in Figures 2.2a and 2.2b, respectively. In Figures 2.2c and 2.2d, the RSM plot of a GeSn film with 3% Sn composition and different thicknesses are presented. The critical thickness for the GeSn epilayer film is the maximum thickness for which the in-plane lattice constant of GeSn remains equivalent to the in-plane lattice constant of the bottom Ge buffer layer [74].

In that condition, the GeSn film on top is called pseudomorphic to the Ge buffer layer, meaning that their lattice constant is the same (Figure 2.2a). Beyond that critical thickness, the GeSn epilayer becomes partially strained, and defects start to be formed at the interface of the Ge and GeSn film. The critical thickness depends on the Sn composition of the GeSn film and increasing the Sn composition lowers the critical thickness of the film. Two different methods, called Matthews-Blakeslee (M-B) and People-Bean (P-B) are available to calculate the critical thickness [106], [107]. Depending on the GeSn device to be grown and fabricated, the critical thickness should be taken into account. Since the formation of the defects has a direct relationship with the critical thickness, for devices that require a very low defect density, the critical thickness should be carefully calculated before the growth process.
Figure 2.2. The RSM plot of (a) a pseudomorphic Ge$_{0.94}$Sn$_{0.06}$ thin film grown on Ge buffer with a thickness lower than critical thickness (b) a partially relaxed Ge$_{0.93}$Sn$_{0.07}$ film grown on Ge buffer with a thickness higher than the critical thickness. The RSM plot of Ge$_{0.97}$Sn$_{0.03}$ films with a thickness of (c) 76 nm and (d) 128 nm [74].

As shown in Figures 2.2c and 2.2d, the thickness of 3% GeSn films is 76 nm and 128 nm indicating that the distance between the GeSn center and pseudomorphic line increases once the thickness of the sample becomes larger. Once the thickness of the GeSn film goes far beyond the critical thickness, the film would be partially relaxed, and the center of GeSn film gets closer to the relaxation line as shown in a dotted line in Figure 2.2b. The advantage of the RSM measurement is the calculation of in-plane strain in the GeSn samples. Strain information is necessary to estimate the bandgap energy of the GeSn films which is a vital parameter for the
performance of GeSn-based optoelectronic devices. The following relation was used to calculate the in-plane strain of GeSn films grown on Ge buffer ($\varepsilon_\parallel$):

$$
\varepsilon_\parallel = \frac{(a_\parallel)_{\text{Ge}} - (a_\parallel)_{\text{GeSn}}}{(a_\parallel)_{\text{GeSn}}}
$$

(Equation 2.1)

where $(a_\parallel)_{\text{Ge}}$ is the in-plane lattice constant of Ge and $(a_\parallel)_{\text{GeSn}}$ is the in-plane lattice constant of the GeSn layer.

Another material characterization technique that examines the crystalline quality and thickness of the grown films is transmission electron microscopy (TEM). Moreover, formation and propagation of the defects inside the epitaxial layers could be analyzed using TEM images of each layer. The TEM images were collected using TITAN 80-300 with 200 KV electron gun source. The results of the GeSn TEM imaging are shown in Figure 2.3.

Figure 2.3. The cross-sectional TEM image of (a) the Ge$_{0.94}$Sn$_{0.06}$ thin film with 85 nm thickness pseudomorphically grown on top of Ge buffer and (b) the thick Ge$_{0.9}$Sn$_{0.1}$ relaxed film with 810 nm total thickness.
Based on the TEM images from the GeSn samples, the Ge buffers and GeSn epilayers had high crystalline quality with threading dislocation density (TDD) of almost $10^7$ cm$^{-2}$ and most of the defects were located at the interface of Si/Ge and Ge/GeSn. Suppressing the defects at the interfaces avoids their propagation toward the epitaxial layers and results in a high crystalline quality of the films.

Figure 2.3a is the TEM image of the pseudomorphic thin GeSn sample with 6% Sn composition grown on Ge buffer layer on Si substrate. Due to the pseudomorphicity of this sample, the epilayer and the Ge/GeSn interface had a low defect density. In Figure 2.3b, the TEM image of a thick GeSn film with 10% Sn incorporation and total GeSn thickness of 810 nm is presented. The high-quality GeSn film with a thickness of 515 nm was formed on the defective intermediate GeSn layer called a sacrificial layer. The first GeSn layer had the threading dislocation defects due to the lattice mismatch between the Ge and GeSn layers and the top GeSn layer had high crystalline quality. Formation of the GeSn sacrificial layer trapped the defects and consequently the top GeSn epilayer turned out to be a high-quality GeSn film. As shown in Figure 2.3b, in the Ge$_{0.9}$Sn$_{0.1}$ sample, two distinctive GeSn layers are presented; the first layer with high threading dislocation densities that trapped the defects and the second layer on top that had less defect and high crystalline quality. The low TDD value in the second GeSn layer is favorable for photonic and optoelectronic GeSn device applications. Later in Chapter 6, the use of thick GeSn films will be discussed in the demonstration of optically-pumped GeSn waveguide lasers.

2.1.2 Growth of SiGeSn films

Similar to the growth of GeSn films, the same RPCVD system was utilized to grow epitaxial SiGeSn films on top of Ge buffer layer. As mentioned, the growth temperature of the
GeSn films was less than 400 °C; however, that temperature is challenging for the growth of SiGeSn films since SiH$_4$ is less reactive at temperatures below 400 °C. Controlling the flow ratio of SiH$_4$/GeH$_4$ and the growth rate eventually provided the desired thin SiGeSn layers. The XRD 2theta-omega scan of SiGeSn films with specified Si and Sn compositions is plotted in Figure 2.4a. The peak related to the SiGeSn samples occurred at lower angles due to the larger out-of-plane lattice constant compared to Ge and Si peaks. The top RSM plot shown in Figure 2.4b is related to the (224) plane of SiGeSn sample with 13% Si and 6.6% Sn and the bottom one is associated with the SiGeSn sample with 19% Si and 2.7% Sn. As indicated in the XRD result, no detectable Si or Sn was incorporated into the film, and the peak for this sample overlaps with Ge peak. The top RSM plot indicates that almost no SiGeSn film was grown. The bottom RSM plot shows the SiGeSn was grown pseudomorphically on top of Ge buffer.

![XRD and RSM plots](image)

Figure 2.4. (a) The XRD 2theta-omega scans of the SiGeSn samples with specified Si and Sn compositions grown on Ge-buffered Si substrate. (b) The (224) RSM contour plot of the Si$_{0.13}$Ge$_{0.804}$Sn$_{0.066}$ shown on top and Si$_{0.19}$Ge$_{0.783}$Sn$_{0.027}$ shown at the bottom [108].

The cross-sectional TEM image of the SiGeSn sample with 13% Si and 6.6% Sn is presented in Figure 2.5a. As noticed in the image, the Ge buffer layer contained most of the
threading dislocations and less defects penetrated to the SiGeSn film. The interface between SiGeSn and Ge obtained with the high-resolution TEM is depicted in Figure 2.5b.

![Figure 2.5](image)

Figure 2.5. (a) The cross-sectional TEM image of the SiGeSn sample with 13% Si and 6.6% Sn. (b) The high-resolution TEM image of the interface between SiGeSn and Ge buffer indicate the high crystalline quality of the film [108].

2.2 Optical characterization testing setups

2.2.1 Photoluminescence setup

In order to explore the bandgap energy of the (Si)GeSn samples, the photoluminescence (PL) measurement of different temperatures was required. Basically, in the PL characterization of (Si)GeSn films, the sample is excited to energies higher than the sample’s bandgap using an laser excitation source. That optical excitation generates electron-hole pairs in the conduction band and the valence band of the (Si)GeSn bandgap. Therefore, the energy of the excitation laser should be above the bandgap of the samples. After generation of electron-hole pairs, they get relaxed to the minimum energy level of the valleys in the bandgap and subsequently recombine leading to an emission equivalent to the bandgap energy [109], [110].

Recombination of electron hole-pairs happens in both radiative and non-radiative procedures [111]. The radiative recombination leads to an emission called PL spectrum
containing useful information about the band structure of the sample. The emitted PL spectrum is collected and delivered to a spectrometer and detector to be analyzed. Although the overall measurement seems rather straightforward, the preparation of PL testing setup requires an appropriate knowledge about the optics in different ranges of wavelengths, understanding the optical and electrical signal detection techniques, and expertise in optical alignment of the optics components. In the characterization lab of this research, a home-built off-axis PL setup was constructed on the standard optical table. The PL setup is capable of measuring PL spectra in the near- and mid-infrared wavelength ranges which matches with the bandgap emission of (Si)GeSn material. The essential components of the PL setup, including the excitation lasers, spectrometer, photodetectors, and the optics were carefully chosen to provide (Si)GeSn PL spectra with high signal-to-noise ratio (SNR) and resolution. The schematic diagram of the standard off-axis infrared PL setup is presented in Figure 2.6. The alignment process is explained in Appendix A.

Figure 2.6. The schematic diagram of the home-built off-axis PL setup designed and constructed for infrared PL measurements from cryogenic to room temperature.
Typically, the aligned laser beam was delivered to the sample in the sample holder of the liquid helium cooled closed-cycle cryostat and the generated PL emission was collected with a lens and eventually delivered to the spectrometer and detectors. The temperature of the sample inside the cryostat was adjusted using a temperature controller. The constructed PL setup had five different excitation lasers integrated to be used for different PL experiments. That unique design provided a variety of laser choices for diverse PL studies, including various excitation powers and wavelengths. Depending on the desired laser power and laser wavelength in different PL measurements, the choice of the excitation laser could be varied. In order to provide high power density and high excitation energy, three different Q-switched pulsed lasers were integrated to the PL setup: 1) a pulsed 1064 nm laser with pulse width of 6 ns and repetition rate which varied from 15 kHz to 80 kHz with maximum power of 15 W; 2) a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser with wavelengths of 266, 355, 532, and 1064 nm – the pulse width of the Nd:YAG laser was 8 ns and the repetition rate was 10 Hz with maximum power of 1 W; and, 3) a Ti:sapphire femtosecond (fs) laser with a pulse width less than 100 fs and repetition rate of 80 MHz and wavelength range from 690 nm to 1040 nm and maximum power of 4 W.

For low power density PL experiments and high excitation energy, a diode-pumped solid state (DPSS) continuous wave (CW) laser with 532 nm wavelength (2.33 eV energy) was exploited. The maximum power of the DPSS CW 532 nm laser was 500 mW. Another laser in the PL setup capable of providing high power, but low excitation energy was a CW 1550 nm (0.8 eV energy) fiber laser with maximum power of 5 W. This laser was suitable for the band minimum excitation studies. In all mentioned lasers, the laser power could be adjusted with the laser controller box, and further adjustment was done using a series of neutral density filters in
the laser beam path. All laser beams were carefully aligned from the laser source to the sample using specific mirrors. A CaF\textsubscript{2} plano-convex lens with focal length of 10 cm was used to focus the laser beam to the sample. CaF\textsubscript{2} material has a transmission above 90\% for the wavelengths between 500 nm to 5000 nm which made this lens a proper choice once different laser sources were available to excite the sample. After excitation of the samples, the generated PL emission was collected using another CaF\textsubscript{2} lens and delivered to the spectrometer using two gold-coated mirrors designed for infrared range. The path of the PL emission from the sample to the spectrometer was carefully aligned using a set of the iris (pin holes). Then, the PL emission was focused to the entrance slit of the spectrometer and dispersed by the specific grating inside the spectrometer. Ultimately, the dispersed beam was focused to the different detectors connected to the spectrometer. The spectrometer used in the PL setup was an iHR320 HORIBA spectrometer with a grating that had the blazing wavelength of 2000 nm and groove (gr) density of 600 gr/mm. All spectrometer functions were computer-controlled using a SynerJY software from HORIBA [112].

Three detectors with different responsivity ranges, bandwidths and signal-to-noise ratio, were available to be attached to the spectrometer. The detector choices were: 1) a liquid nitrogen (LN\textsubscript{2}) cooled extended Indium Gallium Arsenide (ex-InGaAs) with the cut-off wavelength at 2.3 \textmu m; 2) a thermoelectric (TE) cooled Lead Sulphide (PbS) with a cut-off at 3 \textmu m; and, 3) a LN\textsubscript{2} cooled Indium Antimonide (InSb) with a cut-off at 5 \textmu m. Depending on the range of the PL spectra, different detectors were selected. The electric signal generated by the photodetector was amplified using a lock-in technique with an optical chopper. After amplification of the signal, the data was transferred to a laptop, and the PL spectrum was obtained in the SynerJY software.
Figure 2.7 shows the normalized PL spectra of the GeSn films measured using the PL setup. Red-shifted PL peaks were ascribed to the higher Sn compositions and smaller bandgaps, accordingly. Increasing the Sn composition resulted in the bandgap shrinkage and eventually led to a red-shift of the PL peak positions. The PL spectra of samples with lower Sn compositions were measured using extended InGaAs detector (high signal-to-noise ratio) and samples with higher Sn compositions were detected using PbS detector (low signal-to-noise ratio).

Figure 2.7. The normalized room temperature PL spectra of GeSn samples with Sn compositions from 0% to 12%.

2.2.2 Optical pumping setup

Studying the lasing condition of the optically-pumped GeSn waveguide was desired to understand the capability of GeSn material for the future of group IV-based optoelectronic and photonic devices. In Chapter 6, a detailed discussion on the GeSn waveguide and optically pumped GeSn laser is provided. Here, the setup constructed to perform the optical pumping experiment on the GeSn rectangular waveguides is demonstrated. Figure 2.8 shows the optical pumping setup added to the standard off-axis PL setup. In fact, this capability was added to the
The optical pumping setup was added to the PL setup using a careful modification. The closed-cycle cryostat of the PL setup was replaced with a regular vertical Janis cryostat with four windows. In general, the pumping excitation laser was focused on the GeSn waveguides from one direction and the lasing spectrum was collected from another direction which was perpendicular to the incident beam. The reason is that the lasing emission emerges from the facet of the waveguides. The optical pumping process included the excitation of the GeSn waveguides using the 1064 nm pulsed laser. The laser beam was focused to the GeSn waveguide using a cylindrical lens with a focal length of 7.5 nm. The rectangular shape focused beam had a
dimension of 3 mm and 20 µm distributed homogeneously on the GeSn waveguide. The emission from the GeSn waveguide was collected with the same CaF$_2$ collecting lens used in the PL setup. A similar optical path was considered to eventually deliver the GeSn waveguide emission to the spectrometer and detector.

2.2.3 Electroluminescence setup

Similar to the standard PL setup, an electroluminescence (EL) setup was constructed to measure the emission from GeSn light emitting diodes (LEDs). The optics, spectrometer, and detectors were carefully selected to be compatible with the emission wavelengths of the GeSn LEDs. A very low power helium-neon (He-Ne) laser along with a beam splitter and several mirrors were exploited to facilitate the optical alignment of the EL setup. A schematic drawing of the EL setup is given in Figure 2.9. The EL setup featured a probe station for initial current-voltage (I-V) characterization and room temperature EL study. The required current for the EL measurement was provided using a Keithley 236 [113] direct current (DC) source with a maximum current of 100 mA. Also, an ILX Lightwave pulsed current source with a maximum duty cycle of 10%, and a maximum current of 3 A offered higher injection current densities. The probe station consisted of two gold plated needles for electric contacts, and the temperature of the probe station was controlled using a heat sink. Temperatures from 273 K to 350 K could be achieved using the temperature-controlled heat sink. The mentioned probe station was also facilitated with a Fluorine-based optical fiber to collect the room temperature EL emissions from GeSn LEDs and deliver them to the spectrometer and detector. For low temperature I-V and EL measurements on the GeSn LED samples, a standard Janis cryostat [114] with feedthrough capability was prepared. The sample holder inside the cryostat had two gold plated needles that
could be placed on the metal contacts and apply the desired current. The EL emission from the GeSn LED was collected using a CaF$_2$ lens and eventually delivered to the microHR spectrometer and detector. The detected signal was amplified using a lock-in amplifier and an optical chopper. A long pass filter was placed right before the spectrometer entrance slit to avoid the penetration of ambient light.

Figure 2.9. The schematic diagram of the home-built EL setup designed and constructed for infrared EL measurements from cryogenic to room temperature.

The temperature-dependent I-V characteristic and EL spectra of GeSn light emitting devices are thoroughly described in Chapter 5.
Chapter 3. Photoluminescence (PL) study of GeSn films

3.1 Motivation

Group IV-based light-emitting devices, such as LEDs and lasers, have long been desired in Si photonics. Recently, a new technology based on incorporating Sn into Ge has attracted a lot of interest due to the accessibility of the direct bandgap material, the applications of optoelectronic devices operating in near- and mid-infrared, and the compatibility with the CMOS process. GeSn-based optoelectronic devices such as modulators, LEDs and photodetectors have been demonstrated showing a great promise for use in Si photonics. While outstanding progress on GeSn related research has been made, direct bandgap GeSn has yet to be achieved. Without this direct bandgap material, the development of a group IV-based laser to fundamentally address the grand challenge in Si photonics will remain out of reach.

Theoretical work has predicted that 6% or higher of Sn in a relaxed GeSn could result in a direct bandgap [95], [115]. However, because of the compressive strain in the GeSn thin film due to lattice mismatch between the GeSn layer and the substrate (usually Ge or Si), the required Sn composition for indirect-to-direct transition is higher than that in a relaxed one [111].

In this chapter, a temperature dependent PL study on as-grown GeSn thin films with different Sn mole fractions grown using a commercially available CVD system is presented. The room temperature (RT) PL was achieved for as-grown GeSn thin films and the bandgap energies correspond to PL peak emissions were extracted. The temperature-dependent PL measurement from 10 to 300 K was performed on the samples to analyze the behavior of the both direct and the indirect bandgap energies. The temperature-dependent bandgap relation (Varshni’s relation) was utilized to scrutinize the GeSn bandgap behavior in different temperatures and achieve $\alpha$ and $\beta$ parameters in the Varshni’s relation. In all temperatures, reduction of the difference between
the direct and indirect bandgap energies was observed by increasing the Sn composition. A competition between the direct and indirect bandgap optical emission process has been illustrated [116]. The temperature-dependent PL behavior for GeSn alloys with Sn composition near the indirect-to-direct bandgap transition point will be fully investigated in this work.

3.2 Growth and characterization of GeSn films

The GeSn thin films were grown in an industrially available Epsilon® 2000-Plus reduced pressure chemical vapor deposition (RPCVD) reactor with single run epitaxy using commercially available precursor gases [117]. Prior to the growth of GeSn thin films, a strain-relaxed Ge buffer layer was deposited on the Si (100) substrate via a Stranski-Krastanov mechanism. Deposition of the GeSn thin films was performed inside the chamber at temperatures of less than 400 °C using GeH₄, SnCl₄, and H₂, which is compatible with current CMOS techniques. Detailed growth steps of these samples were discussed in Chapter 2 and also in Ref. 75.

The GeSn samples in this study had x = 0, 0.009, 0.032, 0.06, and 0.07 Sn mole fraction, respectively. The Sn mole fraction of each sample was measured using secondary ion mass spectroscopy (SIMS) calibrated for GeSn and X-ray diffraction (XRD). To verify the GeSn and epilayer thickness and its crystallinity, transmission electron microscopy (TEM) images and XRD 2θ-ω scans were employed [117]. The TEM image of the Ge₀.₉₃Sn₀.₀₇ sample is shown in Figure 3.1a. The Ge₀.₉₃Sn₀.₀₇ thin film, Ge buffer layer, and Si substrate can be clearly seen. Due to the high lattice mismatch of GeSn with Si, the Ge buffer layer was grown to improve the GeSn material quality. The TEM image of the Ge₀.₉₃Sn₀.₀₇ layer indicated that the misfit dislocations were confined at the GeSn/Ge interface with no propagation of threading dislocations through the epilayer [117]. The GeSn films were able to lock 80% of the propagated
threading dislocations in the Ge buffer layer [74]. The average threading dislocation density (TDD) was measured to be $9.7 \times 10^8$ cm$^{-2}$ in Ge buffer layer and $3 \times 10^7$ cm$^{-2}$ in GeSn layer. The TDD in the top GeSn layer was verified by etch pit measurement study showing $1.1 \times 10^7$ cm$^{-2}$. The thicknesses of the epilayers were measured by TEM to be 327, 76, 80, and 240 nm for samples with Sn compositions of 0.9, 3.2, 6 and 7%, respectively.

Figure 3.1. (a) High-resolution TEM image of the Ge$_{0.93}$Sn$_{0.07}$ layer grown on a Ge buffer and Si substrate. (b) 2θ-ω scans of the GeSn samples are resolved for each of the different Sn mole fractions [117].

In-plane and out-of-plane lattice constants and the strain in lattice constants were measured by XRD using 2θ-ω scan and reciprocal space map (RSM). Figure. 3.1b shows the XRD 2θ-ω scan from the (004) reflection with the peaks between 66-64° belonging to the GeSn layers. All the samples were partially compressively strained, except Ge$_{0.94}$Sn$_{0.06}$, which was fully compressively strained. This in-plane compressive strain increased the out-of-plane lattice constant which showed up as a reduced angle in the XRD 2θ-ω scan [117]. Information about the thickness, strain and the XRD FWHM of the Ge buffer and GeSn thin films are shown in Table
3.1. As shown in the following table, the Ge sample was tensile strained which indicated as a positive value. Negative values were ascribed to compressive strain.

Table 3.1. Sn Composition, Thickness, Strain, and FWHM of GeSn thin films [117].

<table>
<thead>
<tr>
<th>Sn %</th>
<th>GeSn Thickness (nm)</th>
<th>Ge Buffer Thickness (nm)</th>
<th>In-plane strain Ge Buffer</th>
<th>GeSn</th>
<th>Ge Buffer</th>
<th>GeSn FWHM (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>253</td>
<td>-</td>
<td>-</td>
<td>-0.0018</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td>0.9</td>
<td>327</td>
<td>763</td>
<td>0.0010</td>
<td>-0.0002</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>3.2</td>
<td>76</td>
<td>684</td>
<td>0.0014</td>
<td>-0.0024</td>
<td>0.14</td>
<td>0.20</td>
</tr>
<tr>
<td>6.0</td>
<td>86</td>
<td>700</td>
<td>0.0012</td>
<td>-0.0082</td>
<td>0.16</td>
<td>0.22</td>
</tr>
<tr>
<td>7.0</td>
<td>240</td>
<td>755</td>
<td>0.0009</td>
<td>-0.0045</td>
<td>0.15</td>
<td>0.34</td>
</tr>
</tbody>
</table>

PL measurements were performed using a standard PL setup in an off-axis configuration as explained in Chapter 2. A 532 nm CW diode-pumped solid-state laser with 500 mW power was used as an excitation source, and the laser beam was focused to a 100 μm spot. The GeSn samples were mounted inside a liquid helium-cooled closed-cycle cryostat manufactured by Janis [114]. A spectrometer equipped with a liquid nitrogen cooled extended-InGaAs photodetector with a cut-off at 2.3 μm, along with a lock-in amplifier and the optical chopper, was utilized to collect the emissions from the GeSn samples and provide the PL spectrum [117].

3.3 Photoluminescence measurements of thin GeSn structures

The RT PL spectra, shown in Figure 3.2a, have a clear composition dependent main peak for each sample, showing a red-shift as the Sn mole fraction increases. For samples with Sn content of 0 (Ge reference), 0.9, and 3.2%, a strong high-energy peak and a weak intensity low-energy shoulder were observed corresponding to the direct and indirect bandgap transitions, respectively. For samples with the higher Sn compositions of 6 and 7%, the difference between
the direct and indirect bandgap energies decreased and the emission peaks from the direct and indirect transition overlapped, resulting in a broad peak shown in Figure 3.2a [117].

![Figure 3.2](image)

Figure 3.2. (a) Room temperature PL spectra were collected for the 0% (Ge buffer), 0.9, 3.2, 6 and 7 % Sn mole fraction. (b) The fitting procedure used to extract the different emission spectra (the sample with 3.2% Sn) [117].

The PL peak positions were extracted using a Gaussian fitting as shown for Ge$_{0.968}$Sn$_{0.032}$ in Figure 3.2b. The fitted curve consisted of three peaks, which were assigned to the direct transition of Ge and the direct and indirect transition of GeSn, respectively. The Ge emission peak was observed because of the relatively thin epilayer of the sample with 3.2% Sn content, thus excitation and emission took place in the Ge buffer layer as well. The direct and indirect peak positions, obtained by Gaussian fitting, were plotted as a function of Sn content in Figure 3.3. The closed symbols are extracted data, and the solid lines are theoretical curves based on the Vegard’s law relation [117]:

$$E_{GeSn} = xE_{Sn} + (1 - x)E_{Ge} - x(1 - x)b$$  \hspace{1cm} (Equation 3.1)

where $E_{GeSn}$ is the bandgap energy of GeSn; $E_{Ge}$ and $E_{Sn}$ are the bandgap of Ge and Sn, respectively; $x$ is the Sn mole fraction; and $b$, is the bowing parameter in RT. For the L valley,
b = 0.68 eV and for the Γ valley b = 2.92 eV are considered. At RT, the indirect bandgap of Sn is 0.14 eV, and the direct bandgap is -0.413 eV. For Ge, the indirect and direct bandgaps at RT are equal to 0.66 and 0.8 eV, respectively. Information about the bandgap energy of Ge and Sn and the bowing parameters were given in Chapter 1. As Sn composition increased, the direct bandgap reduced faster than the indirect bandgap, resulting in the continuously reduced separation between the direct Γ-valley and the indirect L-valley in the conduction band, as shown in Figure 3.3. The experimental data agreed with those theoretical calculations for previously measured bowing parameters. A small deviation from the Vegard’s law prediction indicated the role of strain in the bandgap of GeSn films. For more accurate prediction of the direct and indirect bandgap in GeSn alloys, both the Sn incorporation and strain effect should be considered.

![Bandgap energy vs Sn mole fraction](image)

Figure 3.3. The bowed Vegard’s law interpolation for the direct and indirect bandgap of GeSn alloy is plotted for different Sn compositions and is overlaid with experimental data. The asterisks show the indirect bandgaps and the diamonds represent the direct bandgap energy [117,118].

To study the changes in the GeSn bandgap, a temperature-dependent PL measurement was performed. For GeSn samples with Sn composition less than 7%, the following observation was made. At RT, the main peaks were attributed to the direct transition, as aforementioned. As
temperature decreased, the thermally excited electrons that occupy the Γ-valley decreased due to the narrowing of Fermi-Dirac distribution tail. Carriers occupied only the L valley in the indirect gap. Phonon-assisted and impurity-assisted PL was the dominant process at low temperature. Once the required energy for phonon emission and absorption was provided, those phonons conserved the momentum for carrier recombination through the indirect bandgap. This occurrence was almost the same as Ge PL emission at low temperatures [119]–[122]. The GeSn alloys with higher Sn composition tended to be a direct bandgap material. The temperature-dependent bandgap spectra of GeSn thin film with 3.2% Sn composition is presented in Figure 3.4a.

Figure 3.4 (a) Temperature-dependent PL spectra of GeSn sample with 3.2% Sn composition. Curves are stacked for clarity. The direct band gap and indirect bandgap emission peaks are marked by arrows. (b) The ratio between integrated PL intensity of direct and indirect peaks at temperatures from 225 K to 300 K.

The described mechanism of the competition between indirect and direct transition was clearly indicated in the PL spectra from 10 K to 300 K. The ratio between the integrated PL intensity of direct ($I_{\text{direct}}$) and indirect peak ($I_{\text{indirect}}$) at temperatures from 225 K to 300 K is
shown in Figure 3.4b. The ratio shown in Figure 3.4b indicated that an increase in the direct bandgap emission depends upon two parameters: 1) Sn composition of the GeSn alloy; and, 2) temperature of the samples. Higher Sn compositions lowered the $\Gamma$ valley and more carriers were available for the direct bandgap transition. Moreover, higher temperature provided more thermally excited carriers to penetrate the $\Gamma$ valley and participate in the direct bandgap transition with higher recombination rate.

The Ge$_{0.93}$Sn$_{0.07}$ sample was studied under the temperature-dependent PL measurements for further investigation of its bandgap alterations. The Ge$_{0.93}$Sn$_{0.07}$ PL spectra are shown in Figure 3.5 with temperature ranging from 10 K to 300 K. The direct and indirect PL emissions are overlapped and not discernible [117].

![Figure 3.5. Temperature-dependent PL measured on Ge$_{0.93}$Sn$_{0.07}$ illustrates the changes in PL spectra from 10 to 300 K. [117].](image)

At 10 K, a strong PL peak was observed and, in contrast with other samples, no separate PL peaks related to the indirect and direct transition was detected. This verified that the difference between the indirect and direct gap was very small and their PL emissions were
almost overlapped, so the peaks were unresolvable using the Gaussian fitting. It is inferred for sample Ge_{0.93}Sn_{0.07} that the direct and indirect energy gaps were almost equal.

The obtained peak positions from all samples were fitted using an empirical temperature-dependent bandgap Varshni relation. The theoretical calculation of peak position versus temperature for a GeSn bandgap can be described by the Varshni relation [117],

\[
E_{\text{GeSn}}(T) = E_{\text{GeSn}}(0) - \alpha T^2 / (T + \beta)
\]  
(Equation 3.2)

where \( E_{\text{GeSn}}(0) \) is the bandgap at 0 K, and \( \alpha \) and \( \beta \) are the fitting parameters. The peak positions are plotted as a function of temperature in Figure 3.6 for samples with Sn content of 0, 0.9, 3.2 and 6%. The Varshni equation was fitted on the PL peak positions for both direct and indirect emissions. Increasing the Sn mole fraction from 0.9 to 6% reduced the average distance between the direct and indirect gap (\( (\Delta E)_{\text{avg}} \)) in GeSn films from 0 to 6% Sn. For better visibility, the height of the energy axis is kept at 0.25 eV for all samples in a-d. The variance in the fitting process of the temperature-dependent GeSn bandgaps is provided. As indicated before, no thermally generated carrier was available to occupy the \( \Gamma \) valley of the conduction band in low temperature. Therefore, no direct PL peak was observed at temperatures less than 100 K. The direct PL peak for Ge was revealed in temperatures higher than 150 K. In Ge_{0.991}Sn_{0.009} and Ge_{0.968}Sn_{0.032}, the direct PL peaks were distinguished for temperatures higher than 200 K, and in Ge_{0.94}Sn_{0.06} it was observed for temperatures higher than 100 K. These observations depended on the variation in the material quality. In low temperatures, only the phonon-assisted indirect PL could be detected due to the carrier only occupying the \( L \) valley of the conduction band. As indicated in Figure 3.6, in each sample, as the temperature increased from 10 to 300 K, the separation between direct and indirect peaks (\( \Delta E \)) were almost constant, and it decreased as the Sn content increased. The average difference between the direct and the indirect bandgaps


\[ (\Delta E)_{\text{avg}} \] were 0.115, 0.075, 0.043, 0.032 eV for the samples with Sn composition of 0, 0.9, 3.2 and 6%, respectively, which was consistent with the RT PL results. The peak positions in different temperatures for Ge\(_{0.93}\)Sn\(_{0.07}\) could not be accurately determined due to the very small separation between direct and indirect peaks. Only at RT, the difference between the direct and indirect bandgap was identified as \( \Delta E \approx 0.012 \) eV for Ge\(_{0.93}\)Sn\(_{0.07}\) sample. At other temperatures, the indirect and the direct PL peaks were unresolvable.

Figure 3.6. The PL peak positions for different temperatures of the direct (red circles) and indirect (blue triangles) gaps for (a) Ge buffer (0\% Sn), (b) Ge\(_{0.991}\)Sn\(_{0.009}\), (c) Ge\(_{0.968}\)Sn\(_{0.032}\), and (d) Ge\(_{0.94}\)Sn\(_{0.06}\) [117]
The calculated 0 K bandgap of the GeSn alloys and the fitting parameters are given in Table 3.2. The achieved experimental PL data were fitted using the Varshni’s relation (Eq. 2) and the bandgap energy at 0 K, α, and β parameters for the GeSn with different Sn content are presented. No variable was fixed in the fitting process. The values of the variance for the fitting of the direct and the indirect bandgaps in each GeSn sample was calculated and are provided in Figure 3.6. The only constraint that was made on the fitting process was to intentionally maintain the variance less than 0.05 [117].

<table>
<thead>
<tr>
<th>Fitting Parameters</th>
<th>Ge buffer</th>
<th>Ge&lt;sub&gt;0.991&lt;/sub&gt;Sn&lt;sub&gt;0.009&lt;/sub&gt;</th>
<th>Ge&lt;sub&gt;0.918&lt;/sub&gt;Sn&lt;sub&gt;0.032&lt;/sub&gt;</th>
<th>Ge&lt;sub&gt;0.94&lt;/sub&gt;Sn&lt;sub&gt;0.06&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (0) (eV)</td>
<td>Direct</td>
<td>Indirect</td>
<td>Direct</td>
<td>Indirect</td>
</tr>
<tr>
<td></td>
<td>0.861</td>
<td>0.742</td>
<td>0.817</td>
<td>0.741</td>
</tr>
<tr>
<td>α (eV/K)</td>
<td>4.8 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>2.4 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>2.8 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>3.5 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>β (K)</td>
<td>218</td>
<td>254</td>
<td>308</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fitting Parameters</td>
<td>Ge&lt;sub&gt;0.918&lt;/sub&gt;Sn&lt;sub&gt;0.032&lt;/sub&gt;</td>
<td>Ge&lt;sub&gt;0.94&lt;/sub&gt;Sn&lt;sub&gt;0.06&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E (0) (eV)</td>
<td>Direct</td>
<td>Indirect</td>
<td>Direct</td>
<td>Indirect</td>
</tr>
<tr>
<td></td>
<td>0.731</td>
<td>0.690</td>
<td>0.662</td>
<td>0.641</td>
</tr>
<tr>
<td>α (eV/K)</td>
<td>2.7 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>3.3 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>3.0 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>3.6 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>β (K)</td>
<td>298</td>
<td>298</td>
<td>296</td>
<td>195</td>
</tr>
</tbody>
</table>

3.4 Observation of a TRUE direct bandgap GeSn alloy

The nature of GeSn bandgap (directness or indirectness) was determined by Sn composition and strain. Their interrelation is shown in Figure 3.7 with three distinct regions: (1) indirect bandgap material region (marked as "indirect"), (2) direct bandgap material region (marked as "direct"), and (3) uncertain region (marked as "uncertain"). Note that the uncertain
region is not a "specific region"; it only reveals the discrepancy of theoretical calculations based on various models and fitting parameters reported in the literature, in which the predicted values of the transition points for relaxed GeSn with x range from 6 to 10% [81], [95], [123]. Higher Sn composition is required to achieve the transition when compressive strain increases. The two contours of transition points corresponding to the lowest and highest predicted value form the left and right boundaries of the uncertain region. The triangular data points, shown in Figure 3.7, are the PL results of GeSn samples discussed in the previous section of this chapter (section 3.3) and circular data points, are GeSn samples which will be studied in this section.

The schematic band diagrams of direct and indirect GeSn alloys and the mechanism of PL spectra formation are shown as insets in Figure 3.7. In the indirect region where the direct bandgap energy is higher than the indirect bandgap energy, the fraction of electron population in the L valley is higher than that in the Γ valley. Because the probability of radiative recombination in a direct bandgap transition is higher than that in a phonon-assisted indirect bandgap transition, both direct and indirect peaks could be observed. Therefore, the PL spectrum was the superposition of these two peaks. At low Sn composition, both peaks could be identified clearly because of the sufficient energy separation. At higher Sn composition (before reaching the transition point), these two peaks could not be identified due to the reduced bandgap energy difference, resulting in only a single peak with broad line-width. In the direct region, the direct bandgap energy is smaller than the indirect bandgap energy, therefore, more electrons populated the Γ valley. As a result, the direct bandgap transition dominated the PL and, hence, only a single peak could be observed in the PL spectrum. It is worth pointing out that this single-peak spectrum only consisted of the direct peak, therefore, the line-width of the peak was narrower than that for the case in the indirect region with relatively high Sn composition. The uncertain in
Figure 3.7 region reveals the discrepancy of theoretical calculations due to various models and fitting parameters. Materials located in the uncertain region could be either direct or indirect bandgap material. The insets in indirect and direct regions show the schematic band diagrams of GeSn alloy and the mechanism of PL spectra formation for indirect and direct bandgap materials, respectively.

![Figure 3.7](image)

Figure 3.7 The effect of compressive strain and Sn composition in the indirect-to-direct bandgap transition at room temperature. [96].

Investigation on the bandgap characteristics of GeSn thin films was conducted by a systematic temperature-dependent PL study on the GeSn samples with 4, 8, 9, and 10% Sn composition. The XRD and TEM characterizations were done to obtain the thickness and strain information of the GeSn films. Information of the samples is listed in Table 3.3, and the XRD, and TEM results are shown in Figure 3.8. As noticed in the following table, the compressive strain values increased by increasing the Sn composition. It showed that none of those GeSn films were even partially relaxed.
Table 3.3. Information of GeSn samples in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sn (%)</th>
<th>GeSn layer thickness (nm)</th>
<th>Compressive strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4</td>
<td>70</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>8</td>
<td>90</td>
<td>0.8</td>
</tr>
<tr>
<td>C</td>
<td>9</td>
<td>79</td>
<td>1.0</td>
</tr>
<tr>
<td>D</td>
<td>10</td>
<td>95</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Figure 3.8 The TEM image of the Sample D showing the crystal quality of the GeSn epilayer on top of the Ge buffer. Inset figure is the 2θ-ω scan showing the Ge and GeSn peaks in samples A, B, C, and D [96].

The PL measurements were performed using a standard off-axis configuration [124]. A continuous wave (CW) laser with 532 nm wavelength was used as an excitation source. The laser beam was focused down to a 100 μm spot, and the power was measured to be 500 mW. The PL emission was collected by a spectrometer and then sent to a liquid nitrogen-cooled extended-InGaAs detector (cut-off at 2.3 μm, higher signal-to-noise ratio, used for sample A) or a
thermoelectric-cooled lead sulfide detector (cut-off at 3 μm, lower signal-to-noise ratio but with extended spectrum response, used for samples B, C, and D). Temperature-dependent PL spectra of samples A, B, C and D are shown in Figure 3.9a–d. In (a), The direct peaks are marked by upwards arrows, while downward arrows indicate the indirect peaks. In (b) and (c), a broadened PL peak indicates the existence of two peaks with a large spectral overlap. In (d), only a single peak with narrowed line-width was observed, suggesting a direct bandgap material. The detailed discussion is presented as follows:

Figure 3.9. Temperature-dependent PL spectra of (a) sample A, (b) sample B, (c) sample C, and (d) sample D. Each curve is stacked for clarity [96].
For sample A (4% Sn), the PL peaks related to the direct and indirect transitions were clearly seen at each temperature (Figure 3.9a). At 300 K, the peaks at 1800 and 2000 nm were attributed to direct and indirect bandgap transitions, respectively. The direct peak was stronger than the indirect peak due to the strong radiative recombination of the direct bandgap transition. As temperature decreased, the direct peak decreased rapidly while the indirect peak increased. At temperature below 100 K, the indirect bandgap transition began to dominate the PL. Both the direct and indirect peaks experienced a blue shift by decreasing the temperature – the nature of temperature-dependent bandgap tuning. The direct and indirect optical emission competition has been fully investigated in Ref. 111. Furthermore, a small peak at around 1600 nm could be seen in the spectrum at 300 K, which was attributed to the direct bandgap transition in Ge because it matches the wavelength of emission from Ge direct bandgap transition.

For sample B (8% Sn), the PL peaks arising from direct and indirect bandgap optical emission were difficult to be identified due to the small separation between the direct and the indirect bandgap energies. However, a peak with a flat top was observed at 100 K, indicating the existence of two peaks with a large spectral overlap. As temperature decreased from 300 K, the high energy tail of the main peak dropped while the low energy tail grew, reflecting the competing optical emission process. This competition was in agreement with the PL behavior of sample A. Compared with sample A, the position of the main peak in Figure 3.9b was extended to 2100 nm at 300 K as a result of increased Sn composition. Note that the rippling characteristics of PL spectra were due to the relatively low signal-to-noise ratio of the lead sulfide detector (similar features of PL spectra were observed in sample C and D).

Due to further reduced energy separation between direct and indirect bandgap, the direct peak of sample C (9% Sn) nearly coincided with the indirect peak, resulting in observation of
only a single peak with broadened line-width. The line-width of the peak was similar to that of sample B at each temperature, indicating the existence of two overlapped peaks, which implied that sample C was still an indirect bandgap material. The position of the main peak was extended to 2150 nm at 300 K.

For sample D (10% Sn), a comparison of spectra with that of samples B (8% Sn) and C (9% Sn) clearly revealed two major differences: 1) no competition between the high and low energy tails of the observed main peak, indicating that the PL emission could come only from one type of optical transition; and, 2) the line-width of the peak was narrower than that of samples B and C at each temperature, indicating the highly probable existence of a single peak. Since in the radiative recombination rate for direct bandgap, optical transition is higher than that in a phonon-assisted indirect bandgap optical transition, this peak was assigned to a direct-bandgap transition. Therefore, sample D was most likely a direct bandgap material. In addition, the position of the peak in Figure 3.9d was further extended to 2230 nm at 300 K, which is the longest wavelength reported so far for GeSn grown using commercially available precursors (SnCl₄ and GeH₄).

In order to further confirm the direct bandgap of sample D, the PL line-width and PL peak position versus temperature was investigated. The peaks in Figure 3.10 were first fitted by a Gaussian distribution and then the full width at half maximum (FWHM) were extracted to determine the line-width. The plot of line-width as a function of temperature is shown in Figure 3.10a (sample A was not included since its bandgap property was noticeably different). At 300 K, the line-width of samples B and C were 91 and 84 meV, respectively, whereas that of sample D was 53 meV. As temperature decreased, the line-width of samples B, C and D slightly decreased. The line-widths of sample B and C were nearly twice that of the sample D at the
temperature range from 300 to 100 K, implying that only a direct bandgap transition contributed to the PL of sample D. Furthermore, the smooth temperature – line-width curve in sample D indicated the identical mechanism of PL spectra formation at each temperature; therefore, the direct bandgap transition dominated the PL from 300 to 10 K. This fact confirmed that sample D was a direct bandgap material.

Figure 3.10. (a) The line-width of the PL peaks as a function of temperature for samples B, C, and D. (b) Sn composition-dependent bandgap energies at room temperature.

Figure 3.10b shows the Sn composition-dependent bandgap energies (extracted from positions of PL peak in Figure 3.9) at room temperature. Results from previous studies were also plotted to illustrate the transition process of GeSn alloy from indirect to direct bandgap material. There are three regions in Figure 3.10b. Region (i) and (ii) correspond to indirect bandgap material, while region (iii) corresponds to direct bandgap material. The triangular data points are samples used in the previous section, and the circular data points are samples in this section, respectively. Sample D is located in the region (iii), which is determined as a direct bandgap...
material. The solid and dashed lines are eye guidance of direct and indirect bandgap energies, respectively.

In region (i), two PL peaks ascribed to the direct and indirect bandgap transition could be clearly seen. In region (ii), a single PL peak with broadened line-width could be observed. In region (iii), a single PL peak with narrowed line-width could be observed. Sample A was located in the region (i), and samples B and C were in region (ii). Based on the line-width of PL peak study shown in Figure 3.10a, the broadened peak in the region (ii) consisting of two overlapped peaks indicated that region (ii), together with region (i), were linked to the indirect bandgap material (corresponding to the indirect region in Figure 3.7). Region (iii) associated with the sample D, whose PL spectra consisted of a single peak with narrowed line-width. Therefore, sample D was determined as a direct bandgap material. Region (iii) was linked to the direct bandgap material (corresponding to the direct region in Figure 3.7). The dashed and dotted lines were simply linear fitting of direct and indirect bandgap energies for eye guidance purpose. As Sn composition increased, the energy of the direct bandgap reduced more rapidly than that of the indirect bandgap, resulting in the indirect-to-direct bandgap transition taking place at the Sn composition between 9 and 10%, which followed the predicted tendency [124].

In conclusion, material, and optical studies were conducted on GeSn alloys with Sn composition up to 10%. The x-ray measurement revealed that Ge$_{0.9}$Sn$_{0.1}$ alloy was located at the uncertain region. The temperature-dependent PL spectrum of Ge$_{0.9}$Sn$_{0.1}$ alloy showed a single peak with narrowed line-width at each temperature, which was assigned to a direct bandgap transition. These results indicated that the Ge$_{0.9}$Sn$_{0.1}$ alloy was a direct-bandgap material. Furthermore, the wavelength of PL emission from the Ge$_{0.9}$Sn$_{0.1}$ thin film was observed at 2230
nm, which suggested that the operating wavelength of GeSn-based optoelectronic devices could be extended to the mid-infrared range.

3.5 Photoluminescence measurements of thick GeSn films

In the last section, it was shown that increasing Sn composition (≥ 10%) of thin GeSn films eventually led to achievement of a direct bandgap GeSn material favorable for group-IV based light emitters. However, increasing the Sn composition results in Sn segregation and degradation of the material quality once GeSn films are employed in further process for device fabrication. To avoid such a problem, it is required to have direct bandgap GeSn material with lower Sn incorporation. That could be achieved by reducing the compressive strain and increasing the thickness of the film. In this study, the GeSn films were grown with Sn compositions lower than 10%, but thickness of higher than 300 nm. Material characterization showed that the grown thick GeSn films contained two distinguishable layers: 1) a thin (~200 nm) defective strained GeSn layer which is called sacrificial layer; and, 2) a thick (≥ 350 nm) defect-free relaxed layer with high crystalline quality. The room temperature and low temperature PL results clearly showed an enhancement in the optical quality of the direct bandgap thick GeSn films.

3.5.1 Growth mechanism of thick GeSn films

The epitaxial GeSn films were grown on top of 700 nm Ge buffer layer on the Si (100) substrate using ASM Epsilon® 2000-Plus commercially available system. The deposition was done in a single run epitaxy which is an advantage compared to the Ref. 109. A pre-calibrated recipe was used to grow thick GeSn films. Also, a 10 nm Ge cap was grown on top of the structure. The growth temperature was below 400 °C to make sure it was compatible with CMOS
process. The composition of the thick samples was varied from 5% to 10% based on the recipe; however, the actual Sn compositions, thicknesses, and relaxation information were obtained by material characterization.

3.5.2 Material characterization of thick GeSn films

Figure 3.11 shows the cross-sectional TEM and 2θ-ω XRD scan and RSM on the grown thick GeSn samples.

Figure 3.11. (a) The TEM image of the sample with 10.9% Sn composition and ~ 600 nm total thickness of the GeSn layers. (b) The 2θ-ω XRD scan from (004) plane of the thick GeSn films. The RSM plot of sample C is shown in the inset.

The TEM image clearly showed that the defects were located within the Ge/Si interface and Ge/GeSn interface. The formation of threading dislocation at the interfaces stopped the propagation of the defects through the GeSn layer. The defects, trapped at the Ge and GeSn bottom layer interface, provided a defect-free GeSn top layer. The two separate GeSn layers were also identified in the 2θ-ω XRD scan and RSM plot. Si substrate peak at 69° and Ge peak and GeSn peaks are shown at 66.2° and 65°, respectively. The observed shoulder on the GeSn
peaks at 65° represented the GeSn bottom layer. It was also shown in the RSM of sample C presented in the inset of Figure 3.11b that the GeSn top layer was almost relaxed. The results of the material characterization, including the actual Sn composition, layers thicknesses, and relaxation of the GeSn top layer, are provided in Table 3.4.

Table 3.4. Summary of measurement results of samples in this study

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Sn composition (%)</th>
<th>Total GeSn thickness (nm)</th>
<th>Relaxation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GeSn bottom layer</td>
<td>GeSn top layer</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Single GeSn layer with 5.12% Sn</td>
<td>420</td>
<td>72</td>
</tr>
<tr>
<td>B</td>
<td>6.2</td>
<td>7.1</td>
<td>81</td>
</tr>
<tr>
<td>E</td>
<td>8.9</td>
<td>10.6</td>
<td>82</td>
</tr>
</tbody>
</table>

3.5.3 PL measurement on the thick GeSn films

The PL measurement was performed on the GeSn thick films to study the bandgap emission and optical quality of the samples. Photoluminescence (PL) measurement was performed at temperatures of 10 and 300 K. A diode-pumped solid-state CW laser operating at 532 nm with output power of 500 mW was used as excitation source. Emissions from the GeSn samples were collected by a spectrometer, and the collected light was then sent to the detector. A lead sulfide (PbS) detector with a cut-off wavelength at 3 μm was used for detection of the PL spectrum. To eliminate the scattered laser light, a long-pass filter was placed in front of the spectrometer entrance [104].

The normalized room-temperature PL spectra of samples A to C are presented in Figure 3.12. A clear red-shift was detected indicating the shrinkage of the bandgap by increasing the Sn composition. The energy difference between the direct and indirect bandgap for each sample was
small, therefore, two separate peaks related to the direct and indirect emission were not identified. It is worthwhile to mention that the PL peak position of the strain-relaxed thick GeSn samples was shifted towards the longer wavelength compared to the thin GeSn samples with the same Sn composition. Relaxation of the GeSn layer eventually lowers both $\Gamma$ and $L$ valleys in the conduction band and pushes the crossover point (where the difference between the $\Gamma$ and $L$ valleys is zero) toward the lower Sn compositions for GeSn material. This fact obviously shows that less compressive strain and more relaxation in the lattice of the films not only change the GeSn bandgap from indirect to direct but also provides emission at longer wavelength promising for mid-infrared optoelectronic applications.

![Figure 3.12](image)

**Figure 3.12.** The normalized PL spectra of thick GeSn samples (samples A to C) at room temperature [104].

Temperature-dependent PL measurement was conducted on the samples as shown in Figure 3.13. Except for sample A, all samples showed a dramatic enhancement of the PL intensity once temperature was decreased. The PL intensity at low temperature for sample C was
almost 400 times higher than sample A. Higher PL intensity indicates the improvement of the optical quality of sample C. That enhancement, along with the reduction of PL spectra line-width, indicated that the PL emission mainly came from the direct bandgap recombination. The intensity was related to the higher recombination rate for direct gap emission since samples B and C were direct bandgap GeSn. The reduction of the PL spectrum linewidth and a surge in the PL intensity confirmed that judgment.

---

Figure 3.13. The comparison between the PL spectra of sample A and C at 10 K (a) and 300 K (b). (c) The temperature-dependent PL of sample B from 10 K to 300 K.
As mentioned in the PL setup details, the PL measurements were done using 532 nm CW laser. Since the penetration depth of the 532 nm laser is less than 100 nm in the GeSn, it would have been beneficial if an excitation source with a longer wavelength was employed, so it could penetrate more into the sample and generate more carriers which consequently would have increased the PL intensity. That type of excitation is favorable for an optically-pumped GeSn laser which will be discussed in Chapter 6.
Chapter 4. Study of SiGeSn/GeSn/SiGeSn quantum well structures

4.1 Motivation

Developing GeSn-based light-emitting devices has opened a new opportunity for Si-based optoelectronic technology [125]–[127]. The recent demonstration of direct bandgap GeSn [96], [110] and the optically-pumped GeSn laser [92] indicates the great potential of GeSn that can be used as efficient group IV based light emitters. The GeSn light emitting diodes (LEDs) based on advanced structures, such as double heterostructures (DHS) [128]–[133] and a multi quantum well (MQW) [134], [135] have been reported. Compared to DHS, the QW features a higher efficiency of light emission. The QW based GeSn laser are expected to have reduced threshold carrier densities [136]–[141]. It has been reported that the GeSn MQW LED has an improved light emission [135]. However, based on theoretical calculations in the same report, using Ge as a barrier layer cannot achieve Type-I band alignment. In order to gain design flexibility regarding bandgap and lattice constant, a ternary SiGeSn barrier layer has been proposed, featuring separate tuning of the bandgap and lattice constant by incorporating appropriate Si and Sn compositions into Ge. Although the growth of SiGeSn is more challenging particularly when large Si content is required, thanks to the advanced low temperature material growth technique, high material quality of SiGeSn have been reported recently [108], [142].

In this study, the SiGeSn/GeSn/SiGeSn single-QW (SQW) emitters were investigated. The materials were grown on Si using an industry standard chemical vapor deposition reactor with low-cost precursors. The temperature-dependent photoluminescence (PL) was performed, and direct and indirect peaks were identified and analyzed. Moreover, the electronic band structures were studied, which confirmed that the PL emission originates from the QW structure with Type-I band alignment.
4.1 Growth and material characterization of SiGeSn/GeSn QW structures

The SiGeSn/GeSn/SiGeSn QW structures were epitaxially grown on 200 mm Si (100) using an industry standard ASM Epsilon® 2000-Plus reduced pressure chemical vapor deposition (RPCVD) system. Low cost, commercially available SiH₄, GeH₄, and SnCl₄ were used as Si, Ge, and Sn precursors, respectively. A 700 nm thick Ge buffer layer was grown prior to QW growth by a two-step growth method. Two QW structures with a variation of Si and Sn compositions were grown consisting of a 50 nm thick SiGeSn barrier, a 10 nm thick GeSn well, and another 50 nm thick SiGeSn barrier. A 10 nm thick Ge cap layer was deposited at the very top. The Si/Ge/Si₀.₇Ge₀.₈₈Sn₀.₀₅/Ge₀.₉₂Sn₀.₀₈/Si₀.₀₇Ge₀.₈₈Sn₀.₀₅/Ge QW structure and Si/Ge/Si₀.₁₂Ge₀.₇₉Sn₀.₀₉/Ge₀.₉Sn₀.₁/Si₀.₁₂Ge₀.₇₉Sn₀.₀₉/Ge QW structure were labeled as sample A and B, respectively. Schematic of the sample cross-section is shown in Figure 4.1a.

![Figure 4.1](image-url)
After growth, material characterization techniques including cross-sectional transmission electron microscopy (TEM) and high-resolution X-ray diffraction (HRXRD) were employed to investigate the layer thickness, the Si and Sn compositions, and the strain for each sample.

Figure 4.1b shows a typical cross-sectional TEM image of sample B. Each layer could be clearly resolved and featured low defect density. The high material quality was due to the optimized growth of the Ge buffer which localized the defects at the Ge/Si interface allowing almost no threading dislocations to propagate to the active layers. The measured thickness of each layer was consistent with the target value within an error of ±5 nm for the barrier and ±2 nm for the QW region.

The XRD 2θ-ω scan from (004) plane of sample B is shown in Figure 4.2. The gray and red curves were plotted according to experimental data and simulation, respectively. The Ge, SiGeSn, and GeSn peaks were clearly observed. The multiple oscillations were associated with the thickness of multi-layered structure (thickness fringes). Their presence indicated the high quality of the interfaces and permitted the extraction of the thickness of the layers. The experimental data agreed well with the simulation results. The reciprocal space map (RSM) of sample B was performed from asymmetrical plane (224) to find the out of plane lattice constant as well as strain information of the layers. The strain calculation of the layers was made based on the slight tensile strain of the Ge buffer layer. The RSM shown in Figure 4.2 inset revealed that all SiGeSn and GeSn layers were lattice matched (in-plane) to the Ge buffer layer and, thus, featured compressive strain due to their larger lattice constants compared to that of Ge. Due to the realization of the GeSn QW layer, lattice matched to the Ge buffer layer, both QW layers in samples A and B experienced -0.8% and -1.59% compressive strain, respectively. That much strain eventually affected on the bandgap of GeSn QW layers and pushed them to be an indirect
bandgap material. More details will be discussed in section 4.3.

Figure 4.2. The XRD 2θ-ω scan of sample B. The gray and red curves are experimental data and simulation results, respectively. Inset: The RSM shows that each layer was grown pseudomorphically to the Ge buffer.

Characterization results achieved through simulation of the XRD results of these two samples are summarized in Table 4.1.

Table 4.1. Information of QW samples in this study

<table>
<thead>
<tr>
<th></th>
<th>Sample A</th>
<th></th>
<th>Sample B</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si (%)</td>
<td>Sn (%)</td>
<td>Thickness (nm)</td>
<td>Strain (%)</td>
</tr>
<tr>
<td>Ge cap</td>
<td>0</td>
<td>0</td>
<td>11.0</td>
<td>0.01</td>
</tr>
<tr>
<td>SiGeSn barrier</td>
<td>7.00</td>
<td>4.78</td>
<td>50.0</td>
<td>-0.53</td>
</tr>
<tr>
<td>GeSn well</td>
<td>0</td>
<td>6.97</td>
<td>8.0</td>
<td>-0.80</td>
</tr>
<tr>
<td>SiGeSn barrier</td>
<td>7.00</td>
<td>5.61</td>
<td>46.0</td>
<td>-0.41</td>
</tr>
<tr>
<td>Ge buffer</td>
<td>0</td>
<td>0</td>
<td>700.0</td>
<td>0.01</td>
</tr>
</tbody>
</table>
4.2 Photoluminescence study of SiGeSn/GeSn/SiGeSn QW structures

Temperature-dependent PL measurements were performed using a helium cooled closed-cycle cryostat. A continuous wave (CW) 532 nm laser with 500 mW power was used to excite the samples through the standard off-axis configuration with a lock-in technique. The PL emission was delivered to a spectrometer and was then collected onto a thermoelectric-cooled lead sulfide (PbS) detector with the cut-off at 3 µm.

Figure 4.3a shows the temperature-dependent PL spectra of sample A. The Gaussian fitting was used to identify the PL peak position [116], [117]. At room temperature, the PL peak was at 0.647 eV (1917 nm). As the temperature decreased, this peak shifted toward shorter wavelength as expected (marked as a downwards arrow) due to the bandgap increase at a lower temperature. At the same time, the peak intensity monotonically decreased, and almost disappeared at 150 K. This peak was assigned to the direct bandgap transition, whose decreased intensity at a lower temperature could be attributed to the reduced number of carriers populating the Γ valley in the conduction band (CB). The broadened PL peak linewidth was observed at temperatures between 200 and 100 K, indicating the existence of two peaks that partially overlapped. At 200 K, the peak at 0.605 eV (2050 nm) was associated with the indirect bandgap transition.

As the temperature decreased, the intensity of the indirect peak significantly increased and became dominating at temperatures below 100 K (marked as an upwards arrow). This is because the decrease in non-radiative recombination at lower temperature led to band filling in the L valley in CB, resulting in the enhanced PL emission. At 10 K, the indirect peak blue-shifted to 0.642 eV (1931 nm). The sharp peak observed at 2128 nm was the fourth-order diffraction from the 532 nm excitation laser, as it doesn’t shift with the temperature. Later in
section 4.3, the relation between the PL results and the bandgap energy calculations will be discussed.

Figure 4.3. Temperature-dependent PL spectra of (a) sample A and (b) sample B.

The temperature-dependent PL spectra of sample B are plotted in Figure 4.3b. The behavior of PL peak variation was consistent with that of sample A. At 300 K, the direct peak at 0.585 eV (2120 nm) dominated the PL. As temperature decreased, the intensity of the direct peak decreased. At 200 K, the indirect peak at 0.554 eV (2238 nm) emerged. The intensity of the indirect peak increased as the temperature decreased. At the temperatures below 100 K, the indirect peak dominated the PL, and it blue-shifted to 0.585 eV (2120 nm) at 10 K.

The detailed temperature-dependent PL peak positions for both indirect and direct bandgap transitions were fitted using the Varshni relation $E_g(T)=E_g(0)-\alpha T^2/(T+\beta)$, where the $E_g(0)$ is the bandgap energy at 0 K, and $\alpha$ and $\beta$ are the material-dependent parameters related to the thermal coefficient. The parameters are listed Table 4.2 and are beneficial for the temperature-dependent investigation of the bandgap of GeSn QWs.
### Table 4.2. Fitting parameters extracted by Varshni’s relation fitting

<table>
<thead>
<tr>
<th>Fitting Parameters</th>
<th>Sample A</th>
<th></th>
<th></th>
<th>Sample B</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Direct</td>
<td>Indirect</td>
<td></td>
<td>Direct</td>
<td>Indirect</td>
<td></td>
</tr>
<tr>
<td>$E_g(0)$ (eV)</td>
<td>0.704±0.002</td>
<td>0.641±0.004</td>
<td></td>
<td>0.634±0.008</td>
<td>0.592±0.001</td>
<td></td>
</tr>
<tr>
<td>$\alpha$ (eV/K)</td>
<td>$3 \times 10^{-4}$ ± 1.2 $\times 10^{-5}$</td>
<td>$3.3 \times 10^{-4}$ ± $2 \times 10^{-5}$</td>
<td></td>
<td>$1.9 \times 10^{-4}$ ± $6 \times 10^{-5}$</td>
<td>$2.8 \times 10^{-4}$ ± $2.1 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>$\beta$ (K)</td>
<td>172±14</td>
<td>183±11</td>
<td></td>
<td>269±46</td>
<td>172±26</td>
<td></td>
</tr>
</tbody>
</table>

### 4.3 Band structure calculation of SiGeSn/GeSn QWs

In order to further understand the characteristics of the PL emission from the QW structures, the electronic band structures of samples A and B were calculated using the effective mass and 6-band K-P methods for CB and valence band (VB), respectively [136], [143], [144]. The quantized energy levels were obtained using the effective mass approximation. Based on the Ref. 135, the Hamiltonian for the strained 6-band K-P methods attributed to the strained semiconductor with spin-orbit split off ($\Delta$) at the band edge (K=0) is equivalent to:

$$
H = (K = 0) = - \begin{bmatrix}
P_\varepsilon + Q_\varepsilon & 0 & 0 & 0 & 0 & 0 \\
0 & P_\varepsilon - Q_\varepsilon & 0 & 0 & -\sqrt{2}Q_\varepsilon & 0 \\
0 & 0 & P_\varepsilon - Q_\varepsilon & 0 & 0 & \sqrt{2}Q_\varepsilon \\
0 & 0 & 0 & P_\varepsilon + Q_\varepsilon & 0 & 0 \\
0 & -\sqrt{2}Q_\varepsilon & 0 & 0 & P_\varepsilon + \Delta & 0 \\
0 & 0 & \sqrt{2}Q_\varepsilon & 0 & 0 & P_\varepsilon + \Delta 
\end{bmatrix}
$$

(Equation 4.1)

where the band edge energies of the heavy hole (HH) and light hole bands are:

$$
E_{HH}(K = 0) = -(P_\varepsilon + Q_\varepsilon) = \alpha \left( \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \right) + \frac{b}{2} \left( \varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz} \right) 
$$

(Equation 4.2)

$$
E_{LH}(K = 0) = -P_\varepsilon + \frac{1}{2} \left( Q_\varepsilon - \Delta + \sqrt{\Delta^2 + 2\Delta Q + 9Q_\varepsilon^2} \right)
$$

(Equation 4.3)
In the above equation, $\varepsilon_{xx}$ and $\varepsilon_{yy}$ are the in-plane strain and $\varepsilon_{zz}$ is an out-of-plane strain in the lattice constant of each layer. $a_p$ and $b$ are the hydrostatic deformation potential and shear deformation potential of the valence band, respectively. The in-plane strain is related to the top layer lattice constant ($a$) and the bottom layer lattice constant ($a_0$) via the following equation:

$$\varepsilon_{xx} = \varepsilon_{yy} = \frac{a_0 - a}{a} \quad \text{(Equation 4.4)}$$

and the out-of-plane lattice constant is related to the elastic stiffness constants ($C_{11}$ and $C_{12}$) and also the in-plane lattice constant ($\varepsilon_{xx}$).

$$\varepsilon_{zz} = -\frac{2C_{12}}{C_{11}}\varepsilon_{xx} \quad \text{(Equation 4.5)}$$

The conduction band edge energy is also presented as:

$$E_c(K = 0) = E_g + a_c(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \quad \text{(Equation 4.6)}$$

where $E_g$ is the bandgap of the material and $a_c$ is the hydrostatic deformation potential of the conduction band.

All parameters required to calculate the energy levels are listed in the Appendix B.

Using the Vegard’s law, the bandgap energies for the binary GeSn and ternary SiGeSn are introduced as:

$$E_g(\text{Ge}_{1-x}\text{Sn}_x) = E_{g\text{Sn}}(x) + E_{g\text{Ge}}(1-x) - b_{\text{GeSn}x}(1-x) \quad \text{(binary GeSn)} \quad \text{(Equation 4.7)}$$

$$E_g(\text{Si}_{y}\text{Ge}_{1-x-y}\text{Sn}_x) = E_{g\text{Sn}}(x) + E_{g\text{Ge}}(1-x-y) + E_{g\text{Si}}(y) - b_{\text{GeSn}x}(1-x-y) - b_{\text{SiGe}y}(1-x-y) - b_{\text{SiSn}xy} \quad \text{(ternary SiGeSn)} \quad \text{(Equation 4.8)}$$

In the above equations, $b_{\text{GeSn}}$, $b_{\text{SiGe}}$, and $b_{\text{SiSn}}$, are the bowing parameters. Both $\Gamma$ and L valleys have specific bowing parameters that are listed in Table 4.3.
Table 4.3. Bowing parameters of the gamma and L valleys extracted from Ref. [143], [145].

<table>
<thead>
<tr>
<th>Valley</th>
<th>bGeSn</th>
<th>bSiGe</th>
<th>bSiSn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ</td>
<td>2.92</td>
<td>0.2</td>
<td>3.9</td>
</tr>
<tr>
<td>L</td>
<td>0.68</td>
<td>0.33</td>
<td>2.12</td>
</tr>
</tbody>
</table>

Based on Jaros’ band offset theory, the linear interpolation of the average valence band position for the Si$_y$Ge$_{1-x-y}$Sn$_x$ is provided as:

$$E_{v,\text{avg}}(\text{Si}_y\text{Ge}_{1-x-y}\text{Sn}_x) = -0.48y + 0.69x$$  \hspace{1cm} \text{(Equation 4.9)}

Considering the spin-orbit splitting for the Si$_y$Ge$_{1-x-y}$Sn$_x$ as:

$$\Delta_{SO}(\text{Si}_y\text{Ge}_{1-x-y}\text{Sn}_x) = 0.295(1-x-y) + 0.043y + 0.800x$$ \hspace{1cm} \text{(Equation 4.10)}

the relation for the top of the valence band could be simply achieved using

$$E_v(\text{Si}_y\text{Ge}_{1-x-y}\text{Sn}_x) = E_{v,\text{avg}}(\text{Si}_y\text{Ge}_{1-x-y}\text{Sn}_x) + \frac{\Delta_{SO}(\text{Si}_y\text{Ge}_{1-x-y}\text{Sn}_x)}{3}$$ \hspace{1cm} \text{(Equation 4.11)}

In the above calculations, $y$ is equal to zero for the GeSn binary alloy. Thus, the band alignment between the GeSn QWs and SiGeSn barriers for both sample A and B could be obtained. The linear interpolation was utilized to achieve the hydrostatic and shear deformation potential and also the elastic constants for the binary GeSn and ternary SiGeSn. The following equations were applied to calculate the effective mass in the conduction band and for the heavy-hole and light-hole in the valence band [136]. In the following equations, $m_{e-C}$ is the effective mass of the SiGeSn ternary alloy in the conduction band and $m_{e-Ge}$, $m_{e-Si}$, and $m_{e-Sn}$ are the effective masses of Ge, Si, and Sn in the conduction band, respectively.

$$m_{e-C}(\text{Si}_y\text{Ge}_{1-x-y}\text{Sn}_x) = m_{e-Ge}(1-x-y) + m_{e-Si}y + m_{e-Sn}x$$ \hspace{1cm} \text{(Equation 4.12)}
\[ m_{HH} = \frac{m_0}{\gamma_1 - 2\gamma_2} \quad \text{and} \quad m_{LH} = \frac{m_0}{\gamma_1 + 2\gamma_2} \]  
(Equation 4.13)

where \( m_0 \) is the electron mass, \( m_{HH} \) and \( m_{LH} \) are the heavy-hole and light-hole effective masses. \( \gamma_1 \) and \( \gamma_2 \) are Luttinger parameters extracted from Ref. 92. Figure 4.4a shows the electronic band structure of sample A.

Based on Vegard’s law with the selected bowing parameters, the SiGeSn barriers and GeSn QW were indirect bandgap materials. The \( \Gamma \) valley was located above the \( L \) valley in the conduction band of the QW structure. Moreover, Type-I band alignment was achieved at \( \Gamma \) and \( L \) valleys in CB as well as for the heavy hole (HH) and light hole (LH) in VB, which provided a favorable carrier confinement in the GeSn QW region. The barrier heights in CB were \( \Delta E_\Gamma = 177 \) meV and \( \Delta E_L = 11 \) meV at \( \Gamma \) and \( L \) valleys, respectively. Since the \( 11 \) meV at \( L \) valleys was less than the thermal energy \( (1 \ \text{k}_B T \sim 26 \) meV) at room temperature, the SiGeSn barriers, and the GeSn well did not offer sufficient electron confinement for the GeSn well at the \( L \) valley. In addition, at room temperature the \( L \) valley electrons could gain thermal energy and populate the first quantized energy level at \( \Gamma \) valley \( (n_{1\Gamma}) \), resulting in the PL emission being dominated by the direct bandgap transition due to the higher recombination rate of the vertical transition from \( n_{1\Gamma} \) to \( n_{1HH} \). The confinement of holes in HH and LH bands (annotated as \( \Delta E_{HH} \) and \( \Delta E_{LH} \) in Figure 4.4) was calculated, and the barrier heights were 49 and 17 meV, respectively.

Note that the energy \( (\Delta E) \) between the ground-state at the \( \Gamma \) point in CB \( (n_{1\Gamma}) \) and the ground-state in HH band \( (n_{1HH}) \) was calculated to be 0.648 eV, which agreed well with the measured PL spectrum at room temperature (PL peak at 0.647 eV). At lower temperature \((<100 \) K\), due to the decreased thermal energy \( \text{k}_B T \), the SiGeSn barriers and GeSn well offers improved carrier confinement at the \( L \) valley in CB. Furthermore, the reduced non-radiative recombination
velocity and thermally excited carriers enhanced the indirect bandgap transition, therefore leading to the indirect emission dominating the PL at a lower temperature. The electronic band structure of sample B is shown in Figure 4.4b.

Figure 4.4. SiGeSn/GeSn/SiGeSn SQW electronic band structure for (a) sample A and (b) sample B.
Due to the increased Sn composition in the GeSn QW compared to that in sample A, the bandgap energy separation between Γ and L valleys of GeSn was decreased. Nevertheless, due to the quantization effect, the ground state at the Γ point in CB ($n_{1Γ}$) was still higher than the L valley ground state of the QW region and barriers meaning that the sample was an indirect bandgap material. Yet, the probability of the Γ valley being occupied by thermally activated carriers was higher in sample B than that of sample A. This explains that at room temperature, the PL emission intensity was stronger for sample B, as can be seen in Figure 4.4. The energy (ΔE) between the ground-state at Γ point in CB ($n_{1Γ}$) and the ground-state in HH band ($n_{1HH}$) was calculated as 0.585 eV, matching with the PL peak position shown in Figure 4.4b. At lower temperature, the indirect bandgap transition dominated, but the direct bandgap transition contributed to the PL as well, resulting in broader peak linewidth than that of sample A. The detailed band structure calculation results are summarized in Table 4.4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔE$_{Γ}$ (meV)</th>
<th>ΔE$_{L}$ (meV)</th>
<th>ΔE$_{HH}$ (meV)</th>
<th>ΔE$_{LH}$ (meV)</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>177</td>
<td>11</td>
<td>49</td>
<td>17</td>
<td>0.639</td>
</tr>
<tr>
<td>B</td>
<td>284</td>
<td>10</td>
<td>80</td>
<td>34</td>
<td>0.583</td>
</tr>
</tbody>
</table>

Although for sample B the Γ valley minimum of GeSn well was below the L valley minimum of the SiGeSn barrier, the quantization effects make the ground-state at the Γ point of GeSn above the L valley minimum of the SiGeSn barrier, which reduced the electron confinement. To optimize the QW structure for the development of light emitters such as LED and laser, a direct bandgap GeSn well is desired, which can be achieved by incorporating more Sn (> 12%), as demonstrated in Ref. 31. The theoretical study indicated that with 12.5% Sn, the
ground-state at the Γ point could be lower than that of L valley minimum of GeSn well. Since the ternary SiGeSn alloy allows for separate tuning of bandgap energy and lattice constant, a wide bandgap barrier ~ 1 eV with target lattice constant can be obtained. In Chapter 7 (future work), the lattice constant that induces desired compressive strain of the GeSn well will be designed.

4.4 Photoluminescence study of SiGeSn/GeSn/SiGeSn quantum wells using different excitation lasers

In this section, the effect of different excitation lasers on the bandgap emission of the SiGeSn/GeSn QW structures is described. The PL emission of a semiconductor bandgap strongly depends on three parameters: 1) the energy of the excitation laser; 2) laser power density; and, 3) the length in which the laser can penetrate inside the semiconductor. The higher energy and power density of the excitation laser results in the generation of more carriers that eventually participate in the recombination process. Also, the more that the excitation laser penetrates inside the semiconductor, the higher number of carriers were generated. In this study, the effect of three different excitation lasers on the PL emission of SiGeSn/GeSn QW structures was explored. The previous 532 nm CW laser, employed to examine the optical characteristics of QW samples, was limited to the maximum power density of 15 kW/cm². It would be valuable from the physics aspect to use laser sources with higher power densities and scrutinize the QW emission under high power density excitation. The QW structures used in this study were exactly identical to samples A and B in the previous section of this chapter. The laser sources used in this analysis consisted of: 1) a 532 nm continuous wave diode-pumped semiconductor laser; 2) a 1064 nm pulsed laser with a pulse width of 5 ns and repetition rate of 45 kHz; and, 3) a 1550 nm continuous wave fiber laser. The standard off-axis PL setup was exploited to investigate the PL
emission in room temperature and low temperature. Based on the varied power densities and also different penetration depth of the lasers, distinctive PL emission characteristics were observed. Analysis of the PL emission at room temperature and low temperature indicated that the 1064 nm pulsed laser with high power density and large penetration depth increased the carrier concentration in the Ge buffer and cap layers and also SiGeSn layers. That phenomenon suppressed the emission from the GeSn QW region and the PL emission from Ge and SiGeSn were the dominate emissions while using the 1064 nm pulsed laser.

4.4.1 Excitation energy and penetration depth of the different laser sources

The excitation energy of the lasers and also their penetration depth inside the QW samples were different. The 532 nm laser had higher excitation energy ($E_{\text{exc}}=2.33$ eV) than 1064 nm laser ($E_{\text{exc}}=1.2$ eV), and both were higher than 1550 nm laser ($E_{\text{exc}}=0.8$ eV). Moreover, the penetration depths of the lasers were different in each layer of the QW structure due to the change in the layer absorption coefficients. In order to have a better understanding of the penetration depth of each laser employed in this study, the absorption coefficient of Ge, SiGeSn, and GeSn layers in sample A and B is provided. Simply, $1/(\text{absorption coefficient})$ was considered as a nominal penetration depth for lasers presented in Table 4.5.

<table>
<thead>
<tr>
<th></th>
<th>Sample A</th>
<th>Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ge</td>
<td>Si$<em>{0.07}$Ge$</em>{0.88}$Sn$_{0.05}$</td>
</tr>
<tr>
<td>532 nm</td>
<td>38</td>
<td>18</td>
</tr>
<tr>
<td>1064 nm</td>
<td>1006</td>
<td>480</td>
</tr>
<tr>
<td>1550 nm</td>
<td>7758</td>
<td>965</td>
</tr>
</tbody>
</table>
As indicated in Table 4.5, the penetration depth of 532 nm laser in the layers of QW structures was less than 50 nm, however, for 1064 nm and 1550 nm lasers, the penetration depths were almost more than 500 nm indicating that both lasers could excite the Ge buffer layer. Thus, the bandgap emission from Ge buffer layer influenced on the overall emission of the QW structure. Figure 4.5 illustrates the excitation energy (a) and estimated penetration depths (b) of 532 nm, 1064 nm, and 1550 nm lasers.

![Figure 4.5](image)

Figure 4.5. (a) Illustration of excitation energy of the three lasers used to study the emission of the QW samples. (b) Estimated penetration depth of the three lasers inside the QW structures. None of the diagrams are to scale.

As shown in the Figure 4.5a, the 532 nm and 1064 nm lasers were able to excite the carriers higher than the Γ valley and L valley minimum of all layers. Lower excitation energy of the 1550 nm laser reduced the carrier densities in the QW structures. On the other hand, both 1064 nm and 1550 nm lasers penetrated all the way down to the Ge buffer layer that eventually enhanced the carrier density available for the recombination process due to the high thickness of...
the Ge buffer layer. Overall, the 1064 nm laser was able to provide the highest carrier concentration due to its high penetration depth and relatively high excitation energy.

4.4.2 Experimental procedure

To investigate the effect of each laser on the optical emission of QW structures, the PL spectra of samples A and B were examined under different excitation lasers using the standard off axis PL setup. The grown SiGeSn/GeSn QW samples, labeled as samples A and B in the previous section, were mounted inside the closed cycle cryostat of the PL setup. The configuration of the PL setup was similar to the one explained in Chapter 2. Integration of three different laser sources in the PL system is one of the most unique capabilities of the home-built PL setup. Samples A and B were optically excited using excitation lasers CW 532 nm, pulsed 1064 nm, and CW 1550 nm and the PL spectra of each sample were measured at 10 K and 300 K. The repetition rate of the 1064 nm pulsed laser was 45 kHz and the pulse width was 6 ns. To avoid penetration of the laser sources inside the spectrometer, specific longpass filters were placed in front of the spectrometer entrance slit. The PL emission of sample A and B under different excitation power densities was desired. Therefore, the laser powers were adjusted to different values for that purpose.

Table 4.6 presents the power density information of three different excitation lasers used in this study. As indicated in Table 4.6, the power density of the 1550 nm CW laser was almost ten times higher than the one for the 532 nm CW laser. The peak power density of the pulsed laser was one order of magnitude higher than that of 1550 nm and two orders of magnitude higher than that of 532 nm laser. Furthermore, the number of incident photons per second per unit area could be calculated for each laser based on their power densities and wavelengths.
Calculation of the incident photon numbers could be beneficial to understand the generated carrier density in the QW samples.

Table 4.6. The summarized information of the average power, power densities and the number of incident photons on the samples generated by lasers.

<table>
<thead>
<tr>
<th>Excitation laser</th>
<th>Average power (W)</th>
<th>Average power density (kW/cm²)</th>
<th>Peak power density (kW/cm²)</th>
<th>Energy per pulse (J/cm²)</th>
<th>Number of incident photons (cm²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>532 nm CW</td>
<td>0.65</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>4 × 10¹⁹</td>
</tr>
<tr>
<td>1064 nm pulsed</td>
<td>0.2</td>
<td>-</td>
<td>2.7×10⁴</td>
<td>0.13</td>
<td>3 × 10²²</td>
</tr>
<tr>
<td>1550 nm CW</td>
<td>0.7</td>
<td>160</td>
<td>-</td>
<td>-</td>
<td>2 × 10³¹</td>
</tr>
</tbody>
</table>

The number of photons per unit area (cm²) per unit time (s) for the CW lasers was obtained based on the following equation:

$$n = \frac{E\lambda}{hc} = \frac{Pt\lambda}{hc}$$  \hspace{1cm} (Equation 4.14)

where $E$ is photon energy in the unit of Joule, $P$ is the power density, $n$ is the number of photons, $h$ is the Planck constant, $C$ is the light speed, and $\lambda$ is the wavelength of the laser excitation source.

For the pulsed 1064 nm laser, the calculation was different. In the pulsed laser, the energy of each pulse per unit area was calculated using the subsequent equation:

$$E_{pulse} = \frac{P_{avg}}{(R)(Area)}$$  \hspace{1cm} (Equation 4.15)

where $P_{avg}$ is the laser average power and $R$ is the repetition rate of the pulsed laser. Applying the above equation to Equation 4.14 gave the number of photons per unit area per pulse. The
total number of photons per unit area per unit time was achieved by multiplying the above value by the repetition rate (45 kHz). The calculation results are summarized in Table 4.6.

4.4.3 Results of PL measurements on SiGeSn/GeSn QW samples using different excitation lasers

After adjusting the laser powers based on Table 4.6, the laser beam was delivered to the QW samples and the PL spectra were collected at 10 K and 300 K for sample A and B, respectively. The PL peak positions were extracted to analyze the transitions due to the excitation of carriers. Figure 4.6a and 4.6b show the PL spectra of sample A at 10 K and 300 K, and Figure 4.6c and 4.6d indicate the PL spectra of sample B at 10 K and 300 K. The achieved PL spectra from 532 nm, 1064 nm, and 1550 nm lasers are shown in black, red, and blue colors, respectively. All observed peaks in each plot were labeled as numbers in order to clearly identify the peak and describe the related transition. In Figure 4.6a, the PL emissions of sample A at 10 K is presented. Peaks No. (1) and (2) at 1475 nm and 1688 nm were related to the direct and indirect bandgap transition of Ge buffer layer and cap layer. Two possibilities exist for the transition source of peak No. (3) at 1768 nm; first, it might have been related to the indirect bandgap emission of the SiGeSn barriers. It could also be assigned to the n2L-n2HH transition of the GeSn QW. Further evidence in the next section reveals that peak No. (3) was related to the SiGeSn bandgap emission. This emission was fairly identical to the PL emission of a SiGeSn film with the same thickness and compositions of the barriers layer. The PL results of the SiGeSn films with three different excitation lasers at 10 K and 300 K will be discussed later.

Peaks No. (4) and (5) had almost the same positions at 1947 nm which were attributed to the n1L-n1HH transition of the GeSn QW. It is important to notice that for the pulsed laser, the n1L-n1HH transition in the GeSn QW was not dominant. This phenomenon was related to the
high population of the carriers distributed in Ge and SiGeSn layers. High carrier concentrations in the Ge and SiGeSn layers suppressed the emission from GeSn QW due to the loss mechanisms.

Figure 4.6. The PL spectra of sample A at 10 K (a) and 300 K (b) using 532 nm CW laser, 1064 nm pulsed laser and 1550 nm CW laser with different power densities. The PL spectra of sample B at 10 K (c) and 300 K (d) using the same lasers with the same power densities are also presented.
In Figure 4.6a, the PL peak No. (6) and (7) at 2510 nm and 2638 nm were the defect-related emissions. Such an emission from defects has been observed in low temperature PL study of GeSn QWs [146]. Figure 4.6b shows the PL emission of sample A at 300 K. Peak No. (1) and (2) at 1569 nm were related to the direct bandgap transition of Ge buffer layer and cap layer. Peak No. (3) and (4) at 1795 nm were related to the indirect bandgap transition of Ge buffer layer and cap layer. Peak No. (5) and (6) at 1930 nm were related to the n1Γ-n1HH transition. Similar to Figure 4.6a, the PL emission from direct bandgap of Ge was stronger than the PL emission of GeSn QW once the 1064 nm pulsed laser was used. Similarly, it was related to the high carrier density in the Ge and SiGeSn layer that dominated the PL emission.

Figure 4.6c represents the PL emission of sample B at 10 K. Similar to Figure 4.6a, the PL peak No. (1) and (2) were related to the direct and indirect PL emission from Ge buffer and cap layers. Similar to Figure 4.6a, the PL peaks (3), (4), and (5) were related to the indirect bandgap emission of SiGeSn layers. The reason for multiple PL peaks was related to the variation of thickness and also Si and Sn compositions in the barriers. Peaks (6) and (7) were assigned to the n1L-n1HH indirect transition inside the GeSn QW layer. PL peaks (8) to (11) were attributed to the defect-related emissions at low temperatures.

Figure 4.6d depicts the room temperature PL emission spectra from sample B. The peak No. (1) and (2) was related to the direct and indirect bandgap transition of Ge layers. Peak No. (3) was referred to the indirect bandgap emission of the SiGeSn layers. Thus, using 1064 nm pulsed laser led to no GeSn emission at 300 K for sample B. Peaks No. (4) and (5) were related to the n1Γ-n1HH direct transition of GeSn QW. As noticed in the PL measurements of the GeSn QW structures using different excitation lasers, the PL spectra of samples excited with 532 nm and 1550 nm lasers were more similar compared to the one for 1064 nm pulsed laser due to the
difference in the power density and excitation energy. To further understand the effect of the PL emission from SiGeSn barrier layer, the following study was conducted.

4.4.4 PL study of the SiGeSn films identical to the barriers used in SiGeSn/GeSn/SiGeSn QW structure

As discussed in the previous section, in the PL measurements of the SiGeSn/GeSn/SiGeSn samples, several peaks were observed whose transition should be carefully analyzed. The peak No. (3) in Figure 4.6a and peaks No. (3), (4), and (5) in Figure 4.6c were strong PL emissions. The source of those emissions was ascribed to the indirect bandgap emission of SiGeSn barrier layers. To confirm that assumption, it was required to perform PL measurements on the separate SiGeSn films which had the same thickness and compositions as the barrier layers in the QW structures. Direct comparison between the PL of QW and SiGeSn films revealed the sources of questionable peaks observed in the PL spectra of the QW samples.

To achieve that goal, 50 nm Si$_{0.07}$Ge$_{0.88}$Sn$_{0.05}$ and Si$_{0.12}$Ge$_{0.79}$Sn$_{0.09}$ films were grown on top of Ge buffer layer on the Si (100) substrate using SiH$_4$, GeH$_4$, and SnCl$_4$ precursor gases inside the commercially available ASM reduced-pressure CVD system. The growth information and material characterization of Si$_{0.07}$Ge$_{0.88}$Sn$_{0.05}$ and Si$_{0.12}$Ge$_{0.79}$Sn$_{0.09}$ films are described in Ref. 108. Material characterization of Si$_{0.07}$Ge$_{0.88}$Sn$_{0.05}$ and Si$_{0.12}$Ge$_{0.79}$Sn$_{0.09}$ films, labeled as sample C and D, indicated that the Si and Sn composition and also their thicknesses were fairly close to the SiGeSn barriers in sample A and B. Thus, they could be considered as a viable basis to study the optical properties of SiGeSn barriers.

Similar to the PL measurements performed on samples A and B, the PL spectra of samples C and D were measured at 10 K and 300 K using the standard off-axis PL setup. Three excitation laser sources were used to study the PL emission from the bandgap of SiGeSn films.
The results of the PL measurements with different lasers on sample C and D are presented in Figure 4.7 to 4.9 and directly compared with the results obtained from sample A and B, respectively.

The PL spectra in Figure 4.7 were achieved using 532 nm CW laser. The black lines represent the PL spectra of samples A and B and the red lines specify samples C and D. In Figure 4.7a, PL emissions from sample A and C at 10 K using 532 nm laser is provided. Peaks labeled as (a1) and (a2) are the PL emissions from Ge buffer beneath the SiGeSn. Since the thickness of SiGeSn layer in sample C was only ~ 50 nm, the dominate emission would be from Ge buffer in sample C. The peak No. (a3) corresponded to the peak (4) in Figure 4.6a. This peak was related to n1L-n1HH indirect transition.

In Figure 4.7b at 300 K, peaks (a1) and (a2) were related to the direct transition and (a3) and (a4) referred to the indirect transition of Ge buffer layer in both samples A and C. Peak (a5) was the emission of indirect transition in SiGeSn layer in sample C and peak (a6) was related to the direct transition in sample A. Similar Ge PL peak emissions, labeled as peaks (a1) and (a2) were observed at 10 K for sample D in Figure 4.7c. Peak (a3) was related to the SiGeSn indirect bandgap emission at 10 K. Peak (a4) was equivalent to peak (6) in Figure 4.7c, related to the indirect transition in the GeSn QW of sample B. The defect-related emission is shown as peak (a5). Figure 4.7d consists of two peaks, labeled as (a1) and (a2), indicating the PL emission from SiGeSn of sample D (indirect transition) and GeSn QW of sample B (direct transition), respectively. As indicated in this figure, the PL peak emission of the GeSn QW occurred in longer wavelengths compared to the PL peak emission of SiGeSn film. It confirmed that the previous results achieved in section 4.4.3 was valid.
In Figure 4.8, the comparison between the PL measurement spectra of samples A and C and also B and D at 10 K and 300 K using 1064 nm pulsed laser, is provided. Due to the high power density of the 1064 nm pulsed laser, the PL emission from the direct and indirect bandgap of Ge buffer dominated the spectra.
Figure 4.8. The comparison between the PL spectra of samples A and C at 10 K (a) and 300 K (b) and the PL spectra of samples B and D at 10 K (c) and 300 K (d) using 1064 nm pulsed laser.

The PL emissions from the SiGeSn samples and also the GeSn QWs were suppressed by the Ge bandgap emission. Peaks (a1) and (a2) in Figures 4.8a to 4.8d, shows the direct bandgap emission from Ge buffer layers. In Figure 4.8a, peaks (a3) and (a4) were related to the SiGeSn emission at 10 K for samples A and C. The Ge indirect bandgap emissions at room temperature
for sample A and C are presented as peaks (a3) and (a4) in Figure 4.8b. Peak (a5) in the same figure was related to the n1Γ-n1HH in the GeSn QW of sample A.

In Figures 4.8c and 4.8d, the direct bandgap emission of Ge buffer in sample B and D are labeled as (a1) and (a2) and the direct emission from Ge is labeled as (a3). Peaks (a4) and (a5) in Figure 4.8c and (a4) and (a5) in Figure 4.8d were assigned to the SiGeSn indirect bandgap emissions.

Finally, Figure 4.9 was the PL measurement results using 1550 nm CW laser 10 K and 300 K on the samples A and C and also B and D, respectively. The long tail at the left side of the plots was related to the 1550 nm laser line (similar to Figure 4.6). In Figure 4.9a, the peaks (a1) and (a2) were related to the indirect transition in Ge layer. The direct transition peak was overlapped by the strong 1550 nm laser line and cannot be seen. Peak (a3) was the SiGeSn transition, and the main peak (a4) was related to the n1L-n1HH of the GeSn QW in sample A. The defect-related emissions are shown in peaks (a5) and (a6). In Figure 4.9b, the (a1) peak was related to the indirect bandgap emission from Ge and (a2) was assigned to indirect bandgap emission of SiGeSn in sample C. The direct transition in GeSn QW in sample A was labeled as (a3). Similar to Figure 4.9a, the Ge indirect transition was labeled as (a1). The GeSn QW PL emission at 2100 nm was related to indirect n1L-n1HH transition specified as (a2). The (a3) and (a4) were related to the defects in the samples. In Figure 4.9d, the (a1) peak shows PL emission of SiGeSn sample and (a2) referred to the direct transition n1Γ-n1HH of the GeSn QW in sample B. Since the Sn composition of the GeSn QW in sample B was higher than that of sample A, the n1Γ-n1HH transition was stronger in sample B. To further understand the mechanism of carrier generation and recombination in the bandgap of GeSn QW structure, in-depth analysis on the radiative and nonradiative recombination is required.
In summary, SiGeSn/GeSn/SiGeSn QW structures were grown using an industry standard chemical vapor deposition technique. The commercially available low-cost SiH₄, GeH₄, and SnCl₄ were used as precursors. Temperature-dependent PL spectra show that the direct transition peak dominated the PL at temperatures above 200 K while below 100 K the indirect}

77
transition peak dominated. The emission at room temperature was in the technologically important 2 μm wavelength band. The electronic band structure calculation indicated that both samples featured Type-I band alignment. The PL emission was assigned to the transition between the ground-state at the Γ point in CB and the ground-state in the HH band in VB. Due to quantization, the ground-state at the Γ point of GeSn well sat above the L valley of the SiGeSn barriers. In order to improve the electron confinement, a GeSn well with higher Sn composition (> 12%) was proposed, which not only gave a direct bandgap material but also provided a ground-state at the Γ point that could be lower than the L valley minimum. Consequently, the direct bandgap emission was dramatically enhanced.

Moreover, the effects of high power density and different excitation wavelengths on the SiGeSn/GeSn QW structures were studied. The excitation source with high power density and penetration depth and large excitation energy was able to penetrate more in the sample. As a result, carrier density increased dramatically, however, recombination of carriers in the thick Ge buffer layer dominated the overall PL emission and the QW bandgap emission was almost disappeared. Optimization of the GeSn QW structure is in progress and the direct bandgap GeSn QW design, capable of emitting high-intensity emission from the GeSn well region, will be discussed in Chapter 7 as a part of the future work.
Chapter 5. Electroluminescence (EL) study of n-i-p GeSn double heterostructures

5.1 Motivation

Photonic devices operating in the short-wave- and mid-infrared (IR) range (1.5~20 μm) are very useful for diverse fields including chemical and biomedical sensing, gas sensing, military activities and industrial process applications [147], [148]. For instance, characteristic absorption fingerprints of most molecules are identified in the 2.0~10 μm wavelength range, such as water vapor, nitrogen-containing molecules, and hydrocarbon molecules, etc. [149]. Among the many optoelectronics devices, mid-IR light emitting diodes (LEDs) with high power are prospective sources for developing the sensing system. Although III-V based LEDs such as InGaAs, GaSb, InAs, etc. feature mid-IR operation and relatively high efficiency [150], [151], their high cost and incompatibility with current complementary metal–oxide–semiconductor (CMOS) processes exclude them from being widely used in Si photonics, particularly for on-chip integration applications, which play an important role in the emerging field of on-chip biological and chemical sensing [152]. On the other hand, the integratable group-IV based semiconductors Si, Ge, and their alloys suffer from low efficiency due to their indirect bandgap nature, therefore they are not an ideal candidate for light sources.

Recently, studies on group-IV semiconductor GeSn alloys has opened a new window for the development of Si-based optoelectronics active devices [153] . Since a direct bandgap GeSn has been experimentally identified and an optically pumped GeSn-based laser has been demonstrated, the GeSn based light emitter as the low-cost Si-based light source is expected to be efficient, together with all necessary components for mid-IR sensing available on a Si platform. Additionally, by varying the Sn composition in the GeSn alloy, the operating wavelength of GeSn based LED could cover a broad short-wave and mid-IR range, making it
more universal in sensing applications. Investigation of electroluminescence (EL) from GeSn active layers has been conducted by several research groups based on the GeSn double-heterostructure (DHS). A few reports presented GeSn multi-quantum well LEDs with Ge barriers and high EL intensity at low temperatures; however, based on their analysis, the carriers were confined at the Ge barrier due to the lack of Type-I band alignment. The GeSn DHS investigated in this study featured higher density of states in comparison with the GeSn multi-quantum well. Thus, the population of electron-hole in the active region of DHS increased leading to higher intensity EL emissions of the GeSn DHS LED. In this study, a Ge/Ge\textsubscript{0.92}Sn\textsubscript{0.08}/Ge n-i-p DHS surface-emitting and edge-emitting LEDs were demonstrated. Material characterization was done on the Ge/Ge\textsubscript{0.92}Sn\textsubscript{0.08}/Ge n-i-p DHS to investigate the quality of the Ge and GeSn crystalline layers. Optical quality and bandgap energy of the sample was explored using temperature-dependent PL measurements from 77 K to 300 K and supported by theoretical analysis. Once the Ge/Ge\textsubscript{0.92}Sn\textsubscript{0.08}/Ge n-i-p DHS was fabricated into a surface emitting and edge emitting LEDs, the current-voltage characteristic of the devices was studied in different temperature. Finally, the temperature-dependent electroluminescence (EL) spectra of the Ge/Ge\textsubscript{0.92}Sn\textsubscript{0.08}/Ge n-i-p DHS LED device were obtained and analyzed.

5.2 Material Growth and characterization of Ge/Ge\textsubscript{0.92}Sn\textsubscript{0.08}/Ge n-i-p DHS

The GeSn DHS samples were grown using an ASM Epsilon® 2000-Plus reduced pressure chemical vapor deposition (RPCVD) system. The complete layer sequence included: 1) a 700 nm thick p-type doped Ge buffer layer; 2) a 200 nm thick unintentionally doped Ge\textsubscript{0.92}Sn\textsubscript{0.08} active layer; and, 3) a 50-nm thick n-type doped Ge cap layer. The doping concentrations of p- and n-type were measured as $5 \times 10^{18}$ and $1 \times 10^{19}$ cm\textsuperscript{-3}, respectively [153]. The growth temperature was kept below 400 °C to ensure that it is compatible with the Si CMOS process. The detailed
growth method was reported in a prior study of this research group [75]. The thickness of each layer, material quality, and strain information of the GeSn layer were analyzed by TEM and high-resolution XRD techniques. The TEM results in Figure 5.1a indicated that most of the dislocation densities were trapped at the interface of the Ge/Si and GeSn/Ge interfaces. The GeSn layer itself and the Ge cap had low defect density (~10^7 cm^-2). The thickness of the layers measured with TEM agreed well with the initial structure design. The RSM plot of the Ge/Ge_{0.92}Sn_{0.08}/Ge n-i-p DHS and the XRD 2θ-ω scan are shown in Figure 5.1b. The RSM showed that the p-type Ge buffer was partially relaxed. The i-GeSn active layer was compressively strained and the n-type Ge cap layer was a tensile-strained layer due to the lattice mismatch with the GeSn layer.

Figure 5.1 (a) TEM image of the Ge/Ge_{0.92}Sn_{0.08}/Ge nip DHS sample shows thicknesses and the quality of epilayers. (b) The RSM plot from \( \{224\} \) plane of each layer. The GeSn layer was partially relaxed. The 2θ-ω XRD scan is presented in the inset.

Information of the sample after the material characterization is provided in the Table. 5.1. As indicated in Table 5.1, the GeSn active layer had 6.44% Sn composition which was different from the target value (8%) due to unoptimized growth condition. The p-type Ge buffer layer was relaxed and the n-type Ge cap layer had 0.58% compressive strain in the lattice structure. The density of threading dislocation of the GeSn active layer was \( \sim 10^7 \) cm^-2.
Table 5.1. Summary of material characterization of GeSn n-i-p structure.

<table>
<thead>
<tr>
<th></th>
<th>Measured Sn (%) by XRD</th>
<th>p-type Ge strain (in-plane)</th>
<th>GeSn layer strain (in-plane)</th>
<th>n-type Ge strain (in-plane)</th>
<th>Density of threading dislocations (cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.44%</td>
<td>Relaxed</td>
<td>-0.43%</td>
<td>0.58%</td>
<td>3.91×10(^7)</td>
</tr>
</tbody>
</table>

5.3 Optical characterization of Ge/Ge\(_{0.92}\)Sn\(_{0.08}\)/Ge n-i-p DHS

To investigate the optical quality and the bandgap energy of the GeSn DHS, temperature-dependent PL measurements were conducted. The sample was mounted inside a liquid nitrogen cooled cryostat, and the temperature was changed from 77 K to 300 K. The standard off-axis configuration PL setup was utilized along with a lock-in system and optical chopper with 377 Hz frequency. A 532 nm CW laser was utilized to excite the GeSn n-i-p DHS. The PL emission of the samples was collected using a CaF\(_2\) lens and delivered to the spectrometer with an optimized grating (blazes at 2 µm) and a thermo-electric cooled PbS detector with a cut-off at 3 µm.

Detailed explanation of the off-axis PL setup was given in Chapter 2. Figure 5.2a shows the PL spectra of the Ge/Ge\(_{0.92}\)Sn\(_{0.08}\)/Ge n-i-p DHS from 77 K to 300 K. The red-shift noticed for the PL spectra when temperature increased were related to the dependency of the bandgap to the temperature based on Varshni’s relation:

\[
E (T) = E (0) - \alpha T^2 / (T + \beta)
\]

(Equation 5.1)

where E (0) is the bandgap energy at 0 K, and \(\alpha\) and \(\beta\) are the thermal coefficient parameters which are related to the material thermal expansion. It was also noticed that the PL intensity decreased when temperature reduced. This fact was related to the indirect nature of Ge\(_{0.92}\)Sn\(_{0.08}\) bandgap owing a significant amount of compressive strain. The 0.43% compressive strain in the
Ge$_{0.92}$Sn$_{0.08}$ DHS sample maintained the L valley of the conduction band slightly lower than the gamma valley. That small energy difference at room temperature led to the occupation of Γ valley with thermally generated carriers and eventually the transition from Γ valley to the valence band dominates the PL emission at room temperature. Thus, the intensity of PL spectrum was higher at 300 K. Once temperature decreased; carriers did not have sufficient energy to occupy the Γ valley, and they were limited to stay in L valley. The recombination of carriers from L valley to the valence band required phonon or other centers to perform indirect bandgap transition. However, those centers were almost inactive at lower temperatures. Therefore, radiative recombination rate reduced and resulted in the reduction of PL intensity. Due to the small energy difference between the Γ and L valley, it was impossible to observe two separate peaks for the direct and indirect transitions. Broadened PL spectra line-width was attributed to the overlapping of the direct and indirect transitions.

![PL Spectra](image.png)

Figure 5.2. (a) Temperature-dependent PL spectra of Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS sample. (b) Power-dependent PL measurements at 300 K. [132].
To further investigate the optical properties of the Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS, a power-dependent PL measurement was performed on the sample at 300 K (Figure 5.2b). The intensity of the PL spectrum increased by increasing the power of the laser from 60 mW to 440 mW. Direct bandgap transition dominated the PL spectra once power was increased. Increasing the power density builds up the carrier population in the Γ valley and, eventually higher PL intensity was achieved. This fact is related to the band filling of the energy levels at L valley and consequently, an increase in the number of carriers in the Γ valley. The band filling effect and thermally excited carriers increased the Γ valley carrier population and led to the dominant direct bandgap transition. The blue shift noticed in the PL spectra by increasing the pumping power was the result of Γ valley to valence band transition.

To better understand the bandgap characteristics of the Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS, the band structure of the sample was theoretically calculated. The deformation potential model and the quadratic Vegard’s law with bowing parameter was applied to calculate the bandgap energies of each layer and also the barrier heights between the Ge-buffer/GeSn and GeSn/Ge cap layers. The energy band offset was identified based on a technique discussed in Chapter 4. The band alignment of the Ge$_{0.92}$Sn$_{0.08}$ DHS is presented in Figure 5.3. $E_{g\Gamma}$ and $E_{gL}$ are the direct and indirect bandgap energies of the conduction band in each layer, respectively. The difference between the $E_{g\Gamma}$ and $E_{gL}$ is noted as $\Delta E_g$ (≈20 meV). The barrier height at the Γ and L valleys of the conduction band are represented as $\Delta E_c^{\Gamma}$ and $\Delta E_c^{L}$. To calculate these four fundamental energy levels (i.e. Γ, L, HH, and LH) the strain information and Sn composition of GeSn layer were utilized. The change in the Γ and L valley energy level was directly related to the Sn incorporation in the GeSn layer. Also, the separation of the HH and LH energy levels was attributed to the strain in the films.
Figure 5.3. Band alignment of the GeSn together with the p-Ge buffer and n-Ge cap.

As shown in Figure 5.3, the difference between the HH and LH in the Ge buffer layer was negligible since the Ge buffer was partially relaxed. However, the GeSn layer had a 0.43% compressive strain in the lattice resulting in the HH-LH splitting. The HH effective mass was lower than the LH effective mass due to the compressive strain in the GeSn lattice structure; so the HH energy level was closer to the conduction band and, therefore, the dominant transition was $\Gamma$ to HH for higher temperatures and L to HH for lower temperature bandgap emissions. The $\Gamma$ valley barrier height between the Ge buffer and GeSn layer was $\Delta E_c^{\Gamma} \simeq 120$ meV and the L valley barrier height between the Ge buffer, and GeSn layer was $\Delta E_c^{L} \simeq 18$ meV. It should be noted that the Ge cap layer had 0.58% tensile strain; therefore, the LH energy level stayed higher than that of HH in Ge cap layer. The tensile strain in the Ge cap layer reduced the barrier height between the GeSn and Ge cap layers. The $\Gamma$ valley and L valley barrier heights between the GeSn and Ge cap layer was reduced to $\Delta E_c^{\Gamma} \simeq 68$ meV and $\Delta E_c^{L} \simeq 16$ meV, respectively.
Overall, Type-I band alignment was achieved increasing the carrier confinement within the GeSn active layer. The GeSn in the Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS was an indirect bandgap material; however, the dominant transition at room temperature was the $\Gamma$ valley to HH transition. Achieving the Type-I band alignment was one of the advantages in the designed structure. Fundamental transitions happened within the GeSn active layer. The energy difference between the $\Gamma$ valley and the HH was equal to $E_{\GammaHH} = 0.61$ eV (2040 nm) which matched well with the PL peak position at 300 K. The transition from L valley to the HH was equivalent to $E_{LHH} = 0.57$ eV (2180 nm) and it was not clearly obvious in the PL spectrum since the direct bandgap transition ($\Gamma$ to HH) dominated. Although the current barrier height provided enough confinement for the carriers to maintain inside the GeSn layer, better design on the GeSn DHS would improve the confinement and also provide direct bandgap GeSn DHS which is suitable for high efficient LED applications.

5.4 The Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS surface emitting diodes

5.4.1 Fabrication of Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS surface emitting diodes

The Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS was fabricated into a circular mesa LED with 100 µm diameter. Standard photolithography technique, dry etching including reactive ion etching (RIE), and chemical etching were applied to etch the mesa. The gases used in the RIE was 30 sccm tetrafluoromethane (CF$_4$) and 30 sccm Ar. The RIE etching rate was 30 nm/min and depended on Sn composition of the sample. It was noticed that higher Sn composition lowered the etching rate. In contrary, the wet chemical etching exhibited a constant etching rate of 100 nm/min and was Sn composition independent. The chemical etching ratio of the HCl, H$_2$O$_2$, and H$_2$O was 1:1:20, respectively, at room temperature. The plasma enhanced CVD (PECVD) was used to
deposit a 100 nm layer of SiO$_2$ on the device. Once the oxide deposition was done, the windows for metal contacts were prepared by a negative photolithography. Before the metal deposition, the oxide of the windows was removed using wet chemical etching and buffered oxide etch (BOE) with the ratio of BOE: H$_2$O = 5:1. Metal deposition for the p- and n-contacts included 10 nm Cr and 200 nm Au. After the metal deposition and lift-off, the metal contacts were completed. A schematic diagram of the fabricated GeSn DHS surface emitting LED and its optical image top view are shown in Figure 5.4. Large metal contact is favorable for the temperature-dependent measurements in a coplanar scheme.

![Schematic diagram and optical image of GeSn LED device](image)

Figure 5.4. (a) Schematic cross-sectional view of the GeSn LED device. (b) The optical image of the device with 100 µm diameter [154].

5.4.2 Electrical characterization of Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS surface emitting diodes

In order to characterize the electric performance of the fabricated LED, the current-voltage (I-V) characteristic was measured at various temperatures from 80 K to 300 K. The direct current Keithley 236 [113] was employed for I-V measurements. The fabricated GeSn
LED sample was first examined at room temperature to make sure that it had reasonable I-V and EL characteristics. Using the probe station on the EL setup, the I-V and EL results were obtained and confirmed the decent device performance at room temperature. Subsequently, the device was mounted inside the liquid helium cooled cryostat with feedthrough accessories. Since the electric current was required to flow to the device through the metal contacts, gold-coated needles with very tiny tip were precisely placed on the p- and n-contacts of the LED (coplanar scheme). Once the circuit was completed, the I-V characteristic was plotted on the Lab View based software prepared to record the current versus voltage. The rectifying behavior of the diode was observed at all temperatures tested from 80 K to 350 K as shown in Figure 5.5. The decreased slope of I-V characteristics when temperature declined was related to the less thermally activated carriers in the device. This fact led to the increase of the device dynamic resistance once temperature decreased. The dynamic resistance increased from 67 Ω to 218 Ω when temperature reduced from 350 K to 80 K.

![Figure 5.5. The I-V characteristic of the GeSn DHS surface emitting diode.](image-url)
It was important to explore the reason of dark current noticed in the measurement. The dark current was basically related to two parameters: 1) the bulk leakage current that had an exact relation with the area of the device; and, 2) the surface leakage current which was proportional to the periphery of the device. The following explanation reveals the reasons of the generated dark current in the device. (1) The lack of sufficient passivation on the surface and sidewalls of the device increased the peripheral surface leakage current. Decent passivation of the GeSn DHS device reduced the dark current. Recently, a report showed that the performance of the Ge<sub>0.95</sub>Sn<sub>0.05</sub> photodiode device was improved due to the device passivation [155]. (2) Once Sn composition increased in the GeSn, the electronic bandgap shrunk, therefore, more thermally activated carriers contributed to the dark current. (3) More defect densities at the interfaces of the layers, due to the lattice mismatch between Ge and GeSn, produced a leakage current which eventually enhanced the dark current of the device. Optimized design to reduce the number of defects in the structure led to the reduction of dark current and improved the performance of the device.

5.4.3 Optical characterization of Ge/Ge<sub>0.92</sub>Sn<sub>0.08</sub>/Ge n-i-p DHS surface emitting diodes

To investigate the emission of the Ge/Ge<sub>0.92</sub>Sn<sub>0.08</sub>/Ge n-i-p DHS surface emitting diode versus various temperatures, the temperature-dependent electroluminescence (EL) measurement was performed in a fixed current injection density of 6.4 kA/cm<sup>2</sup> (corresponding to 0.5 A of current) to make sure that the device could repeatedly perform without any fluctuation and burning issue. The EL measurements were done at several temperatures from 80 K to 300 K. To obtain the EL spectra, the home-built EL setup explained in Chapter 2 was utilized. The sample was mounted inside the feedthrough-equipped cryostat cooled with liquid nitrogen. The gold-
coated needle tips were placed on the p- and n-contact, and it was ensured that the tip would not move on the metal contact once temperature changed. To reach that purpose, a precise configuration of needle holder including springs and ball bearing provided by Janis company [114] was used. A pulsed current source with a pulse width of 250 µs and the duty cycle of 10% was exploited to achieve the EL emission from the GeSn LED. The 10% duty cycle reduced the effect of Joule heating and prevented device burning. The emitted EL spectrum from the LED was collected using a CaF$_2$ lens and eventually delivered to the microHR spectrometer equipped with a PbS detector with a cut off at 3 µm. The lock-in amplifier and a chopper system with a frequency of 377 Hz (this frequency was selected as a trade-off of detector response frequency and the measurement time) were employed to increase the signal to noise ration of the EL spectra. Once an EL measurement was finished at a desired temperature, the temperature was switched to the new value and then waited for 30 mins to make sure that the device temperature was stabilized. The temperature-dependent EL spectra of the Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS surface emitting diode is presented in Figure 5.6.

![EL spectra of GeSn DHS LED](image)

Figure 5.6. The temperature-dependent EL spectra of the GeSn DHS LED under the injected current density of 6.4 kA/cm$^2$. 

90
The EL peak position was changed from 0.616 eV to 0.606 eV once temperature was increased from 150 K to 300 K. Below 150 K, almost no EL signal was detected. The reduction of EL intensity is clearly indicated in the plot. This phenomenon had the same reason as the PL intensity reduction discussed in the previous section. At higher temperature, thermally generated carriers occupied the $\Gamma$ valley and the direct band-to-band transition dominated the EL emission. Once temperature decreased, the low-intensity indirect bandgap transition dominated and most of the carriers participated in non-radiative (such as Shockley-Read-Hall) recombination.

Moreover, no emission from the Ge layer was detected, indicating the superior carrier confinement in the Ge$_{0.92}$Sn$_{0.08}$ layer due to the DHS. The lock-in amplifier and a chopper at a frequency of 377 Hz averaged the signal over a complete pulse on-and-off cycle (0.2 ms). The selected low duty cycle (10%), and the fact that only the first harmonic was extracted by a lock-in amplifier, resulted in a relatively low signal-to-noise ratio. This could be realized in the non-smooth EL spectra of different temperatures.

5.5 The Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS edge emitting diodes

The realization of edge emitting GeSn LED can be considered as an initial step for the construction of edge emitting electrically-pumped GeSn lasers. The goal of this study was to analyze the EL emission of the edge emitting Ge$_{0.92}$Sn$_{0.08}$ DHS LED, to realize the experimental challenges of the edge emitting devices, and to develop the characterization tools for the future GeSn-based edge emitting LEDs and lasers. The edge emitting Ge$_{0.92}$Sn$_{0.08}$ DHS LED was designed as a waveguide with side walls etched down to the p-Ge buffer. This configuration allowed the Ge$_{0.92}$Sn$_{0.08}$ active layer with refractive index of $n \approx 4.2$ to be confined within the
materials with lower refractive index (Ge layers (n=4) and air (n=1)). That architecture simultaneously provided electrical and optical confinements for the Ge$_{0.92}$Sn$_{0.08}$ active layer. The carriers and the generated light were intended to be confined within the Ge$_{0.92}$Sn$_{0.08}$ active layer. Also, the smooth facets of the Ge$_{0.92}$Sn$_{0.08}$ DHS waveguide acted as mirrors to reflect back the beam and theoretically led to a higher gain in the Ge$_{0.92}$Sn$_{0.08}$ medium. All mentioned parameters contribute to the higher emission efficiency of the edge emitting device. The fabrication process of Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS edge emitting diode was similar to the fabrication of surface emitting devices, except the different mask that was applied to provide the rectangular stripes with specified widths. Standard photolithography, dry and wet chemical etching were used to fabricate rectangular shape stripes of edge emitting Ge$_{0.92}$Sn$_{0.08}$ DHS LED with three different cavity widths including 40 µm, 80 µm, and 120 µm. Reactive ion etching (RIE) was used to etch the structure down to the p-Ge buffer and provide steep sidewalls for the waveguide. The sidewalls were passivated by SiO$_2$ to reduce the surface recombination. The schematic diagram of the edge emitting Ge$_{0.92}$Sn$_{0.08}$ DHS LED is shown in Figure 5.7.

![Schematic diagram of the edge emitting GeSn DHS LED](image)

**Figure 5.7.** (a) The schematic diagram of the GeSn DHS edge emitting LED with 80 µm stripe width. (b) Top view of the microscopic image of the fabricated edge emitting devices with three different stripe widths. The p-contacts had the same widths of 120 µm.
After fabrication, the device was analyzed under the microscope to make sure that there was no undesired feature on the top of the device. In order to have a smooth facet for the edge emitting device, a manual cleaving technique with a diamond scribe was employed. Naturally, the Si crystal orientation could be used to smoothly break the device and provide mirror-like facets. For that purpose, the sample thickness was reduced so that the cleaving process could be done without any unfavorable cracks. The Si substrate had a thickness of \( \sim 800 \, \mu\text{m} \) and could not break easily. A lapping technique was exploited to reduce the thickness of Si substrate so that the fabricated device could be simply cleaved. In the lapping process, the sample was mounted on a glass piece using wax. Then, 15 \( \mu\text{m} \) aluminum powder was used as an abrasive between the sample and the iron plate. By controlling the speed of the iron plate, the Si substrate was smoothly rubbed and its thickness was reduced to almost 80 \( \mu\text{m} \) which was sufficient to perform an uncluttered cleave and provide smooth waveguide facets. Consequently, the sample was cleaved to pieces with 400 \( \mu\text{m} \) and 1 mm strip length containing several devices with different stripe widths of 40 \( \mu\text{m} \), 80 \( \mu\text{m} \), and 120 \( \mu\text{m} \).

After fabrication of the device, the initial electric characterization was performed using I-V measurements on the probe station of the EL setup. The sharp tips of the needles were placed on top of the p- and n-contacts. After several measurements, it was noticed that the needle tip scratched the metal contacts and damaged the device as shown in Figure 5.8. As shown in the figure, the metal contacts were damaged either due to the scratches from the tip of the needles or the Joule heating generated due to the high carrier injection. Two areas related to the needle scratches and two burnt spots due to the heat effect are indicated in Figure 5.8. Those scratches and heated areas gradually degraded the device performance. To avoid any scratch and damage
of the edge emitting devices, different configurations compared to the surface emitting devices were applied.

Figure 5.8. Scratches due to the needles tip and burnt spots that appeared once injected current went beyond 0.5 A.

As shown in Figure 5.9, a proper approach taking advantage of wire-bonding capability was designed to introduce the current to the device and perform the electrical and optical characterizations. A 5 mm x 5 mm Si chip with four gold pads was prepared in the clean room using a metal deposition technique. The purpose of preparing the Si chip with gold pads was to bond the edge emitting device to a stable chip. That design enabled handling the device for further characterization, especially inside the cryostat for temperature-dependent I-V and EL measurements. After attaching the device to the Si chip with silver paste (which provided better thermal conductance and device stability compared to thermal grease), the whole chip was transferred to the assembly lab to perform the wire-bonding process. The wire-bonding mechanism was conducted using a wire-bonding machine with a ball-bonder system. The optimized ball size was around 80 µm. The wire-bonding with smaller ball sizes was not
successful. Better parameters (temperature, distance, and speed) should be selected to achieve ball sizes less than 75 µm.

Figure 5.9. (a) Schematic demonstration of provided chip and wire-bonded edge emitting device. (b) The 75 µm size gold balls on top of the p- and n-contacts of the edge emitting device.

After the wire-bonding process, the electrical characterization was initiated. First, the room temperature I-V was collected using the probe station on the EL setup. A quick room temperature EL measurement was also acquired while injecting 0.5 A current and the emission from the edge was collected using the infrared fluorine-based optical fiber. The EL spectrum was delivered to the spectrometer and detector, accordingly. The results of the room temperature I-V characteristic and EL measurements on the devices with 400 µm length and 80 µm and 120 µm are shown in Figure 5.10. As obvious from the figure, both devices showed rectifying behavior at room temperature; however, the area of the device with 120 µm waveguide width was 2.5 times higher than the 80 µm width device. Therefore, the current density in the 80 µm device was higher compared to 120 µm width device and eventually resulted in higher EL spectrum intensity. For the detailed temperature-dependent characterization, the 80 µm device was selected. In order to perform the temperature-dependent I-V and EL measurements, the device-
containing chip was carefully mounted inside the feedthrough-equipped cryostat, and the needle tips were placed on the large area gold pads.

![Figure 5.10](image)

Figure 5.10. (a) The room temperature I-V characteristic of the GeSn edge emitting LEDs with 80 µm and 120 µm stripe width after the wire-bonding process. (b) The EL spectra of both samples from 1400 nm to 2400 nm wavelength.

The only difference between the measurement setup of the edge emitting LED compared to the surface emitting LED was the sample holder of the cryostat. The EL emission of the edge emitting LED emerged from the facets of the device; therefore, a special cryostat sample holder was designed to easily attach the prepared chip to the sample holder and ensure that the EL emission could be collected and eventually delivered to the spectrometer and detector without any blockade.

Figure 5.11 shows the designed cryostat sample holder and the schematic setup to show how the EL beam was perfectly aligned and transferred to the spectrometer. Careful alignment process was applied to guide the emission from the facet to the spectrometer. As shown in the inset, a part of the sample holder was cut to the half to provide enough path for the EL emission of both surface emitting and edge emitting LEDs. To ensure an appropriate thermal conductivity
between the sample holder and the LED device, a silver paste was applied as an adhesive between the sample holder and the bonded device.

Figure 5.11. The schematic EL setup (described in Chapter 2) and the specifically designed sample holder for the EL measurement of the edge emitting LED.

The I-V characteristics and EL spectra were achieved at different temperatures from 77 K to 300 K. The same EL setup was used to accomplish the measurements. The results of the temperature-dependent I-V characteristics and EL measurements are presented in Figure 5.12. The Ge/Ge$_{0.92}$Sn$_{0.08}$/Ge n-i-p DHS edge emitting diode with the stripe length of 400 µm and a stripe width of 80 µm was selected for the investigation. Figure 5.12a shows the temperature-dependent I-V measurements on the device exhibiting the rectifying behavior at all temperatures tested from 80 K to 300 K. Reduction of the slope of the I-V curves at the forward bias of the measurement once temperature decreased were related to the less thermally activated carriers at low temperatures which consequently increased the device dynamic resistance.
To ensure that injected current was high enough to provide sufficient carrier for radiative recombination and also avoid the device burning due to the Joule heating, a series of room temperature EL measurements in different current densities were conducted. A pulsed current source with a duty cycle of 10% and pulse width of 250 µs was used for the current dependent EL measurements at room temperature. As shown in Figure 5.12b, the current density changed from 0.3 kA/cm² to 1.5 kA/cm². Beyond 1.5 kA/cm², the devices started becoming burnt due to the heat. The 1.5 kA/cm² was selected as the fixed injected current density to perform temperature-dependent EL measurements from 77 K to 300 K.

As presented in Figure 5.12, the EL emission experienced a red shift with increasing temperature and also the intensity of the EL spectra increased. Increase in the EL intensity at higher temperature was related to the rise of the thermally activated carriers populating the Γ valley and participating in the radiative recombination. Similar to the prior study, this observation was attributed to the GeSn indirect bandgap materials in which Γ valley is slightly higher than the L valley in the conduction band. In order to improve the emission efficiency of
the GeSn DHS LED, an optimized structure was required to provide a direct bandgap GeSn active layer with sufficient carrier confinement. Increasing Sn incorporation, thickness of the GeSn layer, and a carefully designed buffer layer (GeSn or SiGeSn instead of Ge), could result in the direct bandgap GeSn with less defects and, consequently, highly efficient emission. In Chapter 7, optimized direct bandgap GeSn-based optoelectronic devices will be further discussed.
Chapter 6. Lasing from optically pumped direct bandgap GeSn ridge waveguides

6.1 Motivation

A Si-based laser has long been desired for the monolithic integration of optoelectronic devices on a complementary metal-oxide-semiconductor (CMOS) platform [6], [37]. Numerous studies have been done to achieve a Si-based laser; the missing component of the all Si-based optical integrated circuit. In 2005, researchers proposed an all-Si Raman laser based on stimulated Raman scattering rather than band-to-band transition [156]. Initial results on optically-pumped and electrically-pumped Ge lasers in 2012 opened an opportunity to further develop the group IV based laser sources [40]. Inherently, Ge is an indirect bandgap semiconductor. Heavily n-type doping or high tensile strain were essential requirements to achieve a lasing from the direct transition in Ge [157]. Technical difficulties in the fabrication of Ge laser devices under the above conditions hindered further explorations of the realization of Ge lasers. On the other hand, the current III-V materials used in laser diodes necessitate use of a wafer bonding process or direct growth on Si substrate leading to either an expensive fabrication process or low device quality [158], [159].

Recently, the demonstration of direct bandgap GeSn, a group IV-based semiconductor, has opened a unique occasion to accomplish monolithically fabricated group IV lasers on Si substrate. In 2015, the PGI-9 group in Germany and their collaborators published the first results of low temperature optically-pumped GeSn waveguide laser [92]. The same group in 2016, reported optically-pumped GeSn microdisk laser operating up to 150 K [160]. The threshold power density in the reported lasers varied between 220 to 325 kW/cm². Those achievements were a breakthrough in the realization of an all group IV based photonic circuit; however, a
practical laser device for group IV-based photonic circuit needs to have lower threshold density and is required to operate at room temperature.

Considering the published results on the GeSn laser, an advanced design of optically pumped GeSn waveguide lasers is introduced based on the Ge/GeSn/Ge double heterostructure (DHS) grown on Si substrate. Later in our investigation, it is indicated that the threshold density of the GeSn laser of this research was reduced to 140 kW/cm² which is almost two times lower than that of reported from the PGI-9 group.

6.2 Growth and characterization of direct bandgap GeSn sample

The device presented in this study was based on a direct bandgap thick GeSn film with 9% Sn composition grown as a Ge/GeSn/Ge DHS on Si (100) substrate. The sample was grown using an ASM Epsilon® 2000-Plus reduced pressure chemical vapor deposition (RPCVD) system. The low cost commercially available GeH₄ and SnCl₄ were used as Ge and Sn precursors, respectively. A 700 nm thick Ge buffer layer was grown on Si to relieve the lattice mismatch between Si and GeSn active layer. Subsequently, a specific recipe was applied to grow 1 µm thick GeSn layer with 9% Sn composition. Finally, a 10 nm-thick Ge cap layer was grown on top of GeSn to form the DHS. A detailed growth process was discussed in Chapter 2.

The thickness of the layers, Sn composition, and strain information of the grown sample were characterized using transmission electron microscopy (TEM) and high-resolution X-ray diffraction (XRD) system. In Figure 6.1a the TEM image of the Ge/GeSn/Ge DHS is presented. Two identified GeSn layers, the 210 nm defective layer and the 760 nm high-quality layer on top were clearly observed in the TEM image. The first thin defective GeSn trap layer with threading dislocation densities (TDD) of 10⁹ cm⁻² originates from the lattice mismatch between Ge and
GeSn. Since the threading dislocation loops occurred in the defective layer, less defect penetrated to the top GeSn layer. Therefore, a thick, high crystalline quality GeSn film with lower TDD ($3 \times 10^6$ cm$^2$) was formed which was favorable for device applications. The Sn composition of the first GeSn layer was 8.9% and for the second GeSn layer was 10.9%. The rate of incorporation of Sn to Ge increased when the film was more relaxed. Thus, the top GeSn layer had higher Sn composition than the bottom layer. The 10 nm GeSn cap layer was not clearly observable in the TEM image; however, the evidence of the Ge cap layer was noticed in the reciprocal space map (RSM) in Figure 6.1b. The RSM plot of the Ge and GeSn layers are presented. Due to the presence of two GeSn layers, the RSM plot became broadened. The first GeSn layer was almost relaxed and the second GeSn layer was $\sim 82\%$ relaxed. The tensile strained Ge cap layer was also detected.

![Figure 6.1](image.png)

Figure 6.1. (a) Cross-sectional TEM image of the 1 µm thick GeSn used in the GeSn waveguide fabrication for optical pumping measurements. (b) RSM of the strain-relaxed GeSn sample with different relaxations and Sn compositions is plotted.

Study of the temperature-dependent photoluminescence (PL) emission of the thick direct bandgap GeSn sample provided beneficial information about the bandgap and optical quality of
the sample. Demonstration of the direct bandgap thin GeSn films and a further increase in the optical quality of the direct bandgap thick GeSn films were thoroughly discussed in Chapter 3. The temperature-dependent PL of the direct bandgap thick GeSn film with 10.9% Sn composition is shown in Figure 6.2. The measurements were conducted using the standard off-axis PL setup with a 532 nm CW laser explained in Chapter 2. As depicted in the figure, the intensity of the PL emission from direct bandgap thick GeSn film increased in lower temperatures due to the efficient direct transition in the bandgap of GeSn sample. Based on the calculation, the linewidth of the PL spectrum at 10 K was 28 meV and at 300 K was 120 mV. A significant increase in the intensity and decrease in the line-width of the PL spectra with temperature reduction was evidence of the direct band gap material with high optical quality. The red-shift of the PL peak position with increasing the temperature followed the Varshni’s temperature-dependent bandgap relation.

![Figure 6.2. Temperature-dependent PL of the direct bandgap thick GeSn film (Sn=10.9%). The inset shows increasing of the integrated PL intensity with decreasing the temperature due to the dominant direct transition and deactivation of the defects.](image)
After examining the bandgap emission of the thick GeSn film, it was fabricated to a ridge waveguide for optical pumping experiments.

6.3 Fabrication of GeSn ridge waveguide

The GeSn with 10.9% Sn composition and 760 nm thickness was used to fabricate ridge waveguides for optical pumping characterization. First, the sample was cleaned with acetone and isopropyl alcohol before spin coating with photoresist AZ4110. A thickness of 1.8 µm was obtained after soft baking at 100 °C for 2 minutes. A set of ridge waveguides with widths of 1 to 5 µm was defined by using photolithography (Figure 6.3).

Figure 6.3. (a) A optical microscopic image of the fabricated GeSn waveguides with cavity widths of 1 to 5 µm. (b) A zoomed-in image of the waveguide with 5 µm cavity width.

A microscope was used to verify the ridge waveguide uniformity and sample cleanliness. Next, the GeSn sample was hard baked at 115 °C for 15 minutes so that the photoresist could serve as an effective mask for the wet chemical etching process. The wet chemical etching process was carried out using a mixture of HCl: H₂O₂: H₂O=1:1:20 at 0 °C. A slow etching rate
of 20 nm/min was measured in the process. In comparison with room temperature etching, smoother side walls were achieved in a low temperature wet chemical etching process. An etching depth of 800 nm was obtained to form the GeSn ridge waveguides.

Figure 6.4. The SEM images of the fabricated GeSn ridge waveguide with (a) 3 µm and (b) 5 µm width.

The SEM images showed that the top width of the waveguide was 3 µm while the bottom width was 5 µm (Figure 6.4). This occurrence was due to lateral etch of the wet chemical etching process. Due to the nature of chemical etching, the side walls at the top were etched more than the bottom portion of the waveguides. Smooth side walls provided by the chemical etching method decreased the scattering loss in the waveguide. All samples were carefully analyzed under the SEM and confirmed that the recipe used in the fabrication of waveguides was a robust and repeatable procedure.

In order to achieve mirror-like facets, the lapping process was required. The fabricated GeSn waveguide samples were lapped to the thickness of ~70 µm and, subsequently, cleaved to form the mirror-like facets.
6.4 Optical pumping measurement on the direct bandgap GeSn

The optical pumping setup described in Chapter 2 was implemented to perform the optical pumping measurements on the fabricated GeSn waveguides. The lapped devices were bonded on a Si chip and then mounted inside the cryostat. The 1064 nm pulsed laser with 45 kHz repetition rate, and 6 ns pulse width was focused on the waveguide sample after passing through a cylindrical lens with a focal length of 7.5 cm. The laser power was attenuated using neutral density filters and adjusted to the desired values with a rotating polarizer right before the cylindrical lens.

To calculate the power density, the effective area of the focused laser beam was critical to be determined. In fact, the area on which the laser beam was distributed homogeneously on the sample was required to calculate accurate power density. To measure the area, the well-known knife-edge technique [161], [162] was used to quantify the length and the width of the rectangular beam shape focused on the sample. The beam length of 3 mm and width of 20 µm was evaluated after the knife-edge measurement. The measured beam area was directly used in the calculation of peak power density.

The pumping laser illuminated homogenously on the GeSn waveguide and the emission from the facet was collected using a CaF₂ lens and eventually delivered to the spectrometer and PbS detector (cut-off at 3.0 µm) to monitor the signal. The integrated intensity of the waveguide emission was measured by adjusting the position of the grating at zero meaning that the grating acted as a mirror to send the waveguide emission output power to the detector. This technique saved a lot of time compared to calculation of integrated intensity from the area below the GeSn waveguide emission spectra. It is worthwhile to mention that longpass filters were placed at the spectrometer entrance to block the penetration of undesirable light.
6.5 Characterization of optically pumped GeSn laser

In order to characterize the lasing performance of the GeSn waveguides, the output power collected from the waveguide versus the incident power of the pumping laser (L-L) was measured at different temperatures. This method clearly indicated the lasing threshold power density and the effect of temperature on the threshold condition. Figure 6.5 presents the temperature-dependent L-L curves of a GeSn waveguide with 5 µm width and 930 µm length. The power density threshold increased from 140 to 350 kW/cm² from 77 K to 110 K. Beyond 110 K no lasing from the GeSn waveguide was observed. The reason to choose a long cavity waveguide was due to the lower mirror loss in longer cavities. Details on the cavity length dependent analysis will be proposed as a part of the future work.

Figure 6.5. The temperature-dependent L-L curves from the GeSn waveguide with 930 µm length and 5 µm width.
Figure 6.5 shows that the threshold power density was less for lower temperature. The threshold power density of 140 kW/cm² was achieved for 77 K and 350 kW/cm² for 110 K. Beyond 110 K, the lasing behavior almost disappeared due to the increase in the thermal loss. A useful parameter that indicates the figure-of-merit in the GeSn waveguide laser is the characteristic temperature ($T_0$). The power density of lasing threshold versus temperature was extracted. The extracted data was fitted using Equation 6.1. $I_0$ was the initial and $I_{th}$ was the threshold intensity, respectively. Based on fitting the following equation on the extracted data points, $T_0$ was calculated to be 65 K. The higher characteristic temperature represents a laser device whose performance was less sensitive to the variation of the temperature. The calculated $T_0$ was comparable with the early results of the III-V optically pumped lasers [163], [164].

$$I_{th} = I_0 \exp\left(\frac{T}{T_0}\right)$$

(Equation 6.1)

The laser emission spectrum of the GeSn waveguide characterized in this study is also presented. The reduction in the linewidth of the laser emission compare to the PL spectrum of the same sample clearly indicated the stimulated emission from the waveguide. The PL spectrum of GeSn sample before fabricating into the waveguide was measured at 77 K and 300 K using standard PL setup. After fabrication of the GeSn waveguide, the emission spectrum from the waveguide facet was measured using optical pumping setup. Results from the PL and optical pumping measurements are plotted in the same graph for comparison in Figure 6.6. As shown in Figure 6.6, the linewidth of the laser spectrum was dramatically reduced to 7 meV compared to the linewidth of the PL spectrum which was 68 meV at the same temperature. The achieved laser spectrum linewidth at 77 K indicates that it could be further reduced once temperature decreased. It should be noted that the power density used in the GeSn laser spectrum measurement was 5 times higher than the threshold power density. The peak position of the laser spectrum was 2476
nm which is the longest wavelength reported for the GeSn waveguide lasers. The double heterostructure design of the Ge/GeSn/Ge sample used in the fabrication of waveguide laser improved the performance of the laser by providing sufficient carrier confinement in the GeSn active region.

![PL spectra of GeSn sample](image)

**Figure 6.6.** The PL spectra of the GeSn sample at 77 K (red color) and 300 K (brown color) before fabricating into a GeSn waveguide and the laser spectrum (blue color) collected from the facet of the waveguide in the optical pumping measurement at 77 K.

To study the distribution of the optical field in the designed structure, the fundamental transverse electric mode (TE₀) was simulated. Using the ellipsometry measurements, the refractive index of the layers was extracted and implemented in the simulation of the Ge/GeSn/Ge waveguide structure. Figure 6.7, shows the distribution of the TE₀ mode in the GeSn waveguide structure. As indicated in Figure 6.7, the main portion of the fundamental TE₀ mode was confined in the top GeSn thick layer. Based on the calculation, the TE₀ mode had 85%
overlap with the top GeSn active layer. Also, the TE\textsubscript{0} mode had 18% overlap with the bottom GeSn layer and 14% overlap with Ge buffer layer. The simulation results indicated the confinement factor of 67% for the optical field in the designed structure.

![Graph showing the 1D optical field distribution of TE\textsubscript{0} mode in the Ge/GeSn/Ge DHS with specified refractive index obtained from ellipsometry measurement.]

To further reduce the threshold and improve the lasing performance of the GeSn ridge waveguide, the following parameters would need to be modified. 1) The Ge buffer and cap layers in the Ge/GeSn/Ge DHS proposed in the study could be replaced by a wider bandgap group IV-based material such as SiGeSn layer, lattice matched with GeSn active layer. The lattice matched SiGeSn layers as a barrier for the GeSn would provide a large barrier height leading to enhancement of the carrier confinement in the GeSn layer. 2) Choosing a thicker cap layer in the DHS design would increase the overlapping of the fundamental TE\textsubscript{0} mode with the
GeSn active region and eventually provide better mode confinement. 3) Optimizing the thickness of the GeSn layer and also the etching depth of the ridge waveguide would increase the modal gain and, consequently, reduce the lasing threshold. 4) Further reduction in the threshold power density could be achieved by designing a direct bandgap SiGeSn/GeSn/SiGeSn quantum well with Type-I band alignment. An initial device design is proposed in the next chapter as a part of the future work.

In summary, the initial lasing results from an optically pumped direct bandgap GeSn ridge waveguide has been studied. The laser structure was grown in a commercially available CVD system with cost effective precursors. The whole layers’ deposition was done in a single run epitaxy process. The growth of thick GeSn film provided a direct bandgap GeSn layer favorable for lasing performance. Implementing the direct bandgap GeSn layer in a Ge/GeSn/Ge DHS increased the carrier confinement within the GeSn active layer and reduced the power density threshold to 87 kW/cm² which was almost five times lower than the threshold reported by PGI-9 group in Germany [92] for their optically pumped GeSn waveguide laser.
Chapter 7. Summary and future work

7.1 Summary and Conclusion

The presented research work provides fundamental vision to the GeSn-based optoelectronic emitters for Si photonics. The main focus of this work was to study the temperature-dependent bandgap emission of GeSn materials and devices with different Sn compositions and structure favorable for the future of photonic integrated circuits. The material characterization of GeSn thin films and subsequently the temperature-dependent PL study of GeSn samples with different Sn compositions was explored.

Two distinctive PL emissions related to the direct and indirect bandgap of GeSn were clearly observed. The PL emissions at low temperatures were assigned to the indirect transitions and at high temperatures were attributed to the direct transitions. Observation of both direct and indirect transitions at different temperatures was a signature of an indirect bandgap GeSn material where the L valley of the indirect bandgap energy remains lower than the Γ valley of the direct bandgap energy. The PL emission was less efficient for the indirect GeSn materials since carriers were distributed in both Γ and L valleys; however, increasing the Sn composition and reduction of compressive strain in the GeSn led to the first observation of a TRUE direct bandgap GeSn material. The GeSn sample with 10% Sn composition and 1.1% compressive strain exhibited different behavior compare to the other strained GeSn samples with lower Sn composition. Analysis of the integrated PL intensity and the line-width of PL spectra at different temperatures along with the theoretical assessments confirmed that only the direct bandgap transition happened at different temperatures. Therefore, carriers only occupied the Γ valley in different temperature. This GeSn bandgap directness was further verified after a series of PL measurements on the strained relaxed GeSn samples with Sn compositions higher than 6%.
Enhancement of the PL intensity, and also reduction of the PL spectra line-width, stated that direct bandgap GeSn material with high optical quality had been achieved. The opportunity of growing direct bandgap GeSn paved the way to achieve the essential component of the group IV-based optoelectronic emitters.

In addition, the temperature-dependent emission of advanced GeSn structures, such as quantum well (QW) and double heterostructure was thoroughly explored. The band structure of the designed SiGeSn/GeSn/SiGeSn single QW was analyzed and band alignment calculations revealed a Type-I band alignment with carrier confinement at low temperatures. After cautious examination of the Si and Sn composition and strain of the QW structure, it was realized that the GeSn QWs were indirect bandgap materials with the L valley lower than the Γ valley; however, the band offset calculations showed that the barrier height between the SiGeSn barriers and GeSn QW could provide sufficient carrier confinement within the QW region at low temperatures. Thus, efficient carrier recombination with high-intensity PL emissions at low temperatures was observed for the GeSn QW.

Although the Type-I band alignment in the SiGeSn/GeSn/SiGeSn QW structure offered the confinement that induced a high-intensity PL emission at low temperatures, the indirectness of the GeSn well region limited its performance as an efficient emitter. The distribution of carriers between Γ valley and L valley in different temperatures reduced the recombination rate from the conduction band to the valence band. Moreover, the designed barrier height was not able to confine the carriers in temperatures higher than 50 K; thus, the PL intensity of GeSn QW decreased for temperatures above 50 K. An optimized QW design is required to achieve direct bandgap GeSn QW with Type-I band alignment. A detailed discussion on the proposed design is provided in the future work of this chapter.
In order to study the GeSn light emitting diodes (LEDs) and their performance in different temperatures under current injections less than 10 kA/cm$^2$, the Ge/GeSn/Ge n-i-p double heterostructure was grown and fabricated into a surface emitting and edge emitting LEDs. The wavelength coverage of the designed GeSn LEDs was beneficial for the gas detection and biochemical sensing for wavelengths from 1.5 µm to 3 µm, known as short-wave infrared. The challenges regarding the characterization of fabricated GeSn LEDs were examined, and the required apparatus were designed and utilized to efficiently measure the LED output emission. The GeSn LED electrical and optical characteristics were investigated from 77 K to 300 K and the electronic band structure was inspected. The Type-I band alignment was observed due to the barrier height between Ge barriers and GeSn active layer. The Sn composition in the GeSn layer combined with the compressive strain in the lattice structure led to an indirectness of the GeSn bandgap. Therefore, the output emission from both surface emitting and edge emitting structures was not quite strong. Optimizing the thickness of GeSn active layer, increasing the Sn composition, reducing the compressive strain, and replacing the Ge barriers with SiGeSn layers could provide direct bandgap GeSn n-i-p double heterostructure LEDs with strong emission.

Lasing performance from relaxed thick GeSn double heterostructure waveguide cavity was investigated as the last assessment of GeSn emitters. The 800 nm thick direct bandgap GeSn waveguides with cavity width of 5 µm and a cavity length of 930 µm was studied under the optical pumping measurements, and the threshold power density and laser spectra were measured at different temperatures. The threshold power density of 87 kW/cm$^2$ measured for the laser at 10 K was the lowest ever reported threshold for the optically-pumped GeSn waveguides, and the observed operation temperature of 110 K was the highest value achieved for such a waveguide laser. The enhancement of the carrier confinement in the Ge/GeSn/Ge double heterostructure
resulted in the lower threshold and higher operation temperature for the presented GeSn laser. However, this accomplishment is still the beginning of a long path to provide room temperature electrically-injected GeSn laser for the integrated Si photonics. A comprehensive study is required to design the advanced structures based on a SiGeSn/GeSn system with high carrier confinement and optical field confinement within the gain medium to exhibit low threshold group IV-based lasers with room temperature operation. Moreover, the theoretical and experimental mode study is required to further analyze the properties of the GeSn laser emission.

7.2 Future work

The SiGeSn/GeSn/SiGeSn QW structure presented in this work could be considered as a fundamental component of future of GeSn-based optoelectronic devices for the infrared wavelength applications. Specifically, direct bandgap QW structure with the Type-I band and large barrier heights are able to provide effective carrier confinement for the low threshold QW LEDs and lasers. Such a confining structure with defect-free layers in its building block could operate at room temperature. The major issues noticed in the current GeSn QW, discussed in Chapter 4, are described as following: i) bandgap indirectness of the GeSn QW; ii) insufficient barrier height between GeSn QW and SiGeSn barriers; and, iii) high compressive strain in the GeSn QW layer. Here, a new design for the GeSn QW structure is proposed in which all the above points have been addressed. Optimization of the GeSn QW presented in this work could eventually provide the desired low threshold GeSn QW LEDs and lasers with room temperature operation.

Figure 7.1 depicts the schematic diagram of the proposed QW structure. The new design is based on the current capability of the growth system. It is already shown that the maximum Sn
composition of the pseudomorphic GeSn QW is 10%. The Ge$_{0.9}$Sn$_{0.1}$ QW, pseudomorphic to the Ge buffer layer, experiences a 1.1% compressive strain in the lattice structure. Based on the results discussed in Chapter 3, the 1.1% compressive strain forces the Ge$_{0.9}$Sn$_{0.1}$ to remain an indirect bandgap material.

Figure 7.1. Proposed structure that offers a direct bandgap GeSn QW with Type-I band alignment and sufficient carrier confinement.

To overcome that constraint, a buffer layer with less lattice mismatch with Ge$_{0.9}$Sn$_{0.1}$ is desired. A thick GeSn buffer layer with low Sn composition has less lattice mismatch with Ge$_{0.9}$Sn$_{0.1}$, so the compressive strain in the lattice structure of Ge$_{0.9}$Sn$_{0.1}$ will be reduced. Therefore, the Ge$_{0.9}$Sn$_{0.1}$ QW could exhibit direct bandgap characteristics favorable for emitting devices. Moreover, to provide sufficient carrier confinement in the GeSn QW layer, a SiGeSn cladding layer lattice matched to the new GeSn buffer is proposed. Inserting that layer ensures the necessary barrier height due to the wider bandgap of SiGeSn compare to GeSn. Finally, a GeSn barrier layer lattice matched to GeSn buffer layer provides another level of confinement.
for the Ge$_{0.9}$Sn$_{0.1}$ QW region. The Sn composition of the GeSn buffer and barrier layers and the Si and Sn compositions of the lattice matched SiGeSn cladding layer should be carefully selected to provide the required direct bandgap Ge$_{0.9}$Sn$_{0.1}$ QW.

In order to determine the Sn composition required for the GeSn buffer layer, a contour plot is provided in Figure 7.2. The negative values represent the indirect band gap GeSn and the positive ones signify the bandgap directness of a pseudomorphic GeSn QW layer. The dashed line is the border indicating the compressive-stained or tensile-strained GeSn QW.

![Contour plot](image)

**Figure 7.2.** Contour plot demonstrating the energy difference between the Γ and L valleys of the pseudomorphic GeSn QW with a relaxed GeSn as a buffer.

Calculation of the bandgap directness of the GeSn QW layer with the contour plot offers a better understanding on the range of Sn compositions that can be used for the relaxed GeSn buffer and pseudomorphic GeSn QW. In the contour plot shown in Figure 7.2, the x-axis is the Sn percentage of the GeSn buffer layer and the y-axis represents the Sn composition for the GeSn QW layer pseudomorphic to GeSn buffer layer. The contour lines are the difference
between the Γ valley and L valley of the conduction band ($\Delta E_{c,QW} = E_L - E_\Gamma$) in the Ge$_{0.9}$Sn$_{0.1}$ QW. The positive values of the contour lines represent the direct bandgap GeSn QW meaning that L valley is higher than the Γ valley energy level. The calculation of the $\Delta E_{c,QW}$ was based on the strain-dependent bandgap calculation discussed in Chapter 4.

Based on the contour plot in Figure 7.2, almost 1% Sn in the GeSn buffer layer is required to achieve direct bandgap pseudomorphic Ge$_{0.9}$Sn$_{0.1}$ QW; however, this is not the only criteria that needs to be considered. Another parameter that plays an important role in the QW confinement is the barrier height between the Ge$_{0.9}$Sn$_{0.1}$ QW and GeSn buffer/barrier layer. The second contour plot was prepared to calculate the highest barrier height ($\Delta E_{c,\text{Barrier-Well}}$) when the Sn composition changes in the GeSn buffer/barrier and QW layers. The largest positive values of the contour lines indicate the highest band offset between the Ge$_{0.9}$Sn$_{0.1}$ QW and GeSn buffer/barrier layer.

Figure 7.3. The conduction band offset between the Ge$_{0.9}$Sn$_{0.1}$ QW and GeSn buffer/barrier layers are shown as contour lines.
As shown in the contour plot of Figure 7.3, the Ge\(_{0.9}\)Sn\(_{0.1}\) QW has the largest conduction band offset with the GeSn layers with Sn compositions between 4.5\% to 5.5\%, the range that is shown between two yellow asterisks in the contour plot (\(\Delta E_{\text{c,Barrier-Well}} \approx 60\) meV). The QW structure design is proposed based on considering the Ge\(_{0.95}\)Sn\(_{0.05}\) as the buffer layer. Another reason that legitimizes using GeSn with 5\% Sn composition is a critical thickness. As mentioned earlier in this section, a GeSn relaxed buffer layer with thickness of \(\sim 400\) nm is required for the new optimized QW structure. To achieve that thickness, the Ge\(_{0.95}\)Sn\(_{0.05}\) buffer layer is the best candidate. GeSn layers with lower Sn compositions would not provide relaxed layer since their critical thicknesses are higher than the one for Ge\(_{0.95}\)Sn\(_{0.05}\). They will be relaxed in thicknesses above \(600\) nm which is beyond the thickness that was designed for the relaxed GeSn buffer layer.

The next step in the QW structure design is to find the SiGeSn cladding layer lattice matched to the Ge\(_{0.95}\)Sn\(_{0.05}\) buffer layer for a separate confinement. A wider bandgap SiGeSn layer provides sufficient carrier confinement for the whole QW structure. Based on Vegard’s law, the lattice constant of the Ge\(_{0.95}\)Sn\(_{0.05}\) buffer layer is 5.7 \(\text{Å}\). Therefore, certain values for Si and Sn compositions are required to provide the SiGeSn cladding layer with an in-plane lattice constant of 5.7 \(\text{Å}\). A lattice matched SiGeSn (relative to the GeSn buffer) with desired band alignment will be achieved by tuning the Si and Sn compositions, separately. Additionally, the band offset between the SiGeSn cladding layer and Ge\(_{0.9}\)Sn\(_{0.1}\) QW for the conduction band (\(\Delta E_{\text{c,cladding-well}}\)) and the valence band (\(\Delta E_{\text{v,cladding-well}}\)) were calculated. In Figure 7.4, the 3D plots represent the correlated Si and Sn compositions required for the SiGeSn lattice matched to Ge\(_{0.95}\)Sn\(_{0.05}\) buffer. The z-axis in the figure signifies the values for \(\Delta E_{\text{c,cladding-well}}\) (Figure 7.4.a) and \(\Delta E_{\text{v,cladding-well}}\) (Figure 7.4.b).
Figure 7.4. (a) Band offset between the conduction band of Ge$_{0.9}$Sn$_{0.1}$ QW and SiGeSn cladding layer lattice matched to Ge$_{0.95}$Sn$_{0.05}$ buffer/barrier. (b) The band offset between the valence band of Ge$_{0.9}$Sn$_{0.1}$ QW and SiGeSn cladding layer lattice matched to Ge$_{0.95}$Sn$_{0.05}$ buffer/barrier.
Based on Figure 7.4, the SiGeSn with 15% Si and 8.8% Sn provides the largest band offsets between the SiGeSn and Ge\(_{0.9}Sn_{0.1}\) QW layer. Therefore, the final GeSn QW structure design with the Si and Sn percentages in the layers will be achieved.

The band structure of the finalized configuration of GeSn QW is shown in Figure 7.5. As indicated in that figure, the Ge\(_{0.9}Sn_{0.1}\) QW in the designed structure is a direct bandgap material which features a Type-I band alignment with Ge\(_{0.95}Sn_{0.05}\) barriers and the Si\(_{0.12}Ge_{0.762}S_{0.088}\) cladding layer.

![Diagram of GeSn QW structure](image)

Figure 7.5. Band alignment of proposed QW structure designed to provide a direct bandgap GeSn QW with Type-I band alignment and sufficient carrier confinement within the QW region.

The provided barrier heights between Ge\(_{0.9}Sn_{0.1}\) QW and Ge\(_{0.95}Sn_{0.05}\) barrier and Si\(_{0.12}Ge_{0.762}S_{0.088}\) cladding layers introduce sufficient confinement for the carriers inside the QW region. The transition energy between the \(E_{c\Gamma 1}\) to \(E_{v\text{HH}1}\) is the dominant transition of the QW
structure that leads to an emission with 2400 nm wavelength. The proposed QW structure could be further improved to be implemented in the electrically-pumped GeSn QW lasers.
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Appendix A: Optical Alignment Procedure

This appendix explains the required procedure for the optical alignment of the PL setup. In fact, the following steps could be employed for every optical characterization setups working based on excitation, collection, and optical detection.

1- Make sure all safety issues (including wearing goggles, turning on the laser lamp sign, …) have been conducted prior to turning on the laser.

2- Turn on the 532 nm CW laser and reduce the power to 5 mW using neutral density filter.

3- Turn on the lock-in amplifier and the chopper.

4- Set the spectrometer entrance and exit slit to zero and set the spectrometer wavelength to the wavelength of the laser.

5- Attach an optical rail to the optical table at least 10 inches far from the laser.

6- Prepare two rail carriers with posts and post holders.

7- Attach the pinholes to the posts on the rail carriers and set the height of the pinholes’ centers to be 5 inches higher than the optical table top.

8- Put one pinhole at the beginning of the rail and another one at the end of the rail.

9- Align the laser beam path, so the laser beam passes exactly through the centers of the pinholes.

10- Use a proper mirror to shine the laser beam to a diffuser (where sample will be mounted).

11- Collect the diffused light in front of the diffuser using a proper collecting lens.

12- Provide a rail and rail carrier system (similar to the one mentioned in 7) and align the beam towards the spectrometer.

13- Use a leveler to properly balance the spectrometer height.
14- Adjust the vertical entrance and exit slits of the spectrometer to be 5 inches higher than the optical table top.

15- Use a proper lens to focus the collected diffused beam to the entrance slit of the spectrometer with the slit width of zero.

16- Continuously monitor the lock-in read out to make sure that the detector and lock-in do not go to saturation and overload condition.

17- Slowly adjust the detector height until maximum signal is achieved by the lock-in.

18- Use the adjustment screws in the detector housing to further maximizing the signal.

19- Once the maximum signal was achieved, properly tighten the detector inside the detector housing.

20- Once the diffuser is replaced by a real sample for the PL measurement, play with the sample-collecting lens distance and focusing lens-spectrometer distance to maximize the PL signal.
## Appendix B: List of Parameters Used in 6-band K.P Bandgap Calculation

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Si</th>
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<td>C12</td>
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<td>(\gamma_1)</td>
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Appendix C: Description of Research for Popular Publication

The 21st century is the information and communication age. Human life closely depends on the information transferred from one place to another. Communication technology has a huge market all around the world, and companies have tried to provide communication devices with high performance and cost effective price for their services to the customers; however, increasing demand for data communication brings about challenges for the traditional devices, such as computers, phones, and the internet. Thus far, the communication technology is based on the conventional digital electronics. Although long-distance telecommunication is benefited by optical fiber technology, the short-distance data transfer still depends upon the transistor-based circuits. Influential companies in the field of data communication have confronted an issue that they are no longer able to reduce the size of the transistors in their integrated circuit packages due to the physical limit. Moreover, the current high-density integrated electronic circuits with billions of transistors generate a huge amount of heat that eventually suppress the efficiency of the devices.

A few decades ago, researchers came up with a new concept called Photonics and Optoelectronics. The concept was based on the exploitation of massless photons instead of electrons in the whole framework of data communication. On the other hand, the well-established Si electronic infrastructure with Si CMOS platform was a powerful basis to develop the photonic and optoelectronic technology. At the beginning of 21st century, Si-based photonics and optoelectronic devices for photonic integrated circuits (PICs) were already introduced and studied. The only obstacle that hinders the commercialization of PICs is a highly efficient Si-based emitter. Even though Si has impressive electronic and photonic capabilities, it is not an efficient emitter for PICs.
A technology based on silicon-germanium-tin (SiGeSn) alloys has demonstrated a specific capability to provide not only highly efficient Si-based emitters, but also a viable platform for the PICs structures. The SiGeSn/GeSn optoelectronic devices cover the wavelengths from 1 µm to 12 µm, suitable for communication, sensing, and military applications.

Currently, the University of Arkansas is one of the pioneers in the SiGeSn/GeSn research in the world. The developed growth capability, device fabrication systems, and characterization equipment are locally prepared to thoroughly investigate the SiGeSn/GeSn technology. A part of SiGeSn/GeSn research was mainly focused on discovering the emission capabilities of GeSn materials for Si-based lasers and light emitting devices. That direction was systematically pursued by Seyed Amir Ghetmiri, a PhD candidate in the Microelectronics-Photonics graduate program at the University of Arkansas. The results of that research were directed to the first demonstration of direct bandgap GeSn material. “The direct bandgap GeSn is the essential component of the highly efficient Si-based GeSn lasers and light emitting diodes,” said Mr. Ghetmiri. “The direct bandgap GeSn lasers can pave the way for commercialization of cost-effective photonic and optoelectronic integrated circuits.” Increasing the efficiency of SiGeSn/GeSn light emitters will be the next stage towards the realization of all-optical photonic circuits for the future of data communication and sensing applications.

The SiGeSn research group under the supervision of Dr. Shui-Qing (Fisher) Yu, Professor of Electrical Engineering, has demonstrated a breakthrough achievement in that research and their accomplishments have been published in tens of peer-reviewed scientific journals and conference proceedings.
Appendix D: Executive Summary of Newly Created Intellectual Property

1. First demonstration of the direct bandgap high quality crystalline GeSn film.

2. A design for integration of multiple optical characterization setups with accurately aligned optical paths to measure photoluminescence with different excitation lasers, optical pumping experiment for lasing study for visible and infrared applications.

3. A method to efficiently bond the lapped edge-emitting devices to a Si chip for temperature-dependent electrical and optical characterizations.

E.1 Patentability of Intellectual Property (Could Each Item be Patented)

The three items listed were considered first from the perspective of whether or not the item could be patented.

1. Demonstration of the first ever reported direct bandgap GeSn crystalline film might be patentable; however, high quality GeSn crystalline films with high Sn composition, achieved by ASM, enabled this demonstration of direct bandgap GeSn. ASM has already filed a patent regarding the growth process of high quality GeSn films.

2. The design for integration of multiple optical characterization setups could not be patented because it would be obvious to those skilled in this research field.

3. The method to efficiently bond the lapped edge-emitting devices to a Si chip for temperature-dependent electrical and optical characterizations could not be patented because it would be obvious to those skilled in this research field.

E.2 Commercialization Prospects (Should Each Item Be Patented)

The three items listed were then considered from the perspective of whether or not the item should be patented.

1. ASM owns the intellectual property for the growth of high quality GeSn. They have filed a patent for the growth technique.

2. Not applicable

3. Not applicable
E.3 Possible Prior Disclosure of IP

The following items were discussed in a public forum or have published information that could impact the patentability of the listed IP.

1. The results of the first demonstration of direct bandgap GeSn high quality crystalline films were publicly disclosed in a journal article (Applied Physics Letters 105 (15) 151109 (2014)) and also presented in the subsequent publications from ASM.

2. Not applicable

3. Not applicable
Appendix F: Broader Impact of Research

F. 1 Applicability of Research Methods to Other Problems

The information provided in this dissertation is a baseline for understanding the GeSn materials for light emitting devices. The analysis applied in this work could even provide necessary information for the other GeSn and SiGeSn optoelectronic devices, such as photodetectors and waveguides for Si photonics.

F. 2 Impact of Research Results on U.S. and Global Society

The commercialization of cost-effective GeSn and SiGeSn lasers and LEDs could make a huge impact on the current expensive III-V optoelectronic devices, such as GaAs-based lasers and LEDs. Reduction of device cost by implementing GeSn and SiGeSn technology in the optoelectronic market saves a huge amount of money and will be profitable for the companies dealing with the production of optoelectronic devices and also the data communication industries. Results achieved in this project can be used to solve a part of the grand challenge of incorporating optical devices into electronic industry by utilizing the infrastructure that has been developed over the last 50 years in the electronics industry. The research demonstrated that devices made from Ge and Sn, which are of the same group of elements in periodic table can resolve the issue of incorporation of photonic devices in a Si chip. More than 250 citations of the GeSn research work in this group in less than four years clearly indicate the significance of this research for the US and global society.

F. 3 Impact of Research Results on the Environment

Solar cells are shown to be a good candidate for a renewable clean energy source that have been used to power civilian sites as well as space exploration missions launched to date. The main
challenges that solar cell technology is facing is high cost and low efficiency. The cost of the cells are due to the substrates as well as the growth and fabrication costs. This work is particularly important to reduce the cost and efficiency of solar cells using GeSn and SiGeSn technology.

The highly efficient light emitters based on GeSn and SiGeSn materials are capable of being used for the gas sensing and bio sensing applications. Short-wave infrared range of spectrum is important since absorption of several toxic gases, including CO and CO\textsubscript{2} takes place in that range of wavelength. Current infrared gas sensors have a reputation for being complicated and expensive. The GeSn light emitting diodes, presented in this work, has a potential to provide less expensive gas sensors compatible with Si substrate platform.

Moreover, the GeSn-based photodetectors could provide a cost effective night vision cameras for both military and civil purposes. The current technology based on III-V materials are not economic to be used for civil applications.
### Appendix G: Microsoft Project for MicroEP PhD Degree Plan

<table>
<thead>
<tr>
<th>Task Name</th>
<th>2012</th>
<th>2013</th>
<th>2014</th>
<th>2015</th>
<th>2016</th>
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<tr>
<td>PhD program</td>
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<td>Registration for PhD study</td>
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<td>Selecting Major Advisor</td>
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<td>Talk with major advisor about whole idea of research</td>
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<td>Selecting committee members</td>
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<td>Literature Review</td>
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<td>Collect information about the characterization setups</td>
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<td>Photoluminescence</td>
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<td>Characterization of GeSn films</td>
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<td>Electroluminescence</td>
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<td>Characterization of GeSn films</td>
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<tr>
<td>Optical pumping measurement on GeSn waveguide samples</td>
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<td>Study the SiGeSn/GeSn QW structures</td>
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<td>Dissertation Writing</td>
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<td>Scheduling defense session</td>
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<td>PhD Defense session</td>
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</table>
Appendix H: Identification of All Software Used in Research and Dissertation Generation

Computer #1:
  Model Number: Asus
  Serial Number: ALTEC– A53E
  Location: Personal Laptop
  Owner: Seyed Amir Ghetmiri

Software #1:
  Name: Microsoft Office 2016
  Purchased by: Electrical Engineering Department, University of Arkansas

Software #2:
  Name: Microsoft Project 2016
  Provided by: Microelectronics-Photonics, University of Arkansas

Software #3:
  Name: Matlab R2016a Student Version
  Provided by: University of Arkansas

Software #4:
  Name: Zotero (Basic)
  Purchased by: Free add-in tab is available online in Fire Fox search engine

Software #5:
  Name: 1D and 2D TEM Solver
  Provided by: Free online link available

Computer #2:
  Model Number: Dell Vostro
  Serial Number: 52M6XK1
  Location: ENRC Room 2923
  Owner: Dr. Shui-Qing Yu

Software #1:
  Name: SynerJY with built-in Origin software
  Purchased by: Dr. Shui-Qing Yu

Software #2:
  Name: LabVIEW 2016
  Purchased by: Electrical Engineering Department, University of Arkansas

Computer #2:
  Model Number: Dell Inspiron
  Serial Number: 52M6XK1
  Location: ENRC Room 2923
  Owner: Dr. Shui-Qing Yu

Software #1:
  Name: SynerJY with built-in Origin software
  Purchased by: Dr. Shui-Qing Yu

Software #2:
  Name: LabVIEW 2016
  Purchased by: Electrical Engineering Department, University of Arkansas
Appendix I: All Publications Published, Submitted and Planned

I. 1 List of Peer Reviewed Published Works (Reverse Chronological)


I. 2 List of Conference Proceedings and Publications


14 W. Du, S. A. Ghetmiri, S. Al-Kabi, A. Mosleh, J. Margetis, J. Tolle, G. Sun, R. A. Soref, B. Li, H. A. Naseem, S.-Q. Yu, M. Mortazavi, “Optical study of Ge_{0.95}Sn_{0.05}/Ge_{0.9}Sn_{0.1}/Ge_{0.95}Sn_{0.05} quantum-well towards group-IV based light source on Si”, accepted for CLEO conference 2016.


I.3 List of Submitted Works

I.4 List of Planned Works


Appendix J. Taken From Author’s Published Works

Chapter 3 is largely reproduced from my publications in the journal of Vacuum Science and Technology B and Applied Physics Letters.


Parts of Chapter 2 to 6 were originally published as:


