

DIRECT BANDGAP GERMANIUM FOR ACTIVE SILICON PHOTONICS
APPLICATIONS

by

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DEDICATION

I dedicated this work to my father (Md. Abdul Jalil), my mother (Most. Shamsun Naher Begum), my siblings, and my loving wife, Luna.

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LIST OF ABBREVIATIONS

Abbreviation	Description
AFM	Atomic Force Microscopy
AHS	Atomic Hydrogen Source
AR	Anti Reflecting
ARSC	Analysis Research Service Center
BEP	Beam Equivalent Pressure
CAR	Continual Azimuthal Rotation
CB	Conduction Band
CEA	Charles Evans Associates
CMOS	Complementary Metal Oxide Semiconductor
CVD	Chemical Vapor Deposition
DFPECVD	Dual Frequency Plasma Enhanced Chemical Vapor Deposition
DH	Double Heterostructure
EPÉE	Epitaxial Photonics & Electronics Engineering
EPIC	Electronic-Photonic integrated Circuit
FTIR	Fourier Transform Infrared
FWHM	Full Width Half Maxima
HFCVD	Hot Filament Chemical Vapor Deposition
HH	Heavy Hole
HR	High Resolution

HRXRD	High Resolution X-ray Diffraction
IVBA	Intervalence Band Absorption
LA	Longitudinal Acoustic
LH	Light Hole
LO	Longitudinal Optical
MBE	Molecular Beam Epitaxy
MBE	Molecular Beam Epitaxy
MFC	Mass Flow Controller
ML	Mono Layer
MSEC	Materials Science, Engineering, and Commercialization
NNIN	National Nanotechnology Infrastructure Network
NRSC	Nano Research Service Center
NSF	National Science Foundation
OCF	Optical Confinement Factor
PL	Photoluminescence
QW	Quantum Well
RBS	Rutherford Backscattering Spectroscopy
RGAs	Residual Gas Analyzer
RHEED	Reflection High Energy Electron Diffraction
RMS	Root Mean Square
RPM	Rotation Per Minutes

RSM	Reciprocal Space Mapping
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectroscopy
SO	Split Off
SOI	Silicon On Insulator
SRH	Shockley Reed Hall recombination
SRO	Shared Research Operations
TC	Thermocouple
TO	Transverse Optical
UCSB	University of California Santa Barbara
UHP	Ultra High Pure
UHV	Ultra High Vacuum
VASP	Vienna Ab-initio Simulation Packages
WDM	Wave Division Multiplexing
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

ABSTRACT

Machine learning and data centers require data interconnects with orders of magnitude more bandwidth. This could be achieved using optical interconnects, but the Group IV semiconductors compatible with silicon fabrication (Si, Ge, C, and Sn) emit almost no light. All Group IV elements have an indirect bandgap that prevents light emission but applying strong tensile strain to Ge or alloying it with C or Sn could induce a direct bandgap. This dissertation focused on three such projects.

In the first project, I successfully incorporated C in Ge using CBr_4 as a C precursor. Reflection high energy electron diffraction (RHEED) and atomic force microscopy (AFM) showed better surface reconstruction and lower surface roughness for the lowest growth temperature, $T_{\text{sub}} = 215^\circ\text{C}$. Increasing growth temperatures turned the RHEED pattern spotty and increased the surface roughness. High resolution x-ray diffraction (HRXRD) confirmed the RHEED and AFM results, showing better crystal quality at $T_{\text{sub}} = 215^\circ\text{C}$, with a higher-angle peak corresponding to tensile strain from a nominally substitutional carbon content of 0.71%. We believe this is a lower limit for the total composition of C in the sample, because ab-initio simulations showed that Ge vacancies could not explain the peak shift, and C interstitials would push the lattice toward compressive strain. Raman spectroscopy showed a clear Ge-C local mode at 530 cm^{-1} for growths from $215\text{-}324^\circ\text{C}$, confirming the substitutional carbon incorporation in germanium. In contrast with previous reports of Ge:C growth, these samples showed no amorphous or graphitic carbon in Raman. Furthermore, these samples produced the first

reported photoluminescence (PL) below the Ge bandgap, near 0.61 eV at 83 K, in agreement with band anti-crossing and computational models.

In the second project, I added a beam of atomic H to the $\text{Ge}_{1-x}\text{C}_x$ growth to reduce undesirable C-C bonds and similar C clusters on the growth surface. Unlike the H-free growths, these samples showed the smoothest surface and narrowest XRD linewidth at higher temperatures: $T_{\text{sub}} = 324^\circ\text{C}$. More significantly, Raman spectroscopy showed a 4x stronger Ge-C local mode peak intensity compared to the samples grown without H, which suggests a much larger fraction of C substitutional in the lattice. Again, PL showed emission below the Ge bandgap in these samples, near 0.60 eV at 83 K.

Finally, in the third project, I modeled ridge waveguide lasers using tensile strained Ge for the active region, with stress provided by SiNx stress liners. I performed 2.5D mechanical stress modeling in COMSOL Multiphysics, then combined the strain profile with ab-initio data to produce gain/absorption and refractive index profiles across the waveguide. From these, I calculated the optical mode profile, modal gain, and material losses in the laser. Intervalence band absorption loss was found to be the dominant loss. The threshold current density was found to be 1.4 kA/cm^2 , which was almost $10\times$ higher than typical GaAs-based lasers. Therefore, strain alone is insufficient to produce efficient lasers, although it could aid in producing a direct bandgap from Ge alloys. Together, these results offer a route to lasers and other active photonic devices on silicon.

1. INTRODUCTION

1.1 Overview and Motivation

The invention of the transistor [1], [2] was one of the most significant breakthroughs in modern science. Since then, the size of the transistor has been decreasing exponentially. In 1975 Gordon Moore predicted that the number of transistors on a chip at the lowest cost point would double every two years. In other words, the area of the transistor would halve every two years [3], [4]. Transistor size shrinkage allows more devices on a wafer, but the challenge is integrating the high-speed interconnects with the transistor without significant time delay and with a small energy budget [5], [6]. The increasing number of transistors require additional interconnects, which increases the total length of interconnects and decreases the cross-sectional area of the wires as well. Following $R = \rho \frac{L}{A}$ (where R is resistivity, L is wire length, and A is its cross-sectional area) the resistivity R increases. Similarly, as wires get closer together, the parasitic fringing capacitance between the wires increases. The line-to-substrate capacitance is $C_{ox} = K_{ox}\epsilon_o(WL/X_{ox})$, where X_{ox} , W , L and K_{ox} are the oxide thickness, width of the interconnects, length of the interconnects and dielectric constant, respectively, and ϵ_o is the permittivity of the free space. The capacitance between two interconnect lines is $C_I = K_{ox}\epsilon_o(HL/L_s)$, where L_s and H are the distance between the two lines and the height of the interconnects respectively. The total capacitance can be approximated by $C = K_I(C_{ox}+C_I)$, where K_I considers the fringing fields to the substrate and is approximately equal to 2 [7]. The resistance may be negligible for very short distance interconnects (local interconnects that are used for very short interconnects at the device level), such as between neighboring transistors, but the resistance dominates wires longer than one-tenth

of the chip edge length (for example, global interconnects used to connect long interconnects between cores, including memory buses and clock distribution) [8]. Chen et al. have shown that replacing the electrical interconnects with optical interconnects between nearby transistors will not improve the overall data transfer rate because, at a short distance, the data transfer rate between electrical and optical interconnects are comparable [8]. However, optical interconnects integrated with CMOS could transfer the data between the chips or on high bandwidth data buses within the chip.

The technology of integrating photonics on a Si wafer is known as silicon photonics. In silicon photonics [9]–[13], Group IV materials are used to shape or modulate, transmit, and receive data optically. In current silicon photonics devices, an off-chip or wafer bonded laser diode is coupled to waveguides on an integrated circuit. Then a modulator imposes data onto the laser beam, which then travels through an optical fiber or on-chip waveguide to a photodetector, which detects the signal and converts it back into an electrical signal again (Figure 1.1).

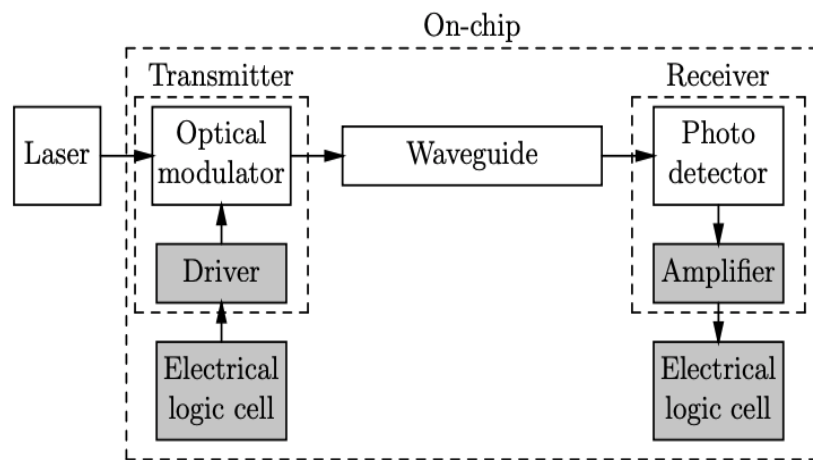


Figure 1.1: An on-chip optical interconnect data path [8].

The current need for high-speed data transfer rates has made silicon photonics a

major research area, particularly for the past decade. But the major shortcoming of silicon photonics is the lack of a laser compatible with an existing Si CMOS fabrication [14]. Among the semiconductor materials, Group III-V materials are excellent light emitters that could theoretically be integrated with Si through a highly complex and expensive fabrication process with sufficient strict contamination control, but even then, a 100% yield factor is virtually impossible. In addition, III-V materials diffuse into the Si at high temperatures and act as unwanted dopants. On the other hand, Group IV materials are CMOS compatible but are extremely weak light emitters because of their indirect bandgap.

It has been a longstanding goal of many groups to develop a CMOS-compatible laser source. Ge could fill up this gap due to its unique band structure and compatibility with CMOS.

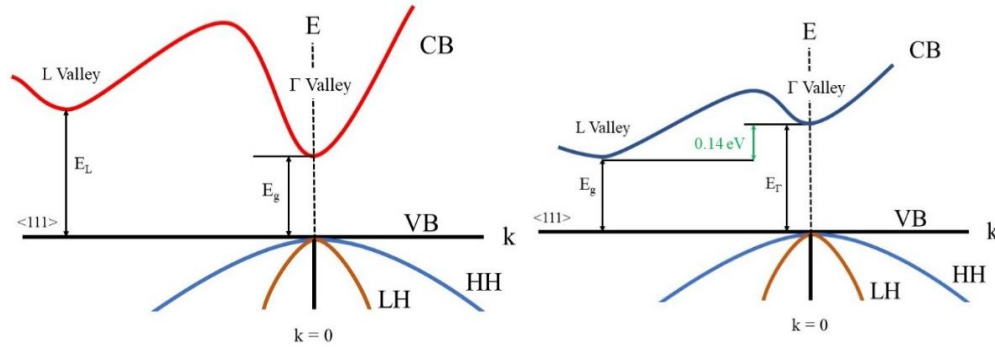


Figure 1.2: (a) Schematic band diagram of a direct bandgap semiconductor; (b) Schematic band diagram of an indirect bandgap semiconductor (Ge)

Figure 1.2 illustrates the schematic band diagram of a direct and an indirect bandgap semiconductor. GaAs is an excellent example of a direct bandgap material; the valence band maxima and the conduction band minimum are at the same crystal momentum (Γ point, or $k=0$). As a result, an electron in the lowest excited state in the conduction band valley in GaAs can lose its energy and drop to the ground state or recombine with a hole

in the valence band maxima by simply emitting that energy as a photon. Photons have almost no momentum, and this process does not require a change in momentum, so momentum is conserved, and the recombination is favorable over other, nonradiative processes. On the other hand, Ge is an indirect bandgap material; the valence band maximum ($k=0$) is at a different crystal momentum than the conduction band minimum. As a result, an electron in one of the lowest conduction band valleys requires significant momentum transfer to recombine with a hole. Unfortunately, photons have very little momentum. Hence, to have optical emission from Si or Ge requires the simultaneous participation of a photon and a phonon, which makes this an improbable and weak process. The result is effectively no light emission from Ge.

Although Ge is an indirect bandgap material, if we look at the band structure in Figure 1.2(b), the energy difference between the valence band maximum and the conduction band minimum at the Γ valley is only slightly larger than the L valley (~ 140 meV). The energy difference between the direct and the indirect valley is so slight that it can be overcome by applying tensile strain or alloying with other group IV materials [9], [15]–[22].

1.2 Direct Bandgap Germanium

The two most common routes to create a direct bandgap are tensile strain [15]–[19], [23]–[26], and alloying Ge with other Group IV materials [27]–[31]. Several research groups have shown direct or nearly-direct bandgap and optical emission from tensile strained Ge both theoretically and experimentally [17], [23], [25], [32]–[35]. Unfortunately, demonstrated lasers required high current density, and the strained Ge showed a tendency to form new dislocations or dark line defects [36], [37].

Many research groups have demonstrated successful epitaxial growth of GeSn [30], [31], [38], [39], but reported lasers only operate cryogenically and with high current densities [22], [40]–[43]. This may be due to the very small effective mass in the GeSn conduction band (CB) at Γ , which produces much stronger confinement energy, pushing the Γ CB valley higher than the L valley and losing the direct bandgap [44]–[49].

The substitutional incorporation of C onto Ge lattice sites offers an additional degree of freedom in these germanium carbides to engineer the band structure. Computational modeling has shown a direct bandgap for a dilute germanium carbide alloy having less than one percent of C substituted into Ge [27], [28], [50]. The C state in $\text{Ge}_{1-x}\text{C}_x$ splits the CB into two different bands, E^+ and E^- . At Γ , the E^- band moves downward below the L valley to create a direct bandgap. In this research, I investigated two different novel approaches to make Ge a direct bandgap material. The first approach is alloying Ge with C; the epitaxial growth of dilute germanium carbide ($\text{Ge}_{1-x}\text{C}_x$) with and without the presence of atomic H and is described in section 1.3. The second approach is by applying a biaxial tensile strain by these of SiN_x stress liners and will be discussed in section 1.5.

1.3 $\text{Ge}_{1-x}\text{C}_x$ and Band Anti-crossing

The idea of dilute germanium carbide came from band anti-crossing in dilute nitrides. Incorporating a small percentage of nitrogen in GaAs resulting in strong band bowing and a surprising *reduction* in the overall bandgap, which was unexpected because GaN has a larger bandgap than GaAs. In-band anti-crossing, a localized impurity state is introduced *above* the bandgap; in the case of GaAs:N and $\text{Ge}_{1-x}\text{C}_x$, it is just above the conduction band minimum. In comparing the GaAs:N and $\text{Ge}_{1-x}\text{C}_x$ systems, Ge lies

between Ga and As in row four of the periodic table, while C is next to N in row two, as shown in Figure 1.3. This means a similar size difference between the As, N, and Ge, C atoms. There is also a similar difference in electronegativity.

IIIA	IVA	VA
Boron (B) $Z = 5$ $A = 10.81$ amu Electronegativity: 2.04 Electron affinity: 26.7 kJ/mol	Carbon (C) $Z = 6$ $A = 12.011$ amu Electronegativity: 2.55 Electron affinity: 153.9 kJ/mol	Nitrogen (N) $Z = 7$ $A = 14.007$ amu Electronegativity: 3.04 Electron affinity: 7 kJ/mol
Aluminium (Al) $Z = 13$ $A = 26.982$ amu Electronegativity: 1.61 Electron affinity: 42.5 kJ/mol	Silicon (Si) $Z = 14$ $A = 28.085$ amu Electronegativity: 1.90 Electron affinity: 133.6 kJ/mol	Phosphorus (P) $Z = 15$ $A = 30.974$ amu Electronegativity: 2.19 Electron affinity: 72 kJ/mol
Gallium (Ga) $Z = 31$ $A = 69.723$ amu Electronegativity: 1.81 Electron affinity: 28.9 kJ/mol	Germanium (Ge) $Z = 32$ $A = 72.63$ amu Electronegativity: 2.01 Electron affinity: 19 kJ/mol	Arsenic (As) $Z = 33$ $A = 74.922$ amu Electronegativity: 2.18 Electron affinity: 78 kJ/mol

Figure 1.3: Difference in atom size and electronegativity between Ge and C is similar to the difference between As and N atoms

When a C atom is substituted into Ge with sp^3 bonds, the new electron state has a spherically symmetric s orbital-like character. Similarly, Ge's conduction band minima at the Γ valley also comes from spherically symmetric s orbitals. The Pauli exclusion principle states that these two states with the same spherical symmetry cannot exist at the same energy simultaneously, so there is a strong repulsion between the conduction band edge and the impurity level above the conduction band edge at the Γ point. This is known as an anti-crossing or an avoided crossing. However, the X and L valleys are not affected as much by the C defect perturbation effect [51]. The addition of C will push the Γ valley down faster than the indirect X or L valleys. With enough C, the E- band will drop below the indirect L valley, making $Ge_{1-x}C_x$ a direct bandgap material [28], [50], [52]. The computational results have shown a direct bandgap on dilute germanium carbide alloy for

nearly one percent substitutional incorporation of C onto Ge. Chapter 3 and 4 of this dissertation will demonstrate the successful growth of $\text{Ge}_{1-x}\text{C}_x$ alloy to validate the computational findings [28], [50], [52].

1.4 Growth and characterization of dilute $\text{Ge}_{1-x}\text{C}_x$

The growth of the $\text{Ge}_{1-x}\text{C}_x$ has been performed on a hybrid source Varian Gen II MBE system using both solid and gas sources. We used the state-of-the-art characterization facilities in the Analysis RSC at Texas State University to characterize the films. We also worked closely with collaborators at the University of Texas at Austin, Seth Bank and Aaron Muhowski, for low-temperature photoluminescence (PL) and secondary ion mass spectroscopy (SIMS) measurements, as well as Rachel Goldman's group at the University of Michigan at Ann Arbor for Rutherford backscattering spectroscopy (RBS).

1.5 Tensile strained Ge

The second approach is applying biaxial tensile strain on Ge waveguides using SiN_x stress liners. Ge may convert to a direct bandgap material under sufficient amounts ($\sim 2\%$) of biaxial tensile strain [16], [17], [32]. As mentioned above, a strong direct bandgap would make Ge an effective light emitter and possible laser material for silicon photonics. The most common way to strain a semiconductor is to grow it on another semiconductor with a different lattice constant.

Ge can be stretched in two directions for tensile strain by growing it on a semiconductor with a slightly larger lattice constant (Figure 1.4). Strain generated in two directions in this manner is known as biaxial tensile strain. Figure 1.5 shows how the band edges are expected to change with the biaxial strain. Ge could be converted into a

direct bandgap semiconductor with between 1.4% and 2% biaxial tensile strain [14], [54]–[56].

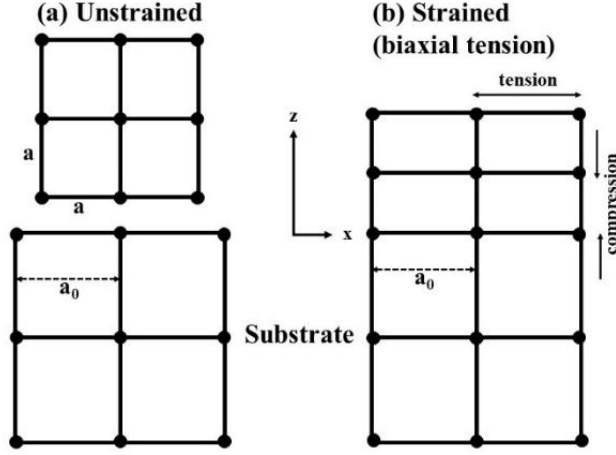


Figure 1.4: Biaxial tensile strain in a crystal. Redrawn from [53].

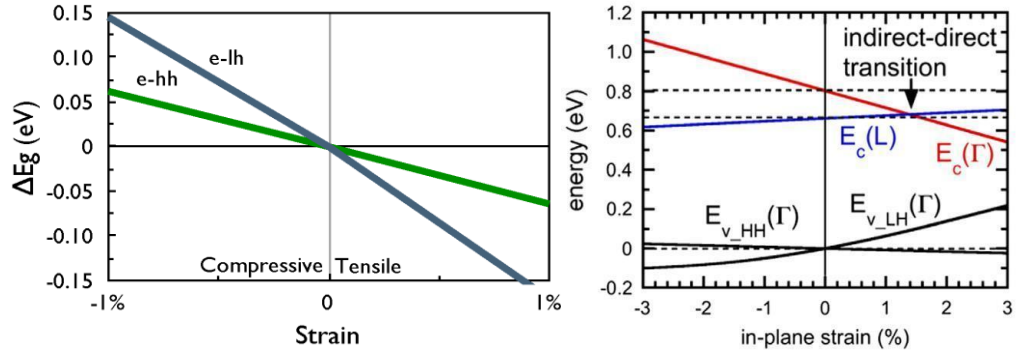


Figure 1. 5: (Left) Calculated change in direct bandgap energy with strain. The bandgap increases with compressive strain and decreases with tensile strain (After [50]). (Right) Simulation of how the band edges change with strain. Negative strain is compressive and positive strain is tensile [14].

Chapter 5 of this thesis focuses on modeling various shapes of Ge waveguide wrapped with a SiN_x stress liner to induce artificial strain on Ge, and the expected laser performance that would result. We calculated optical gain, losses, net gain, and threshold current density to understand whether it is possible to achieve lasing from strained Ge or not.

1.6 Summary

In summary, this work investigated different growth techniques for making a direct bandgap material using Group IV materials, especially Ge-based, for lasers, amplifiers, and compact modulators directly on CMOS. Group IV lasers would be a tremendous advantage in the semiconductor industry for silicon photonics. This thesis is divided as follows: Chapter 2 explains the epitaxial growth techniques of semiconductor thin films and their characterization using various tools. Chapters 3 and 4 primarily focus on the epitaxial growth of Ge and its alloys using two different methods towards direct bandgap material. The band properties, material composition, and crystal quality studied by using different characterization tools at Texas State University will also be reported. Chapter 5 describes simulations of tensile strained Ge to investigate the possible band properties, optical gain, threshold current density, and lasing capability of Ge waveguides at different tensile strains. Finally, Chapter 6 presents the summary of this dissertation and the scope of proposed future research.

2. EPITAXIAL GROWTH AND SEMICONDUCTOR THIN FILM CHARACTERIZATION TECHNIQUES

2.1 Molecular Beam Epitaxy (MBE)

MBE is a commonly used semiconductor material growth tool. It was developed in the early 1970s as a means of growing high-purity epitaxial layers of compound semiconductors. MBE can produce high-quality layers with a very abrupt interface and well controlled thickness, doping, and composition. In MBE, atoms of different elements are deposited directly onto a hot wafer, allowing the arriving particles to migrate to locations that maintain the underlying crystal order of the wafer. There is a movable shutter in front of every element's source to provide strict control over the thickness and composition of different layers. In solid-source MBE, Knudsen effusion cells with ultra-high purity (UHP) solid or liquid source materials supply the elemental atoms by evaporation. In gas source MBE, gas precursors are used instead, allowing a much more versatile supply of precursor gases instead of specific evaporated elements. This work used a hybrid combination of both solid and gas sources. As I will describe in Chapter 3, gas source precursors are very tricky to control. We use a combination of computer-controlled leak valves, pneumatic valves, needle valves, and mass flow controllers (MFC) to control the beam equivalent pressure (BEP) of the gas source precursors. Usually, gas passes through the metal tube, and the tubes are wrapped with heating tape to prevent gas condensation on the pipe's wall. On the other hand, the solid source precursors are relatively easy to control. The BEP is controlled by the thermal heating of that particular material through a Eurotherm PID controller and feedback loop.

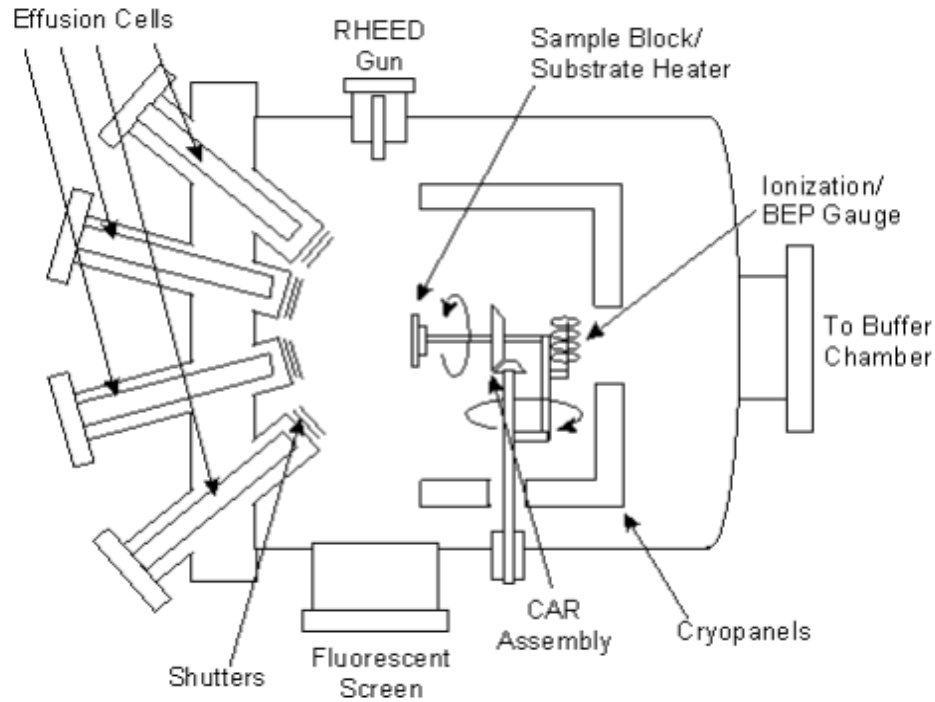


Figure 2.1: Schematic diagram of a Varian Gen II MBE system [57].

The growth chamber of an MBE is always kept under an ultra-high vacuum (UHV) condition. The average pressure inside of a typical MBE growth chamber is $\sim 10^{-10}$ Torr. An ion gauge inside the growth chamber is used to monitor the pressure. The effusion cells are installed in a source flange directed toward the continual azimuthal rotation (CAR) assembly (also known as the substrate manipulator), which holds the wafer for growth. The CAR heats the substrate during growth, and it can rotate the wafer continuously around its azimuth to help improve the uniformity of deposition. Another ion gauge is connected to the CAR to measure the BEP of source materials. Based on the BEP, one can calibrate the growth rate and control the composition during growth. A mass spectrometer or residual gas analyzer (RGA) inside the chamber monitors the gas molecules inside the chamber, both intentional and background impurities. The RGA is also used for leak detection in the MBE system.

Different kinds of vacuum pumps work simultaneously to maintain the ultra-low pressure inside the growth chamber, including turbomolecular pumps, ion pumps, and scroll pumps.

The MBE system we used for this research at Texas State University consists of two ultra-high vacuum chambers and an airlock (load chamber) connected through a buffer chamber. The load lock chamber is isolated from the buffer and growth chamber by a UHV shutter. It can be pumped down and vented to the atmosphere quickly and baked independently from another chamber to evaporate most of the water and hydrocarbons from the wafer before being transferred onto the buffer chamber. The buffer chamber is a UHV chamber ($\sim 10^{-10}$ Torr) where the samples are stored between growths and transferred between other chambers. The buffer contains a heater station where the wafers are baked individually at higher temperatures, up to 400 °C, to remove further contaminants before loading the wafer into the growth chamber.

At Texas State University, the Wistey group (EPEE Lab) owns two MBE systems: one for solid source III-V MBE and another for Group IV materials. The III-V MBE is a Veeco Gen 930, containing Ga, In, and Al for group III materials and As, Sb, and P source for group V materials. An additional Ge cell allows easy combinations of III-V and Group IV growth, including n-doped Ge under an arsenic flux. The Group IV MBE is a Mod Gen II Varian MBE, and it has eight source cells, two of which are gas injectors. We have solid-source Ge as well as digermane and trisilane gas sources, with the flexibility to add custom precursor gases and do mixtures during growth. This MBE was rebuilt specially for gas-source Group IV growth, including a corrosive-rated Pfeiffer 1200C turbomolecular pump and a substrate manipulator capable of reaching 1200 °C.

The gas manifold allows maximum flexibility in the growth of different materials. This manifold can accurately and precisely control extremely low flow rates into the vacuum of the MBE chamber, including mixing multiple gases through the use of mass flow controllers and computer-controlled leak valves. This MBE also has a thermally cracked hydrogen source where the surface of the wafer can be cleaned using highly reactive pure atomic hydrogen. Hydrogen cleaning is typically used before regrowth in MBE when the surface needs to be completely oxygen and carbon-free after exposure to chemics or other fabrication processes. We added a platinum membrane hydrogen purifier to eliminate any traces of water or oxygen in our hydrogen.

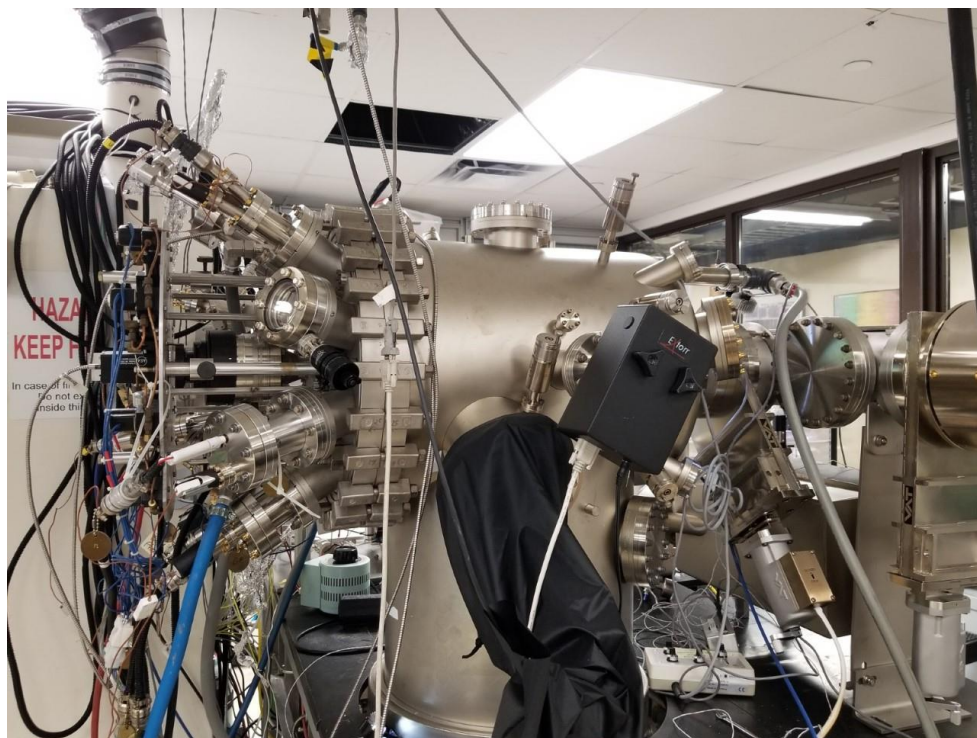


Figure 2.2: Wistey Group: EPEE Lab Varian Gen II Group IV MBE system

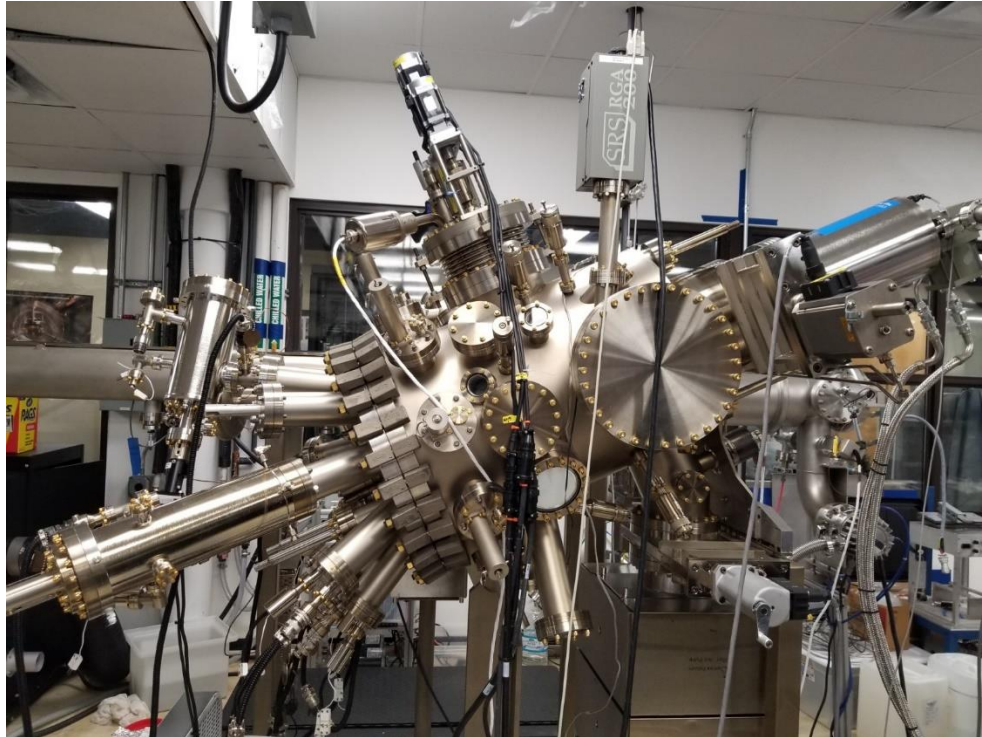


Figure 2.3: Wistey Group: EPEE Lab Veeco Gen 930 III-V MBE system

2.2 X-Ray Diffraction (XRD) System

X-ray diffraction (XRD) is one of the most fundamental studies used to characterize the structure and composition of materials. English physicists Sir William H. Bragg and his son Sir William L. Bragg developed a relationship $n\lambda = 2d\sin\theta$ in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence. The variable d is the distance between atomic layers in crystal, and the variable λ is the wavelength of the incident X-ray beam; n is an integer. This observation is an example of X-ray wave interference, commonly known as X-ray diffraction (XRD). The father-son duo was awarded the Nobel prize in physics in 1915 for their groundbreaking discovery in determining crystal structures.

In XRD, the crystal works as a 3D diffraction grating. Therefore, by adjusting the source and detector positions relative to the sample/crystal, a 3D array of diffraction

maxima can be probed. These diffraction maxima are also known as diffraction spots.

Each diffraction spot is related to the reciprocal lattice created by periodic crystal planes.

Thereby the diffracted X-ray beam is detected as a 3D reciprocal lattice.

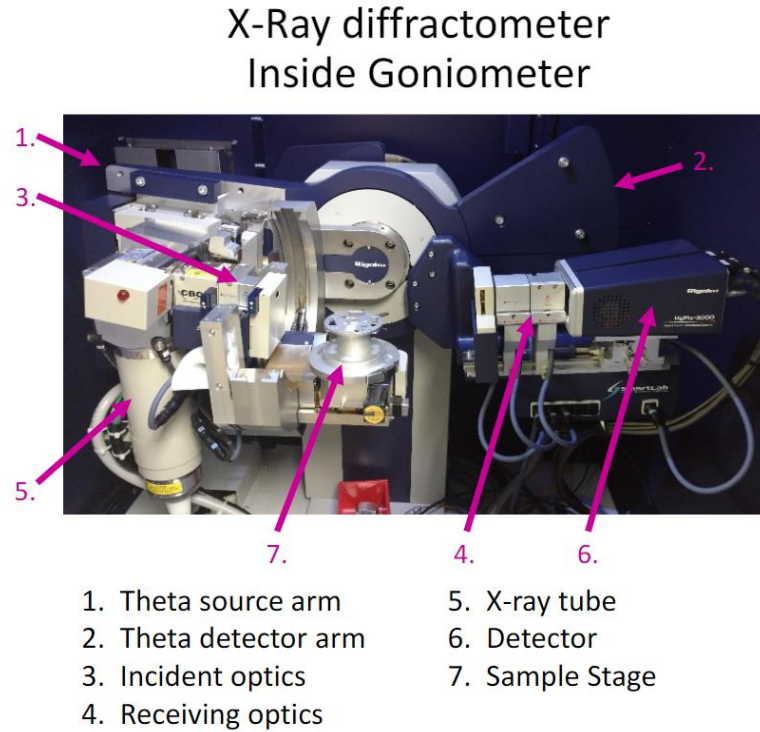


Figure 2.4: Inside of the Rigaku XRD system at Texas State University (courtesy TXST SRO)

A Rigaku SmartLab XRD system was employed as shown in Figure 2.4 to study the structural properties of the films deposited during this dissertation research. The wavelength used for the measurements was $\text{Cu K}\alpha \lambda = 1.5418 \text{ \AA}$, and the X-ray tube operates at 40 kV and 44 mA. In addition to the standard $\omega/2\theta$ scan, several other scans were employed to study the crystal quality and strain on the thin film. To investigate the quality of crystal and defects in the samples, we also performed rocking curve measurements: ω scan of a specific plane. An extended rocking curve between $2\theta = 65^\circ$ to 67° of $\text{Ge}_{1-x}\text{C}_x/\text{Ge}/\text{GaAs}$ revealed the (004) planes of these materials, which was often used as a quick determination of crystal quality. To observe whether the $\text{Ge}_{1-x}\text{C}_x$ layer is

strained with the substrate or not, reciprocal space mapping (RSM) was performed around the (115) asymmetric plane.

In the $2\theta/\omega$ measurement, the direction of the scattering vector $\mathbf{K}$ is fixed, and only the length of $\mathbf{K}$ is changed. If the measured lattice planes are parallel to the sample surface, the incident X-ray beam is diffracted by the lattice planes, which direction matches the scattering vector. In all XRD measurements, it is necessary to carefully adjust the beam alignment and angles to identify reciprocal lattice points in the scattering plane. This operation is termed a tilting axis adjustment.

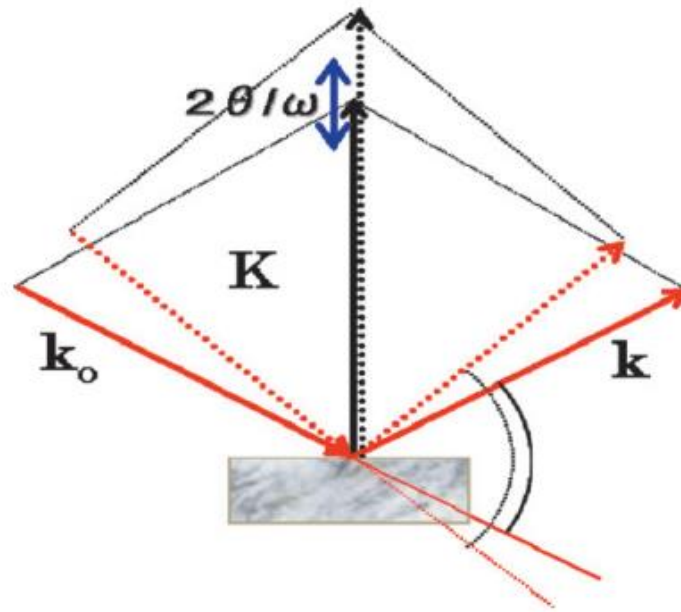


Figure 2.5: Rocking curve measurement [58].

The reciprocal space mapping measurement records diffraction intensity distributions by scanning the diffraction angle and sample rotation axes and plots the result in the reciprocal space. The reciprocal lattice map can provide information on the crystal structure, crystal orientation relationships, strain relaxation, and crystallinity of the sample. The central coordinates, shapes, and positional relationships of the reciprocal

lattice points appearing in two-dimensional (or three-dimensional) data plotted in the reciprocal space provide a wide range of information on the crystal structure.

2.3 Raman Spectroscopy

Raman scattering is an inelastic light scattering process that involves the absorption of high-intensity laser light by a polarizable sample. It causes a transition from the ground electronic state to a virtual state. The energetic system then goes through a radiative relaxation via transition from the virtual state to a lower energy electronic state by spontaneous emission of a phonon and either creating (Stokes process) or absorbing (anti-Stokes process) a vibrational quantum of energy (a phonon in crystal) [59]. The emitted photon has a shifted energy from the incident excitation photon energy ($\hbar\omega_L$) by the phonon energy. In conventional Raman spectroscopy, only the Stokes process is studied because of its higher intensity. The Raman spectra of intensity versus emission photon energy exhibit peaks at energy $E_s = \hbar\omega_s$ which corresponds to the vibrational energies involved in the process[60]. Note that in Raman spectroscopy, a change in vibration energy is traditionally reported as the inverse of the wavelength, such as $1/\lambda$ (cm^{-1}) = $\Delta E/\hbar c$, where

$$\Delta E = \hbar\omega_L - \hbar\omega_s.$$

Not all lattice vibrations produce Raman scattering, but only those that satisfy the Raman selection rule [60], conserving energy and momentum: [61],

$$\hbar\omega = \hbar\omega_1 - \hbar\omega_2 \quad (2.1)$$

$$\vec{k} = \vec{q} = \vec{k}_1 - \vec{k}_2 \quad (2.2)$$

$\hbar\omega$ and $\hbar k$ represent energy and momentum, respectively, where ω and k are frequency and wave vectors of crystal excitation respectively. Since Equation (2.2) is a vector sum,

the magnitude of k depends on the direction of scattering. For forward scattering, $|k|$ is minimum. For first-order inelastic scattering such as Raman scattering, the difference in wave vectors k_1 and k_2 is small, and the range of q is very small. This is only possible at the zone center of the first Brillouin zone. Thus, Raman scattering will only take place if the optical vibration is zone centered or $k=0$. A complete version of Equation (2.3) can be given by [61],

$$k = \vec{q} = \vec{k}_1 - \vec{k}_2 + \vec{K} \quad (2.3)$$

Where K is the reciprocal space vector or the separation between zone centers, that means a Raman scattering will occur when the difference between the wave vectors of two excitations is very small and close to the zone center so that the momentum is conserved. It is important to note that the zone center optical vibration refers to retaining the crystal's full symmetry and having non-zero energy at the zone center [60].

In this research, we used a Horiba Scientific LabRAM HR Evolution visible micro-Raman system. Figure 2.11 shows the image of the visible Raman system at Texas State University. The visible system is equipped with three class 3B lasers emitting at 532 nm, 633 nm, and 785 nm, with maximum intensities of 103 mW, 20.3 mW, and 84.9 mW, respectively, at the laser head. The laser is focused onto the sample through a 50x microscope objective. A standard silicon wafer is used to calibrate the system before taking any measurements. This dissertation used a 532 nm laser with a 10% ND filter to reduce the beam power and avoid sample heating. The penetration depth of 532 nm light in Ge is 19.5 nm, which is enough to penetrate the cap layer but not enough to pass the 150 nm active layer. Horiba Scientific LabSpec 6 software was used to collect and analyze the spectra.



Figure 2.6: Horiba LabRAM HR Evolution Raman system. (Photo courtesy Horiba Scientific)

2.4 Atomic Force Microscope (AFM)

AFM microscopes are among the best solutions for measuring the nanoscale surface metrology and material properties of samples. A conventional compound light microscope is limited to a maximum sample magnification of approximately 1000 $\times$, a limit imposed by the diffraction of visible light. This provides a resolution of approximately 0.2 μm , which means it is impossible to distinguish two points that are closer together than around 200 nm. These bottlenecks were resolved with the genesis of advanced technologies like scanning electron microscopy (SEM) and atomic force microscopy (AFM). AFM microscopes are based on a non-optical surface interrogation technique using a physical probe to measure the surface features of samples with atomic resolution for lateral and height measurements [62].

AFM microscopes operate by bringing an extremely sharp tip on a flexible cantilever in contact with the surface. The cantilever is rastered across the surface to create a height map. As the tip contacts the surface, the cantilever bends, and the bending

is detected using a laser diode and a split photodetector. This bending is indicative of the tip-sample interaction force. If the tip is atomically sharp and the surface is clean, AFM can image individual atoms on the surface. The tip is pressed into the surface in contact mode, and an electronic feedback loop monitors the tip-sample interaction force to keep the deflection constant throughout raster scanning. Tapping mode limits the contact between the sample surface and the tip to protect both from damage. In this mode, the cantilever is caused to vibrate near its resonance frequency. The tip subsequently oscillates up and down at or near its resonant frequency. This motion is changed by attractive or repulsive interactions as it comes near the sample. A feedback loop is used in a similar fashion to contact mode, except it keeps the amplitude of this tapping motion constant rather than the quasistatic deflection. By doing so, the topography of the sample is traced line by line.

The AFM used for this dissertation was Bruker dimension ICON, as shown in Figure 2.7. The measurements were performed in soft tapping mode using the non-conductive HQ.NSC14/Al BS tip with a spring constant of 5 N/m. Various operating parameters can control the AFM imaging; the proportional/integral gain is the most important one. The gain parameters determine the sensitivity of control over the surface features. Depending on the gain parameters, the noise level can be high or low. To get accurate results, the gain parameters must be set in a way so that the trace and retrace lines overlap. In the Bruker ICON system, auto-tuning is also a user-friendly option to adjust the gain parameters. The cantilever setting system automatically optimizes the rest of the scan parameters for the most accurate scan during the auto-tuning. Various parameters can be obtained from the AFM, but in this dissertation, AFM was used to

measure the root mean square (RMS) roughness of the thin film. RMS roughness was calculated by the system using the equation

$$R_q = \sqrt{\frac{1}{L} \int_0^L |Z^2(x)| dx} \quad (2.4)$$

Where $Z(x)$ is the function that describes the surface profile analyzed in terms of height (Z) and position (x) over the evaluation length L .

1. Scan Head
2. Vacuum Sample Stage
3. Probe Holder Base
4. Objective & Camera
5. Vacuum toggle switch
6. Photodetector signal display



Figure 2.7: Bruker Dimension ICON AFM system at Texas State University. (Courtesy TXST SRO)

2.5 Other Techniques

Besides MBE, XRD, Raman, and AFM, several other tools were also used to characterize the materials in this dissertation. A Bruker surface profilometer was used to measure film thicknesses to calibrate growth rates. X-ray photoelectron spectroscopy (XPS) was used to analyze the thin film composition and identify unwanted molecules on the film. The Nexsa XPS at Texas State University has the capability to sputter etch the sample, which allows measurement of the composition as a function of depth into the sample.

PL was used to measure the optical emission from the $\text{Ge}_{1-x}\text{C}_x$ active layers. The total emission from the samples was measured using a micro-PL setup. The samples were

held in a temperature-controlled cryostat with a ZnSe window. The sample was optically pumped by a 1 W, 808 nm laser modulated at 10 kHz. The pump laser light was passed through a 3 μm dichroic beam splitter and focused onto the sample using an all-reflective parabolic mirror through an antireflection-coated (3-5 μm) Si window onto liquid nitrogen cooled InSb detector. The Si window was used to filter laser light. The detector signal was demodulated by a lock-in amplifier and recorded for each temperature of the sample. For weak PL signals farther into the infrared, emitted light was passed into a Fourier transform infrared (FTIR) spectrometer after being reflected from the dichroic beam splitter. The FTIR is run in the step-scan mode to reduce infrared background dramatically. The input power was approximately 240 mW, focused into an ellipse of $200 \times 40 \mu\text{m}^2$. The PL measurements were carried by Aaron Muhowski, a postdoc working for Seth Bank's and Dan Wasserman at the University of Texas at Austin.

A linear 4-point probe was used to measure the sheet resistance and the resistivity of the thin film, and the contactless mobility system was used to measure the mobility. Finally, the Cronus system was used to perform C-V measurements and quantify the defects on the thin film.

3. GROWTH OF DILUTE GERMANIUM CARBIDE USING CBr_4 AS A PRECURSOR FOR CARBON

3.1 *Prior Literature*

Only a few groups have studied the theory and growth of $\text{Ge}_{1-x}\text{C}_x$. Even fewer grew $\text{Ge}_{1-x}\text{C}_x$ epitaxially using MBE or CVD, with various growth temperatures reported from 200 – 600 °C [52], [63]–[71] and C fraction x varying between 0 to 10% [63], [69], [70]. Due to the low solid solubility of C in Ge, past attempts showed poor C incorporation onto crystal lattice sites, and growth was often dominated by C-C defects and other types of C cluster in the Ge and/or on the film surface.

Another common reason for the formation of C-C defects in previous attempts was the use of sources of carbon that emitted C clusters, such as pyrolytic graphite filaments, rod-fed carbon, or destructive high energy sources such as e-beams [63], [68], [69], [71]–[75]. For example, Kolodzey et al. showed that C triplets are the most common species evaporated from high-purity graphite sources [76]. The problem is that C atoms sitting on the Ge surface can easily reduce their energy by bonding to each other, causing a C-C defect in the film. Gall et al. predicted a 170 meV decrease in formation energy per C atom when C bonds with one other C, and an 800 meV decrease when bonding with two C atoms [65], as shown in Figure 2.1. This means clusters of C are more stable than substitutional C; once formed, C-C split interstitial pairs and similar defects are unlikely to dissociate during growth or annealing. These C clusters form mid-gap trap states that can act as non-radiative recombination centers in $\text{Ge}_{1-x}\text{C}_x$. Okinaka et al. reported MBE-grown $\text{Ge}_{1-x}\text{C}_x$ epilayers on Si substrates using an arc plasma gun [77]. They reported getting up to 2% of C incorporation with Ge as shown by XRD measurements, and a

significant band bowing was observed, i.e. the bandgap was smaller than would be expected from a linear interpolation of the alloy endpoints (Vegard's Law). The sublimation of pyrolytic graphite filament (PGF) [76] or electron-beam (EB) evaporation of a rod-fed C source [78] was used to generate the molecular C beam. Recently, an investigation on $\text{Ge}_{1-x}\text{C}_x/\text{Ge}(001)$ epilayers using a hyperthermal C beam from a new ultrahigh vacuum Kaufman type broad ion-beam source has been reported [66]. They achieved a C concentration of 2% at growth temperature from 200 °C to 500 °C.

Most reported experimental studies focused on the direct growth $\text{Ge}_{1-x}\text{C}_x$ on Si(001). In this case, the substrate-induced compressive strain led to relaxation beyond a few monolayers of growth [63], [70], [71], [75]. Relaxed $\text{Ge}_{1-x}\text{C}_x/\text{Si}(001)$ thick layers exhibit highly defective microstructure containing a large concentration of misfit dislocations, which act as a sink for incorporated C. Osten et al. used Sb as a surfactant to prevent Stranski-Krastanov 3D island formation during the growth of $\text{Ge}_{1-x}\text{C}_x$ film on Si(001) [71], [75]. Yang et al. reported low temperature (~ 200 °C) MBE-grown $\text{Ge}_{1-x}\text{C}_x$ alloys on Si(100) and Ge substrates with C concentration reported between 0 to $\sim 10\%$, estimated by Rutherford backscattering spectroscopy [78]. The microstructure showed an increase in planar defect (stacking fault and microtwins) density with increasing C concentration. X-ray diffraction showed that the lattice parameter decreased with increased C concentration and that a maximum of 1% C was incorporated substitutionally in Ge. Though Raman data did not reflect any clear evidence of a peak at 530 cm^{-1} corresponding to Ge-C, films with nominal C concentrations greater than 2 to 3% showed clear evidence for amorphous C. The authors concluded that the nominal C in excess of about 2-3% remains on the surface as amorphous C and plays an important role in 3D

island and defect formation [78]. Later, the same group saw the Ge-C local mode in Raman shift near 530 cm^{-1} for the samples grown on Ge(100) substrates [79]–[81].

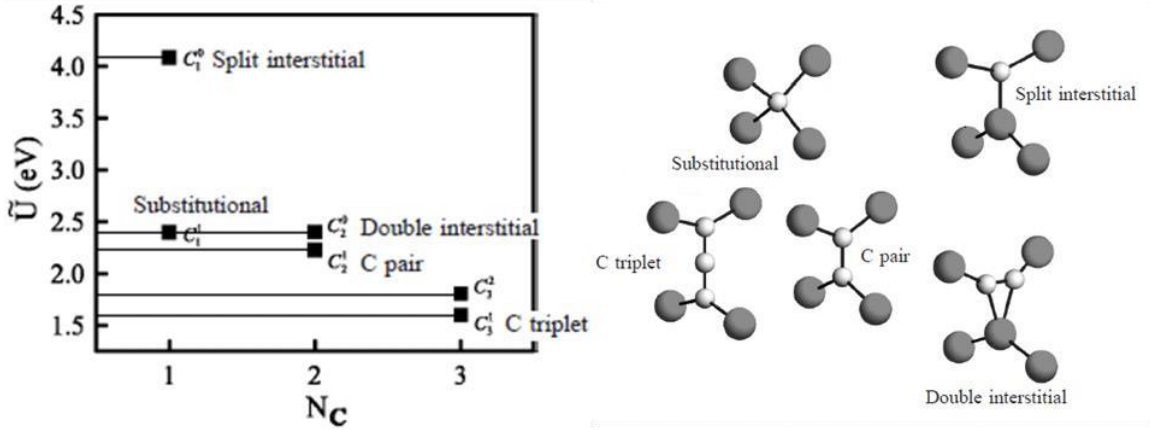


Figure 3.1: Calculated formation energies of various C configurations. From ref [65].

A few other groups later were able to show substitutional C in a $\text{Ge}_{1-x}\text{C}_x$ using Raman spectroscopy. They also identified a local mode near 530 cm^{-1} coming from Ge-C vibrational state [68], [69], [74], [79], [82]. Park et al. concluded that “it is not possible by MBE to obtain fully substitutional C incorporation in $\text{Ge}_{1-x}\text{C}_x$ (001) alloys” using traditional Ge and C source materials [69]. Other growth methods like pulsed laser deposition or ion implantation produce amorphous [83] or polycrystalline [67] films and phase segregation with C precipitates. There are few reports of optical emission from the $\text{Ge}_{1-x}\text{C}_x$, although Dashiell et al. observed near-band-edge photoluminescence (PL) at 735 meV assisted by transverse acoustic (TA) photons [74], [84].

To limit the possible C defects, in this work, we provided C to the growth surface using a different precursor, CBr_4 as a source of C. CBr_4 is commonly used as a p-type dopant in GaAs growth but not typically used for Group IV growth. The CBr_4 was supplied to the chamber through a cold gas injector attached to the MBE system. Some of the CBr_4 thermally cracks on the substrate surface and produces atomic C and Br_2 . The

Br_2 evaporates from the surface, leaving the lone C atom to bond with Ge. For the Ge source, 6N pure Ge was evaporated from a Knudsen trumpet-style effusion cell. For the work described in this Chapter, I grew and characterized $\text{Ge}_{1-x}\text{C}_x$ thin-film grown at several growth temperatures. RHEED, AFM, XRD, Raman, and PL were used to characterize and show the successful incorporation of C into Ge crystal lattice sites.

3.2 New Precursor: CBr_4

As a solid, carbon tetra-bromide (CBr_4) is a monoclinic crystalline material with a boiling point of 189.5 °C. It slowly sublimates at room temperature, with a modest vapor pressure of about 1 Torr at 300K, which is useful for MBE. In this dissertation, we used CBr_4 as the precursor gas for C. There are three main reasons for choosing CBr_4 over other sources of C. First, it does not damage the wafer surface. Second, it has a low cracking temperature compatible with $\text{Ge}_{1-x}\text{C}_x$ growth. Finally, it deposits individual atoms rather than clusters of C on the growth surface. In addition, research-grade pure CBr_4 can be purchased commercially, saving a significant amount of time for precursor synthesis.

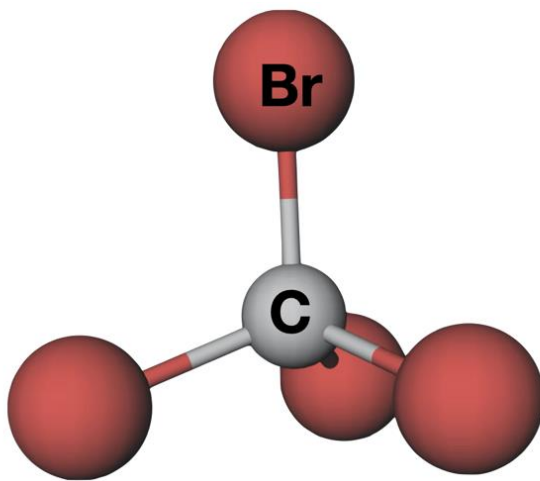


Figure 3.2: Chemical structure of carbon tetra-bromide (CBr_4).

3.3 Controlling Gas Precursor

Controlling gas precursors is very tricky as they are not as well behaved as solid precursors. CBr_4 in particular comes with its own set of challenges. With its low vapor pressure, the sublimated CBr_4 is very sticky and wants to stick to the walls of the tube. To prevent that issue, we covered all gas lines with heating tape. To control the beam equivalent pressure (BEP), we used a combination of a computer control leak valve, needle valve, pneumatic valve, all-metal valve, and mass flow controllers (MFC). Two Baratrons were used to monitor the pressure inside the metal pipes. Constant reading on Baratron is also an indication of continuous gas flow to the chamber.

As I mentioned above, CBr_4 is a sticky gas; hence getting the flow of CBr_4 to reach a constant BEP at the start of the growth was challenging. To stabilize the CBr_4 BEP, we initially overflow the gas to the growth chamber by opening the needle valve more than it should be. Once the gas flow stabilizes, we slowly dialed down the needle valve to its original position. This entire process takes 45 minutes to 1 hour. The gas flow stabilization was recorded using Molly EpiTrend.

Hydrogen was the second gas we used during the growth to clean the native oxide layer. Since the Hydrogen atom is very small in size and extremely reactive, we used an extra layer of protection during the growth. The hydrogen cylinder is connected to the mainline through a two-stage controller to prevent accidental overflow. Before hydrogen goes into the chamber, we flow it through the platinum membrane hydrogen purifier to eliminate any traces of water vapor or oxygen that comes with the hydrogen.

3.4 Growth Techniques

As I mentioned before, CBr_4 and 6N pure Ge were used as precursors for the epitaxial growth of $\text{Ge}_{1-x}\text{C}_x$ using a hybrid source MBE. This section discusses growth techniques.

I used a hybrid source Varian Mod GEN II MBE system to perform the growth. The MBE operates in an ultra-high vacuum condition, which offers a large mean free path for the evaporated materials, and the substrate surface remains ultra-clean. During the growth of an alloy in an MBE system, the fluxes of solid source elements can be controlled with very high precision to achieve the correct ratios of constitutive elements in the epitaxial layers. In addition, MBE is a slow growth process (on the order of 1-2 μm per hour), allowing it to have the control needed to grow high-quality thin structures.

The substrate manipulator thermocouple required calibrating before growth. The substrate temperature is normally measured using a C-type thermocouple behind the wafer on the substrate manipulator. However, the thermocouple does not directly contact the wafer, so the thermocouple reading can vary from the actual substrate temperature by 100 °C or more. Furthermore, the contact between the sample and the silicon backing wafer may vary, especially if there is any dust or previous growth material between the sample and the backing wafer, further changing the thermocouple reading. To measure the temperature accurately, we had planned to use an optical thermometry system (k•space BandiT) through a viewport. Unfortunately, BandiT was not working in time for this work. Therefore, we used the melting point of indium dots to calibrate the thermocouple and measure the growth temperature accurately in this study. Indium droplets were placed on a quarter of a 3-inch GaAs wafer, from center to edge, during the

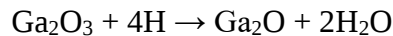
calibration process. The wafer was then loaded into the MBE and heated slowly until the indium melted. The melting temperature of each droplet was observed through the viewport. We noticed a 7 °C temperature difference in melting point between droplets at the center (hotter) and the edge (colder) of the substrate. The thermocouple read the correct temperature at room temperature, and the correction was assumed to be approximately linear as follows:

$$T_{sub} = \frac{TC - T_R}{TC_{In} - T_R} * (T_{In} - T_R) + T_R \dots \dots \dots (1)$$

where T_{sub} , TC , TC_{In} , T_{In} and T_R are the actual substrate temperature, thermocouple reading during growth, the melting point of indium thermocouple reading, the actual melting point of indium, and the room temperature, respectively. Unless otherwise noted, growth temperatures in this work were corrected from thermocouple temperatures using the technique above. Finally, we used chilled water to cool the MBE system instead of traditional liquid nitrogen cooling to avoid the gas condensation into the growth chamber wall.

3.4.1 Hydrogen Cell and Atomic H Cleaning

Immediately before each growth, we used atomic hydrogen to clean the native oxide from the GaAs substrate. Atomic hydrogen cleaning has been shown to be effective for preparing As-rich surfaces on GaAs substrate [85]–[87]. GaAs must typically be heated up to 580 °C under an As-overpressure to remove Ga_2O_3 prior to epitaxial growth. However, if GaAs is exposed to hydrogen radicals, Ga_2O_3 becomes Ga_2O , which is volatile at 400 °C, as indicated by the reaction –



It has been shown that such hydrogen cleaning of GaAs produces an As-rich surface without an As-overpressure during heating [87]. The atomic hydrogen was generated by a Veeco Atomic Hydrogen Source (AHS) cell with a tungsten filament heated above 2250 °C to give approximately 10% hydrogen cracking efficiency. The operating current and voltage were 8.5 A and 22.5 V, respectively. A Sorenson DC power supply powered the cell, and it operates in current mode. Based on the manufacture specifications, 8.5 A produces nearly 2250 °C. Figure 3.3 shows the schematic diagram of the cell.

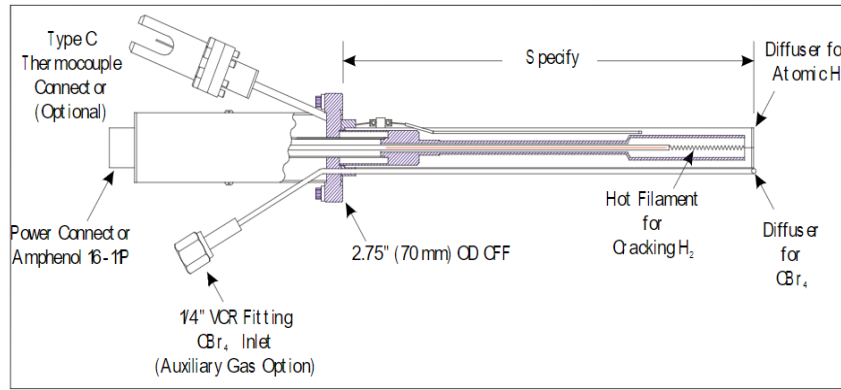


Figure 3.3: Schematic diagram of an Atomic H cell. (Source: Veeco AHS manual)

3.5 Experimental

3.5.1 Germanium carbon epitaxial growth process

The $\text{Ge}_{1-x}\text{C}_x$ film were grown on a quarter of a 3-inch epi-ready GaAs wafer baked in the load chamber overnight at 200 °C. Before starting the oxide desorption, the wafer was baked one more time on a heating station at 400 °C for 1.5 hours. Finally, the oxide removal was performed inside the growth chamber under a flux of thermally cracked H at $T_{\text{sub}} = 406$ °C for 20 minutes. Sharp 2×4 diffraction patterns in the high-energy electron diffraction (RHEED) (not shown) indicated the surface was essentially free of oxides. Germanium (Ge) was deposited from a previously calibrated Knudsen source at ~ 3 nm/min, and the carbon (C) was deposited from a CBr_4 gas source. We also

noticed indium dots melted at substrate temperatures 5 °C colder when the H cell was hot with its shutter open, indicating 5 °C of sample heating by the hot H cell. During these growths, we kept the H₂ cell hot, but the shutters were closed.

Before growing the active layer of Ge_{1-x}C_x, we grew 90 nm of Ge as a buffer layer at 406 °C. RHEED showed a sharp 2×2 reconstruction (not shown), which indicated smooth 2D growth of Ge, and X-ray rocking curve analysis confirmed fully strained buffer layers (not shown). Following the buffer layer, we deposited 170 nm Ge_{1-x}C_x for the active layer. Due to its low cracking efficiency and higher sensitivity in the beam flux ion gauge, the BEP reported by the ion gauge for CBr₄ 4.02×10^{-7} Torr was higher than that of Ge during the growth 3.01×10^{-7} Torr even though the targeted composition of C was much smaller (~1%). In-situ RHEED and ex-situ AFM, XRD, and Raman spectroscopy were used to analyze the film surface, crystal quality, and composition. Finally, all growths were concluded with a 10 nm Ge cap layer grown at 401 °C to aid with carrier confinement for later PL. X-ray reciprocal space maps confirmed that the buffer layer and Ge_{1-x}C_x were fully coherent, without relaxation.

3.5.2 RHEED and AFM

RHEED was used to monitor real-time surface reconstruction during growth. The growth temperature of the Ge buffer was consistent for all samples, and we observed a sharp, 2×2 streaky RHEED pattern indicating smooth, 2D growth. For the Ge_{1-x}C_x active layer, the observed evolution of RHEED patterns depended on the substrate temperature and CBr₄ flux. At 215 °C substrate temperature, the 2×2 reconstruction is a stable and streaky RHEED pattern throughout the growth, indicating 2D layer growth on the surface; this means we should expect a smooth surface with very low root-mean-square

(RMS) roughness. However, for higher growth temperatures (270 °C and 324 °C), the initial few monolayers (ML) showed 2×2 streaky patterns but slowly became spotty, indicating a rough surface. Figure 3.4 (a)-(c) shows RHEED patterns observed during the growth of $\text{Ge}_{1-x}\text{C}_x$ at various temperatures.

We did an ex-situ AFM analysis to understand the RHEED results better and found that $\text{Ge}_{1-x}\text{C}_x$ film grown at 215 °C exhibited very low surface roughness of 0.63 nm RMS over a $5 \times 5 \mu\text{m}$ scanning area. Samples grown at 270 °C and 324 °C showed significantly higher RMS roughness of 8.56 nm and 7.53 nm, consistent with the RHEED results.

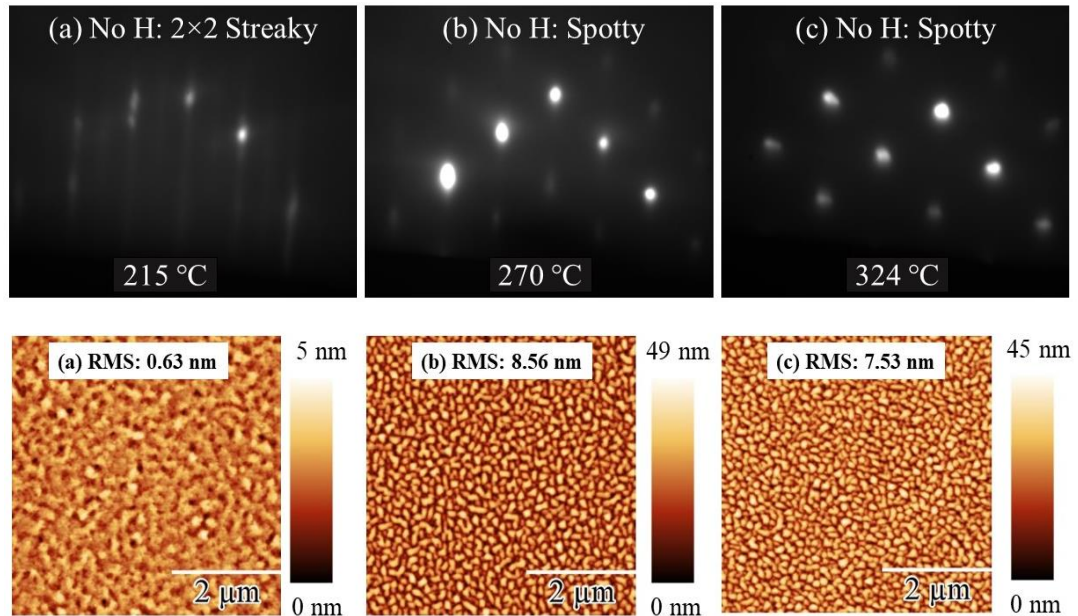


Figure 3.4: (a-c) RHEED image during $\text{Ge}_{1-x}\text{C}_x$ active layer grown at 215 °C, 270 °C, and 324 °C, respectively. (d-f) AFM image of $\text{Ge}_{1-x}\text{C}_x$ active layer grown at 215 °C (cap layer), 270 °C (cap layer), and 324 °C (no cap layer), respectively.

3.5.3 X-ray Diffraction

To see whether the surface profiles correlated with composition and crystal quality, high-Resolution X-ray diffraction (HRXRD) couple scans were measured on the symmetric (004) plane. Figure 3.4 shows the (004) $2\theta/\omega$ scans of $\text{Ge}_{1-x}\text{C}_x$ as a function of

growth temperature. All sample peak positions were compared with baseline undoped Ge grown at $T = 433\text{ }^{\circ}\text{C}$. The sharp peaks at 66.05° correspond to the GaAs substrate. The Ge-C peaks were observed at higher diffraction angles, consistent with tensile strain, which is expected from the growth of $\text{Ge}_{1-x}\text{C}_x$ with a smaller lattice constant than the underlying GaAs substrate. Using a Lorentz fit, we found that the peak position of the Ge-C (004) plane shifts by 0.23° , 0.24° , and 0.26° towards the larger angle at a respective growth temperature of $215\text{ }^{\circ}\text{C}$, $270\text{ }^{\circ}\text{C}$, and $324\text{ }^{\circ}\text{C}$ signifying increased substitutional C incorporation with increasing growth temperature. Using Global Fit software to fit the data, the substitutional C percentage was found to be roughly 0.72-0.75% for all three samples. Interestingly, the Ge-C peak starts to shift to smaller angles if we keep increasing the growth temperature. It eventually vanishes after $379\text{ }^{\circ}\text{C}$ (not shown), consistent with previous reports of the segregation of C at higher growth temperatures. The lowest full width half maximum (FWHM) of 0.05° was observed for the sample grown at $215\text{ }^{\circ}\text{C}$ (Figure 3.5). Sharp Pendellösung fringes on the same sample confirmed sharp interface boundaries and a smooth surface, consistent with the RHEED and AFM results. With the increasing growth temperature, the $\text{Ge}_{1-x}\text{C}_x$ diffraction broadens, with a maximum FWHM of 0.15° at a growth temperature of $324\text{ }^{\circ}\text{C}$ (Figure 3.6). It is noticeable that the Pendellösung fringes begin to disappear at higher growth temperatures, consistent with the comparatively rough surface and again consistent with RHEED and AFM.

Taken together, we interpret the RHEED, AFM, and XRD data as indicating $215\text{ }^{\circ}\text{C}$ is the suitable temperature to grow good quality $\text{Ge}_{1-x}\text{C}_x$ films.

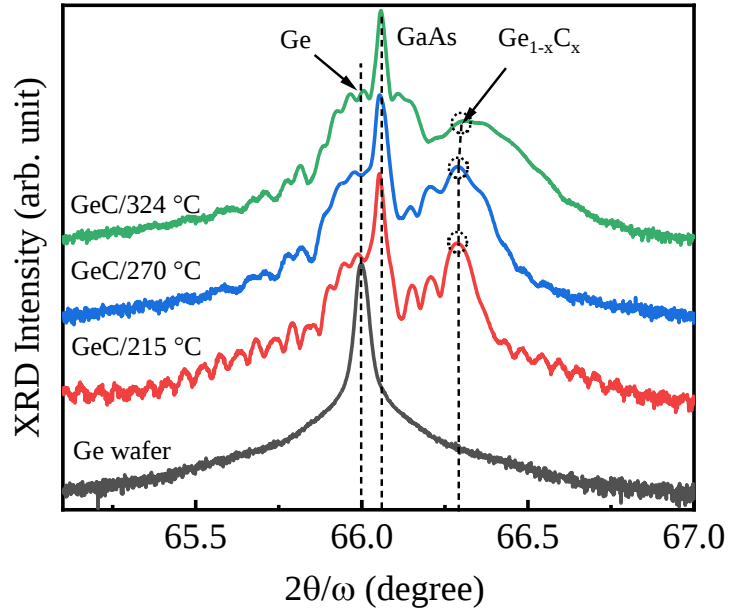


Figure 3.5: $\text{Ge}_{1-x}\text{C}_x$ X-ray couple scan shows increasing tensile strain from C but significant broadening at higher growth temperatures.

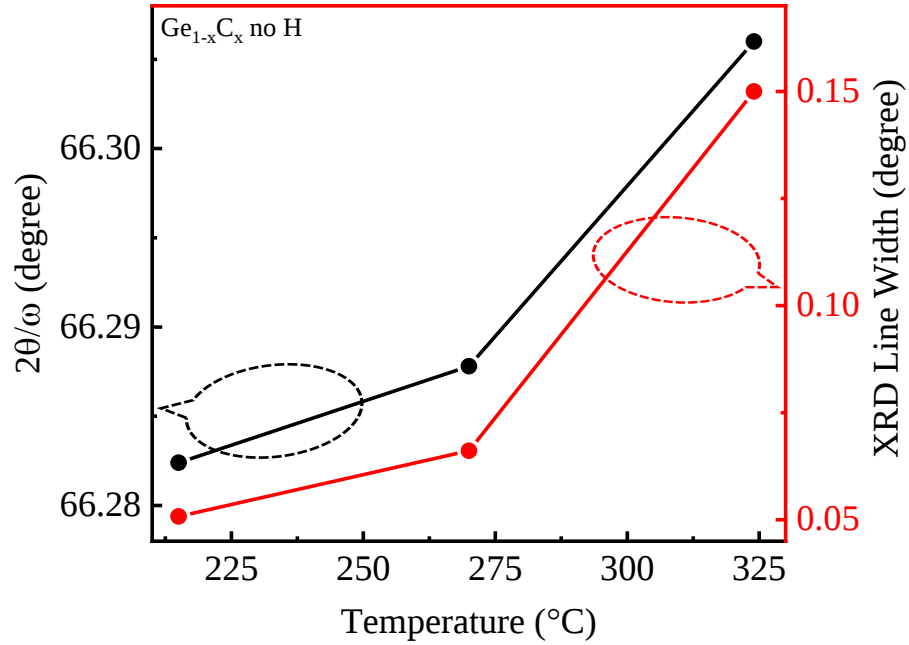


Figure 3.6: Change in X-ray FWHM and 2θ with temperature

Reciprocal space mapping (RSM) was performed on all samples around the asymmetric (115) reflection from $\text{Ge}_{1-x}\text{C}_x$ layers to look for relaxation. Figure 3.7 shows the RSM of $\text{Ge}_{1-x}\text{C}_x$ grown at 215 °C, where the substrate and the film peaks are perfectly

aligned with Q_x (reciprocal spacing parallel to the surface), indicating the Ge buffer and $\text{Ge}_{1-x}\text{C}_x$ alloy layers are completely coherent with a negligible in-plane strain relaxation, and the growth was pseudomorphic. Figure 3.6 further confirms the $\text{Ge}_{1-x}\text{C}_x$ alloy layer grown at $T_{\text{sub}}=215^\circ\text{C}$ to be under tensile strain. The samples grown at 270°C and 324°C also showed similar results in RSM (not shown).

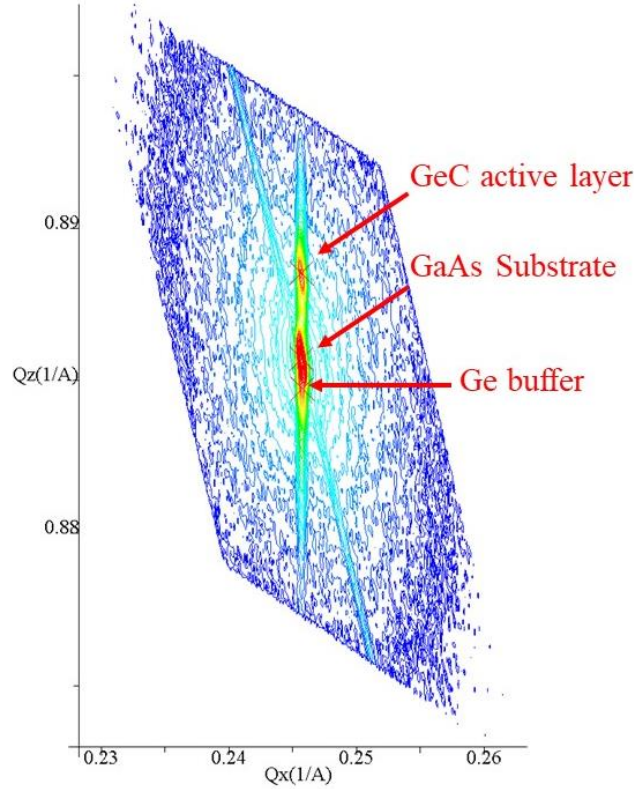


Figure 3.7: RSM around the asymmetric (115) Bragg peaks from $\text{Ge}_{1-x}\text{C}_x$ alloy layers deposited at $T_{\text{sub}} = 215^\circ\text{C}$ shows Ge and $\text{Ge}_{1-x}\text{C}_x$ are fully strained to the GaAs substrate.

Figure 3.8(a) shows the correlations between the temperature and C%. We noticed that the C percentage initially increases with increased temperature, but above 324°C , the nominal C percentage as extracted from XRD starts to fall and eventually becomes zero (not shown). At higher temperature, the thermal cracking efficiency of CBr_4 increases, so more C becomes available on the film surface, while the solubility of C in Ge also decreases; hence C is more likely to form clusters of C on the surface, or

enter in a interstitial site as a defect, contributing to 3D island growth as observed in the previous RHEED and AFM results. The increase in %C would be desirable, but not if it comes with increased fractions of interstitial C or C clusters, which appears to be the case at growth temperatures above 270 °C, resulting in wider XRD FWHM. However, it is noteworthy that neither XRD nor AFM can probe the bonding configuration of the alloy, and XRD can only show net strain; it cannot easily distinguish whether the film contains purely substitutional C or a mix of substitutional C (tensile) and C-C defects (compressive), which would partially compensate each other.

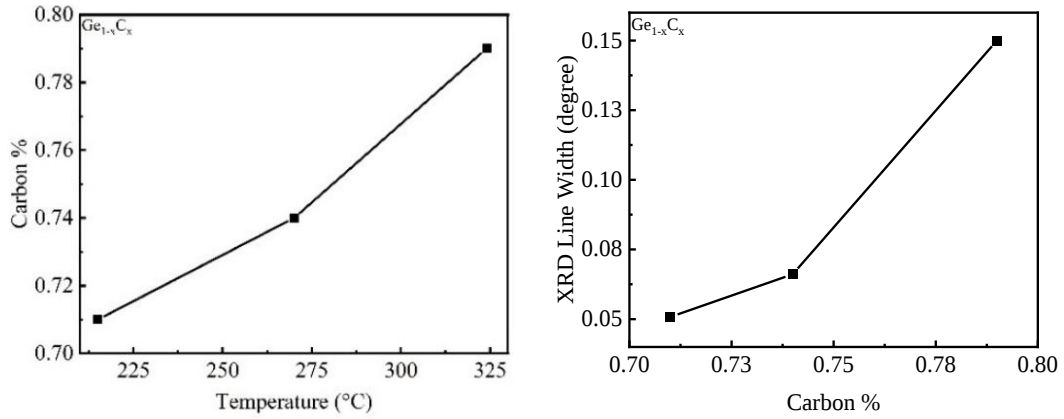


Figure 3.8: The relations between the C % in $\text{Ge}_{1-x}\text{C}_x$ and XRD line width.

3.5.4 Raman

As a preliminary study of the bonding of Ge and C and to validate XRD results, Raman measurements were performed. The measurements were obtained using a Horiba (LabRam HR Evolution) microscope with 532 nm excitation. At this wavelength, the optical penetration depth $d_{opt} \sim \frac{1}{2\alpha} \sim \approx 20$ nm in Ge, where α is the absorption coefficient [88]. This serves as a good estimate for d_{opt} in $\text{Ge}_{1-x}\text{C}_x$ at low x . Therefore, in our measurements, the majority of Raman scattering will originate from the alloy (and Ge cap, when present). Figure 3.8 shows the Raman spectrum from the samples previously

shown in Figure 3.3. The Ge reference material exhibits strong first-order scattering near 300 cm^{-1} from the Raman-allowed phonon, Figure. 3.8.

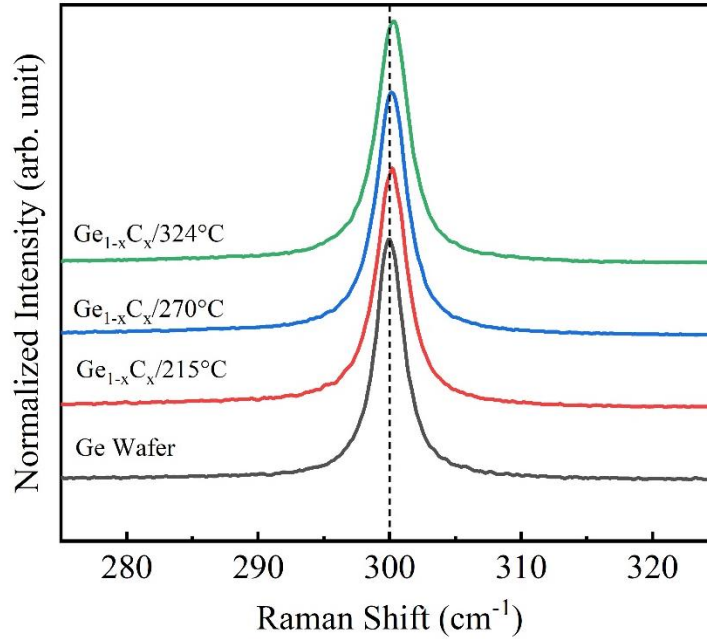


Figure 3.9: First order Ge Raman spectra showed slight blue shifts due to C incorporation with Ge, which we attribute to the slight tensile strain.

Also observed, in Figure 3.9, are weaker second-order bands from the Ge. These same features are also observed in the $\text{Ge}_{1-x}\text{C}_x$ alloy samples. Most importantly, spectra from the alloy samples exhibit a sharp mode near 530 cm^{-1} that has been previously identified as the Ge-C local vibrational mode [79], [81]. Observation of this band directly confirms the desired substitutional C incorporation. Based on fits to the data, the Ge-C local mode varies in position between 529.6 and 530.1 cm^{-1} , with FWHM between 6.95 and 7.25 cm^{-1} . The position and line width are in good agreement with prior reports [74], [79].

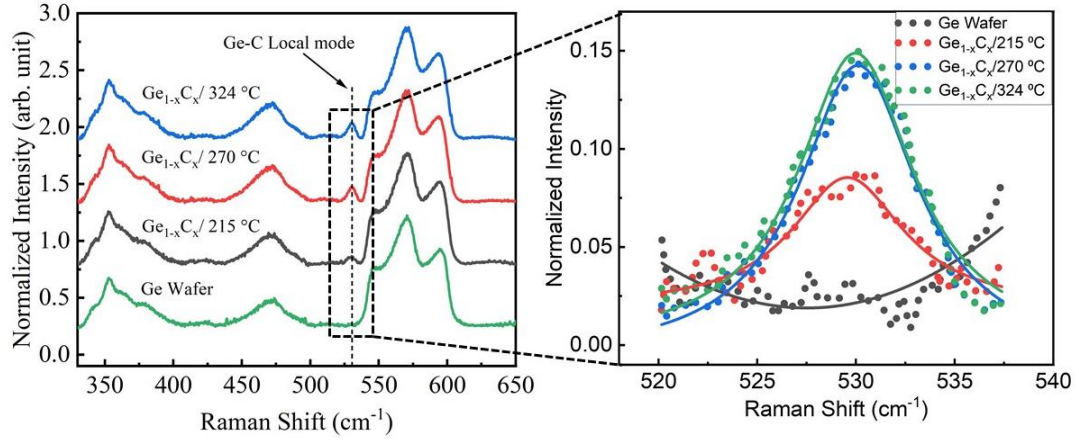


Figure 3.10: Raman spectra near the 530 cm⁻¹ Ge-C local modes from (a) Ge wafer, (b) Fitted Raman spectrum of Ge-C local mode near 530 cm⁻¹ after subtracting the background.

The Ge-Ge bands in the alloy spectra are found to be blue shifted from that of the reference material by $\Delta\omega = +0.2 \text{ cm}^{-1}$ based on fits using Lorentzian line shapes. This small shift is the result of contributions from the substrate-induced biaxial tensile strain (red shift) and the effect of alloying on the vibrational band structure and may be written

$$\Delta\omega = \Delta\omega_{bi} + \Delta\omega_{alloy}$$

with obvious notation. Based on our X-ray data, we estimate the strain to be +0.1%. Using the dependence on strain previously reported [89] the +0.1% strain will produce a phonon shift of $\Delta\omega_{bi} = -0.2 \text{ cm}^{-1}$. Taking this into account with the measured $\Delta\omega$ value, the net result is an alloy-induced blue shift of $\Delta\omega_{alloy}$ is approximately 0.2 cm^{-1} .

Previous Raman reports on germanium carbide showed substantial intensity from disordered C phases [78], [80]. The presence of these phases was attributed to excess C accumulating at the surface rather than the desired substitutional incorporation into Ge_{1-x}C_x during growth. The signature broad bands from these materials, whether primarily sp² or sp³ coordinated, are in the 1250 to 1650 cm⁻¹ range. However, as shown in Figure

3.13, there are no peaks visible in this range in Raman. From this we conclude that there is little if any residual C on the surface following the MBE growth process used here.

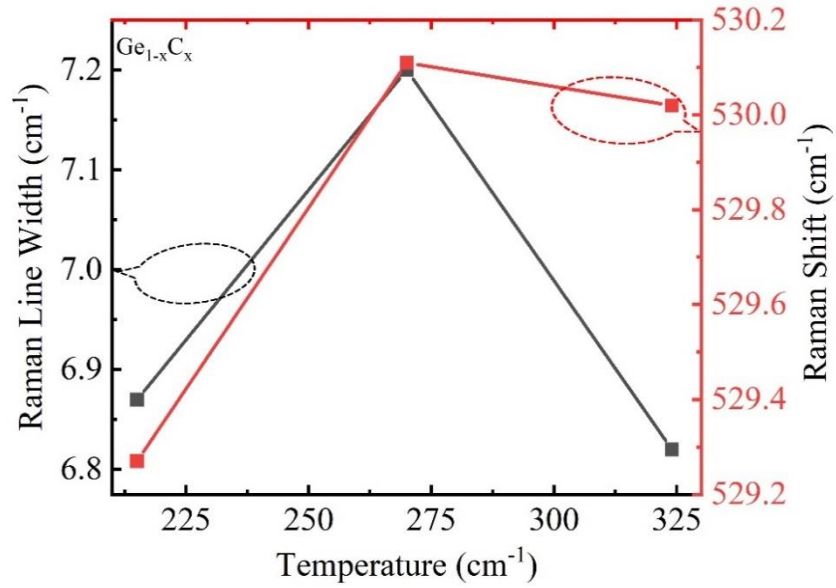


Figure 3.11: Relations between the Raman line width and peak position of Ge-C mode, fitted to peaks in Figure. 3.8.

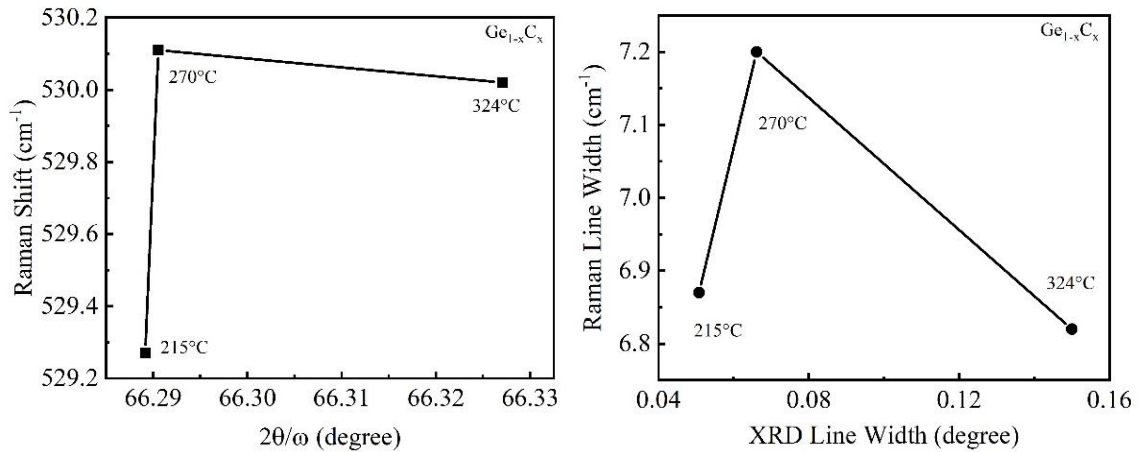


Figure 3.12: (a) Relations between the Raman shift and XRD peak position of $\text{Ge}_{1-x}\text{C}_x$ film. (b) Relations between the Raman line width and XRD line width of $\text{Ge}_{1-x}\text{C}_x$ film.

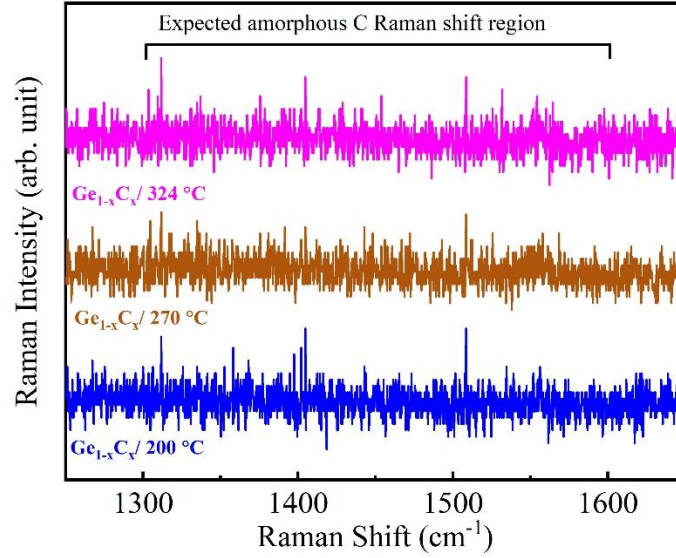


Figure 3.13: Raman spectrum of expected amorphous C region.

3.5.5 Photoluminescence

To see the change in bandgap and optical emission, low temperature micro-PL was performed on all three samples grown. The sample is held in a temperature-controlled cryostat with a ZnSe window, optically pumped by a 1 W, 808 nm laser modulated at 10 kHz. The pump laser light is passed through a 3 μm dichroic beam splitter and focused onto the sample using an all-reflective parabolic mirror through an antireflection-coated (3-5 μm) Si window onto a liquid nitrogen cooled InSb detector. The Si window is used to filter laser light. The detector signal is demodulated by lock-in amplifier and recorded for each temperature of the sample. For spectrally resolved PL measurements, emitted infrared light is passed into a Fourier transform infrared (FTIR) spectrometer after being reflected from the dichroic. The FTIR is run in the step-scan mode to dramatically reduce infrared background. The input power was approximately 240 mW, focused into an ellipse of $200 \times 40 \mu\text{m}^2$

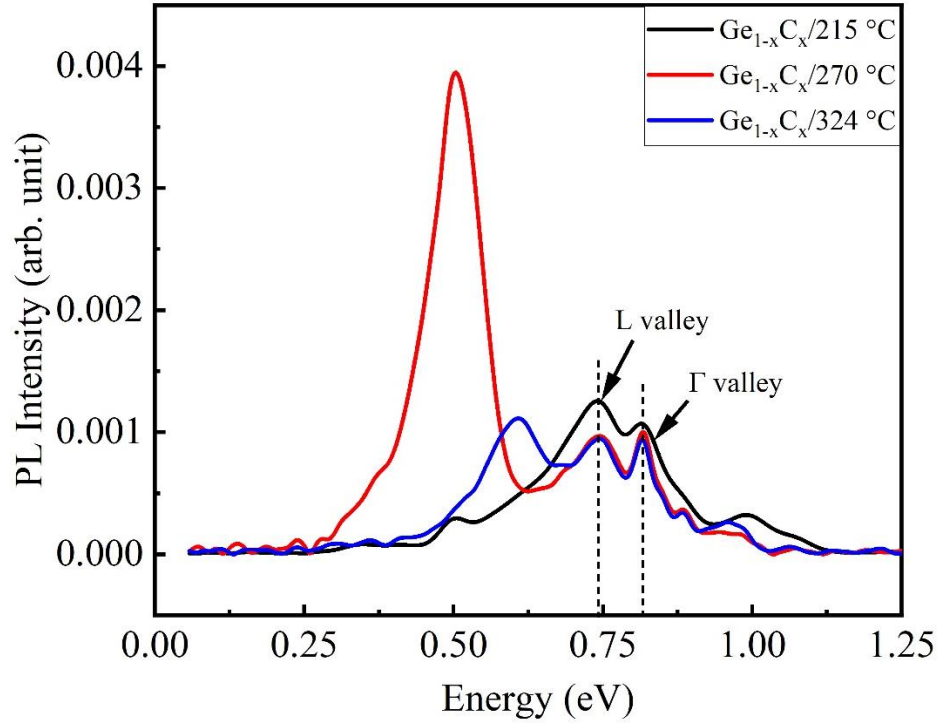


Figure 3.14: PL spectrum from Ge_{1-x}C_x thin film

Weak PL at 80 K was observed at 0.61 eV from the film grown at 324 °C. No PL was visible from the 215 °C sample, which we attribute to the creation of point defects such as Ge vacancies during this low-temperature growth. Further study using capacitance-voltage techniques is underway to try to quantify vacancies and other point defects in the Ge_{1-x}C_x. The use of atomic H surfactants to reduce point defects will be reported in Chapter 4. Also, my colleague Tuhin Dey is currently investigating the impact of adding Sn in Ge_{1-x}C_x as a surfactant to further reduce defects. The sample grown at 270 °C shows relatively strong emission at 0.5 eV; however, we observed similar emissions from Ge grown at 412 °C as shown in Figure 3.14. Therefore, we attribute the PL emission from Ge and Ge_{1-x}C_x has grown 270 °C to be emission from a defect state. Further study is necessary to verify and identify the type of defect.

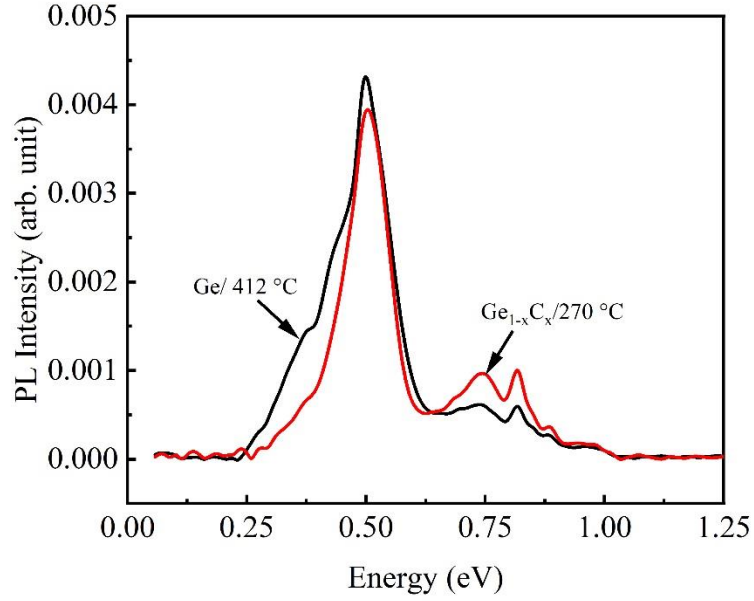


Figure 3.15: PL spectra from Ge ($T_{sub} = 412$ °C) and $Ge_{1-x}C_x$ ($T_{sub} = 270$ °C) thin film show similar features.

Table 3.1: Data from the characterization of $Ge_{1-x}C_x$

T_{sub} °C	H/ No H	RMS Rough ness (nm)	RHEED Pattern	XRD Peak (degree)	XRD FWHM (degree)	%C	Raman Peak (cm ⁻¹)		PL (eV)
							Ge	$Ge_{1-x}C_x$	
215	No H	0.63	Streaky	66.28	0.051	0.71	300.14	529.27	No PL
270	No H	8.56	Spotty	66.29	0.067	0.74	300.13	530.11	0.50
324	No H	7.53	Spotty	66.31	0.155	0.79	300.21	530.02	0.61

3.6 Summary and Conclusion

In summary, we showed successful incorporation of C in Ge using CBr_4 as a C precursor for the first time. The HR-XRD couple scan confirmed a maximum of 0.76% C in $Ge_{1-x}C_x$ at $T_{sub} = 324$ °C. Furthermore, XRD tensile shift and the G-C local mode in the Raman spectrum ensure the substitutional C. The Raman spectrum also confirmed the amorphous C free surface. RHEED, AFM, and XRD measurements indicate smooth surface and better crystal quality at $T_{sub} = 215$ °C. Most importantly, we demonstrate PL at 0.5 and 0.61 eV from the samples grown at 270 and 324 °C, respectively. This is a

significant step forward to achieve lasing from Group IV materials on Si. However, we noticed similar PL emission at 0.5 eV from Ge film grown at 412 °C. Hence, it may be possible that the PL emission at 0.5 eV from the sample grown at the coldest temperature (270 °C) could come from a defective state rather than band to band emission. Further study is necessary to understand this phenomenon.

4. EFFECT OF ATOMIC H DURING THE EPITAXIAL GROWTH OF DILUTE GERMANIUM CARBIDE

4.1 Introduction

The primary challenge for $\text{Ge}_{1-x}\text{C}_x$ growth is avoiding C-C bonds, which form a stable defect and midgap trap in Ge [73]. This tendency is aggravated by the fact that energetic sources of C cause surface damage [65], and graphite-based C sources deposit C_2 , C_3 , or larger clusters of C atoms [76], [90], [91]. John Arthur and Alfred Cho said at the 2014 International MBE conference that evaporated graphite release C_8 or C_7 clusters [92]. Even if individual C atoms are deposited, surface segregation and surface diffusion of excess C adatoms will lead to C-C bonds, which incorporate as defects.

In this work, to address the C-C defect, we combined a low-energy CBr_4 carbon source with a beam of thermally cracked H, which has long been used for removing hydrocarbons from MBE surfaces [85], [87]. The idea of adding hydrogen came from the difficulty in the chemical synthesis of the C source precursor gas $(\text{GeH}_3)_4\text{C}$ from its preceding step, $(\text{GeBrCl}_3)_4\text{C}$; the latter is relatively easy to make by itself, but the subsequent hydrogenation step to replace Br and Cl with H is slow, difficult, and has low yield. Instead, we chose to try the hydrogenation of a simpler C precursor in the MBE itself using a beam of low energy, thermally cracked H. Furthermore, it has previously been shown that atomic H preferentially removes sp^2 -bonded C from surfaces [93]–[96], which can prevent graphite formation during diamond growth by hot-filament chemical vapor deposition (HFCVD). In diamond growth, atomic hydrogen plays several roles in the deposition process: (1) preferential etching of graphite by hydrogen atoms; (2) production of CH_3 radicals; (3) stabilization of the diamond surface by prevention of

reconstruction; (4) suppression of aromatic species; and (5) promotion of the gas phase production of acetylene, which evaporates from the surface [97]–[99]. Increasing the gas flow rate of hydrogen significantly decreases diamond growth rate. Growth temperature also plays an important role, with higher quality and growth rate at higher temperatures [95], [96], [100]. However, to date, no research group has reported using atomic hydrogen during the growth of $\text{Ge}_{1-x}\text{C}_x$ by MBE.

In this chapter, we examine the possible reaction mechanisms and their impacts on film growth in detail. We understand that comparing diamond growth in an HFCVD system is significantly different from growing $\text{Ge}_{1-x}\text{C}_x$ in an MBE system. In particular, the growth temperatures of diamond and $\text{Ge}_{1-x}\text{C}_x$ lie in opposite ends of the spectrum; diamonds grow best at high temperatures above 700 °C, while $\text{Ge}_{1-x}\text{C}_x$ must be grown at relatively low temperatures (200–400 °C) where kinetic limitations prevent segregation of C and Ge. We also use orders of magnitude lower beam equivalent pressure (BEP) of the precursors.

As in the previous chapter, CBr_4 was used as the C precursor for $\text{Ge}_{1-x}\text{C}_x$ growth. In this chapter, the addition of atomic H during the growth of $\text{Ge}_{1-x}\text{C}_x$ is explained in detail. The cracking of CBr_4 is a low-energy process that allows breaking the C-Br bond on the substrate surface at temperatures of 172 °C or even lower. In addition to the thermal cracking, highly reactive atomic H can also help crack some of the CBr_4 by removing Br as HBr. After cracking, bromine evaporates from the surface leaving individual C atoms. As mentioned above, bare C atoms on the surface are likely to bond to each other and form undesirable C-C clusters, which create mid-gap trap states in Ge. Having atomic H during the growth could prevent or remove these C clusters by breaking

the C-C bond and/or removing excess C from the surface. Thus, the only C remaining in the film would be C that is already bonded and buried under Ge atoms. We used a semi-insulating GaAs substrate because GaAs is highly transparent at photon energies near the Ge and $\text{Ge}_{1-x}\text{C}_x$ bandgaps, which allows us to do optical absorption measurements near the band edge of Ge. As mentioned in Chapter 1, all substrate temperatures reported here were calibrated to the melting point of indium droplets on a similar wafer surface.

4.2 Experimental

4.2.1 Germanium carbon epitaxial growth process

As was described in the previous chapter, the $\text{Ge}_{1-x}\text{C}_x$ films were grown in an MBE modified for gas growth by addition of a gas mixing system, a corrosive rated turbomolecular pump, a higher temperature substrate manipulator, and Pirani gauges to measure pressures higher than ion gauges can handle. As was mentioned in Chapter 3, the chilled water was used rather than liquid nitrogen to cool down the MBE system.

To grow $\text{Ge}_{1-x}\text{C}_x$, 3-inch epi-ready GaAs wafers were cleaved into quarters, baked in a vacuum overnight at 200 °C, then baked individually for 1.5 hours at 400 °C. Oxide removal was performed inside the growth chamber using atomic H at 406 °C for 20 minutes. A sharp 2×4 diffraction pattern on the RHEED screen indicated an oxide-free clean surface. A 90 nm buffer layer was grown at $T_{\text{sub}} = 406$ °C, followed by 150 nm of $\text{Ge}_{1-x}\text{C}_x$ at temperatures T_{sub} between 215 °C and 324 °C, in the presence of atomic H. In-situ RHEED was used to monitor the growth in real-time. Any Ge cap layer was omitted intentionally so the surface roughness of the active layer could be directly measured using AFM. To keep the consistency between growths, the beam equivalent pressure (BEP) for CBr_4 and Ge were kept same as mentioned in Chapter 3. The H_2 gas was

supplied to the chamber through the hydrogen cell. The chamber base pressure was 2.5×10^{-5} Torr during the growth. The ion pump on the MBE is usually very good at pumping down light gases such as H_2 but introducing too much H_2 at once overwhelms the pump. Therefore, during the growth of the active layer in the presence of atomic H, the ion pump was shutdown intentionally. Also, because H_2 can diffuse backward through both the turbo pump and scroll pump, a slow but constant bleed of N_2 sealing gas was supplied through the turbo bearings for the entire growth period, to help push the H_2 through the backing pump. The wafer was rotated around its azimuth at 10 RPM. Based on the growth rate calibration, the total growth time was 1 hour and 35 mins, excluding desorption of the native oxide from the substrate.

4.3 Characterization

The deposited film thickness was calibrated using a micro stylus profilometer while estimated total C concentrations in as-deposited layers were determined using symmetric plane X-Ray rocking curves near the (004) plane. Further characterization, for example, Rutherford Backscattering (RBS) or secondary-ion mass spectrometer (SIMS), would be necessary to determine C concentration in absolute terms; these measurements are underway but have not been completed as of this writing. *In situ* RHEED operates at 10 kV, and 1.5 A was used to monitor real-time surface reconstruction. The incident electron beam hits the wafer surface at a grazing angle of $\sim 2^\circ$, and the reflected beam was collected on a phosphorus screen. A Bruker atomic force microscopy (AFM) system was used to measure the surface roughness of the films. A non-conductive HQ.NSC14/AlBS AFM tip with a stiffness of 5 N/m was used to scan $5 \times 5 \mu m^2$ areas.

HR-XRD was performed using a Rigaku SmartLab XRD system with Cu $K\alpha_1$ radiation ($\lambda = 1.540597 \text{ \AA}$) from a four-crystal Ge(220) monochromator, which provides an angular divergence of $<12 \text{ arcsec}$ with wavelength spread of $\Delta\lambda/\lambda \approx 7 \times 10^{-5}$. 2θ - ω coupled scans were taken around the symmetric (004) plane. Data fitting was performed using the Global Fit simulator to understand crystal quality and C concentration.

To verify the substitutional and graphitic C incorporation on $\text{Ge}_{1-x}\text{C}_x$ film, Raman measurements were performed using the Horiba LabRAM HR Evolution system equipped with a 532 nm line from a solid-state laser. The 103-mW laser beam was incident to the sample normal and focused to a spot size of $\approx 3 \text{ }\mu\text{m}$. At this wavelength, the optical penetration depth is $\approx 20 \text{ nm}$, enough to penetrate the cap layer but much smaller than the alloy layer thickness. A standard Si wafer was used to calibrate the spectrometer lasers and gratings. The laser spot was focused on the sample surface using a microscope and a camera.

To study and optimize optical emission, photoluminescence measurements were carried out on all samples. The total emission from the samples was measured using a micro photoluminescence setup at UT Austin. The sample is held in a temperature-controlled cryostat with a ZnSe window. The sample is optically pumped by an 808 nm laser outputting 1 W and modulated at 10 kHz. The pump laser light is passed through a 3 μm dichroic beam splitter and focused onto the sample using an all-reflective parabolic mirror through an AR-coated (3-5 μm) Si window onto liquid nitrogen cooled InSb detector. The Si window is used to filter laser light. The detector signal is demodulated by a lock-in amplifier and recorded for each temperature of the sample. For spectrally resolved photoluminescence measurements, infrared light is passed into a Fourier

transform infrared (FTIR) setup after being reflected from the dichroic. The FTIR is run in the step-scan mode to reduce infrared background dramatically. The input power was approximately 240 mW, focused into an ellipse of $215 \times 40 \mu\text{m}^2$. All results were compared with corresponding samples from Chapter 3 that were grown without H.

4.4 Experimental Results

4.4.1 Film Growth - RHEED

In-situ RHEED was used to monitor the growth and surface reconstruction in real-time. The growth temperature of the Ge buffer layers, which were grown without H, was constant for all samples, and we observed a sharp 2×2 streaky RHEED pattern, indicating smooth, 2D growth of the Ge on the GaAs substrate. In the $\text{Ge}_{1-x}\text{C}_x$ active layer, the observed RHEED patterns depended on atomic H, substrate temperature, and CBr_4 flux. For the samples grown in the presence of atomic H, at the highest growth temperature in this study, $T_{\text{sub}} = 324^\circ\text{C}$ growth temperature, the 2×2 RHEED reconstruction was stable and streaky throughout the growth. However, for lower growth temperatures (215°C and 270°C), the initial few ML showed 2×2 streaky patterns and slowly became spotty, indicating 3D island growth and a rough surface. Figure 4.(1a- 1c) shows RHEED patterns observed during the growth of $\text{Ge}_{1-x}\text{C}_x$ at various temperatures.

To check the RHEED results, ex-situ AFM was performed on all six samples. As with RHEED, the combinations producing the smoothest surfaces were low T_{sub} without H, and high T_{sub} with H. Indeed, the only sample showing extended atomic terraces in AFM was $\text{Ge}_{1-x}\text{C}_x + \text{H}$ at 324°C , with an RMS roughness of just 0.11 nm over $5 \times 5 \mu\text{m}^2$. The samples grown with H at 215°C and 270°C showed higher RMS roughness of 1.40 nm and 4.76 nm, respectively as shown in Figure 4.(2a - 2c).

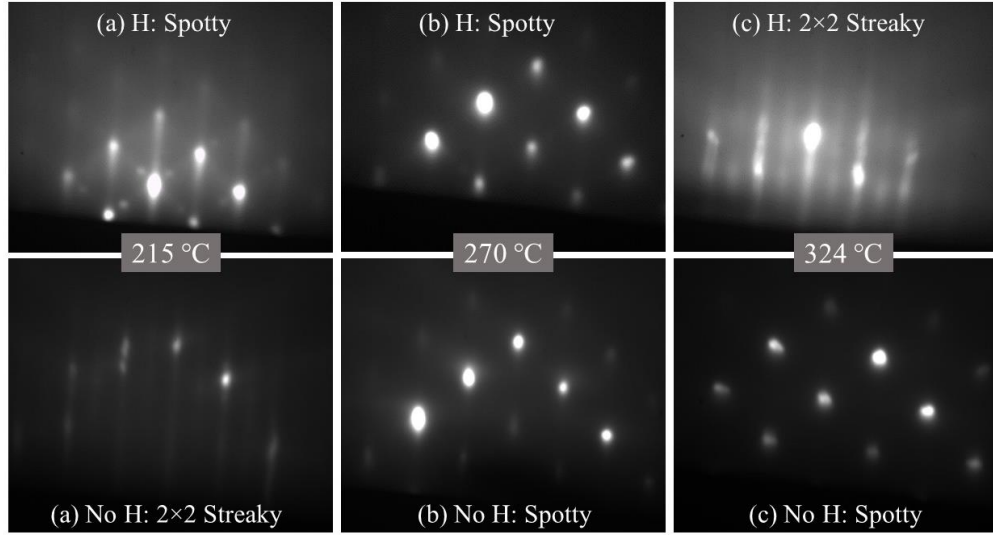


Figure 4.1: (a-c) RHEED images of samples grown with H at 215 °C, 270 °C, and 324 °C, respectively. (d-f) RHEED images of samples grown without H at 215 °C, 270 °C, and 324 °C, respectively.

In contrast, samples grown without atomic H had an RMS roughness of 0.63 nm, 8.56 nm, and 7.53 nm for T_{sub} of 215 °C, 270 °C, and 324 °C, respectively, these results are also shown in Table 4.1

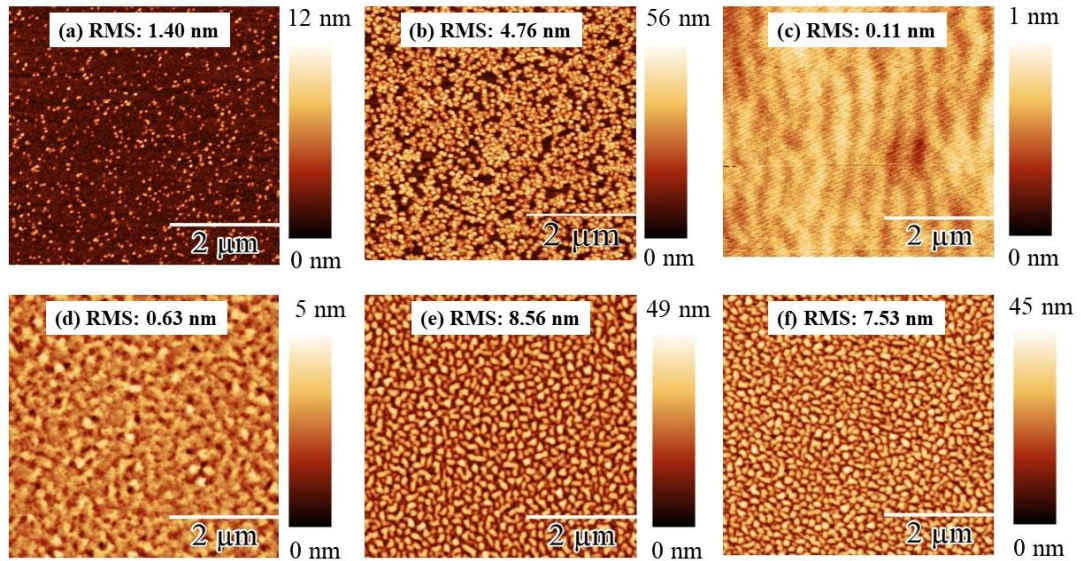


Figure 4.2: (a-c) 5×5 μm² AFM images of samples grown with H at 215 °C, 270 °C, and 324 °C, respectively. (d-f) 5×5 μm² AFM images of samples grown without H at 215 °C, 270 °C, and 324 °C, respectively.

We interpret the RHEED data as follows. At low $T_{sub} = 215\text{ }^{\circ}\text{C}$, atomic H does not start to remove surface C until $T_{sub} \sim 324\text{ }^{\circ}\text{C}$, leaving more C on the surface. XRD similarly showed more C on the film, as discussed further in the following section (section 4.4.2). Excess C segregates on the surface, creating facets, eventually leading to 3D island growth and rough surface. This faceting was also previously observed at high C concentrations using a different precursor [28]. At higher $T_{sub}=324\text{ }^{\circ}\text{C}$, thermal cracking of CBr_4 increases, so more C might be expected to incorporate with Ge; but instead, the opposite happens. At higher T_{sub} , atomic H is able to react with and remove surface C at a much higher rate. Hence, the C percentage on $\text{Ge}_{1-x}\text{C}_x$ film appears to be much lower than the other two samples as discussed below (section 4.4.2). Now comparing the results from Chapter 3 for the samples grown without atomic H, the RHEED pattern was stable and streaky at $215\text{ }^{\circ}\text{C}$ and became spotty at $270\text{ }^{\circ}\text{C}$ and $324\text{ }^{\circ}\text{C}$ (Figure 4.(1d-1f)). This is quite opposite trend from what was observed in growths that included atomic H. Figure 4.(1d-1f) shows the RHEED pattern during the growth of $\text{Ge}_{1-x}\text{C}_x$ in absence of C.

4.4.2 XRD: Composition and Strain

The RHEED and AFM results raised the question whether H might simply be removing *all* types of C during the growth, rather than just unwanted C-C bonds. In an effort to determine the fraction of C in the alloy, and get a rough measure of crystal quality, HR-XRD $2\theta/\omega$ (004) scans were performed on all six samples, shown in Figure (4.3). The sharp peaks at 66.05° correspond to the GaAs substrate. The Ge-C peak was observed to the right of the substrate, indicating the layer is tensile strained, as it should be if small C atoms are substituting for Ge in the lattice.

A HR-XRD scan on a sample grown in the presence of atomic H at $T_{sub} = 324\text{ }^{\circ}\text{C}$ exhibits a sharp layer peak, with a full-width half maxima (FWHM) of 0.06 degree, which suggests high quality crystal growth. The positive angular separation between substrate and layer peaks demonstrates that the film is in a state of tensile strain. Furthermore, the finite-thickness fringes are visible, indicating that the layer is very smooth in the plane of the substrate, again agreeing with the streaky RHEED and smooth AFM results. Rigaku Global Fit was used to determine the C percentage by simulating the $\text{Ge}_{1-x}\text{C}_x$ layer structure based on the dynamical formalism of Takagi and Taupin [101], [102]. The simulation and fit were carried out assuming a perfectly abrupt and coherent film/buffer-layer interface with all C atoms residing in substitutional sites. We assumed that non-substitutional C atoms exert negligible in-plane strain in the Ge lattice [69], [74], [80], yielding a substitutional C concentration of only $0.45 \pm 0.02\%$. Using a similar method, samples grown at a lower $T_{sub} = 215\text{ }^{\circ}\text{C}$ and $270\text{ }^{\circ}\text{C}$ showed a significantly higher C composition of 1.15 and 1.10% and relatively wider FWHM of 0.17 and 0.22 degrees, respectively (Figure 4.4).

To interpret these results, we note that in both CVD diamond growth and surface cleaning of Ge and III-V wafers, atomic H bonds to the surface but lacks sufficient thermal energy below $\sim 300\text{ }^{\circ}\text{C}$ to remove C [93]–[96]. At higher temperatures, we believe H removes not only graphitic C, but also some substitutional C, which explains the sharply reduced amount of C at $T_{sub} = 324\text{ }^{\circ}\text{C}$. Because atomic H still preferentially removes the graphitic C at high temperature [97], [99], we observed smooth 2D growth with no formation of C clusters, consistent with RHEED and AFM results. This explains

that the high T_{sub} offers excellent crystal quality with a smooth surface. Also, at a higher T_{sub} , Ge adatoms have higher surface mobility, allowing them to fill surface vacancies.

Note that atomic H produces a surprising but consistent reversal: In contrast with H-free growths in Chapter 3, where low temperature produced smoother surfaces, the addition of atomic H raises the optimal growth temperature by almost 100 °C. Comparing this with the results from Chapter 3 for the samples grown without atomic H, they show opposite phenomenon with sharp layer peak with clear Pendellösung fringes at low T_{sub} = 215 °C, with the increasing growth temperature, the layer peak starts to widen, and fringes start to disappear, although the C concentration was consistent over a T_{sub} range between 215 °C - 324 °C (Figure 4.3).

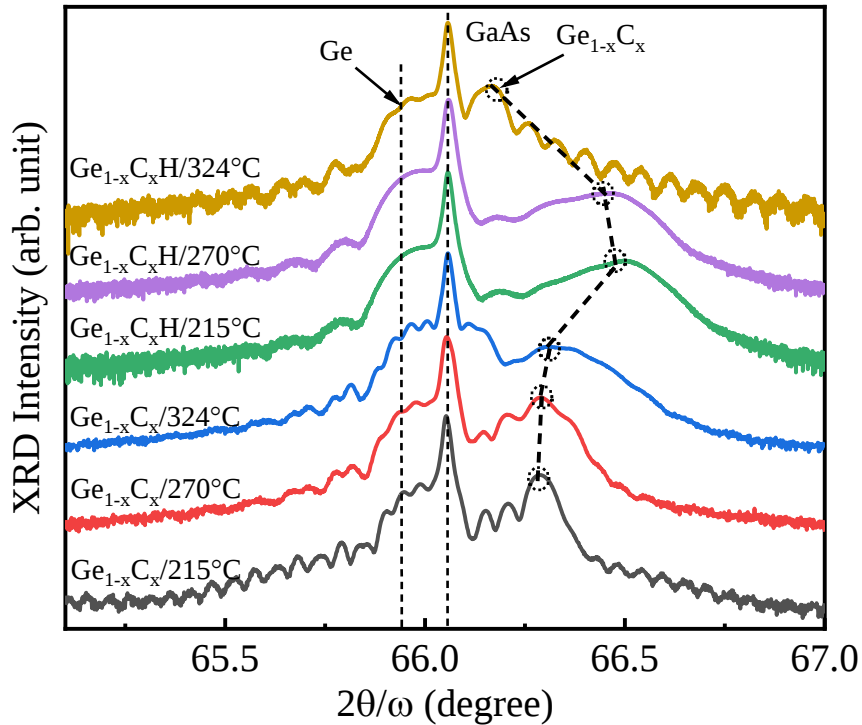


Figure 4.3: HRXRD $2\theta/\omega$ couple scan of $\text{Ge}_{1-x}\text{C}_x$ with and without H_2

Furthermore, the narrow FWHM of 0.05 degree was observed at T_{sub} = 215 °C, and it widened to 0.155 degrees at T_{sub} = 324 °C (Figure 4.4b), which explains samples grown

without H show excellent crystal quality at low T_{sub} . On the flip side, at low T_{sub} Ge leaves vacancies on the films to act as a trap state. That concludes that introducing atomic H during growth offers high-temperature growth of $Ge_{1-x}C_x$ with better crystal quality and relatively fewer Ge vacancies/trap states.

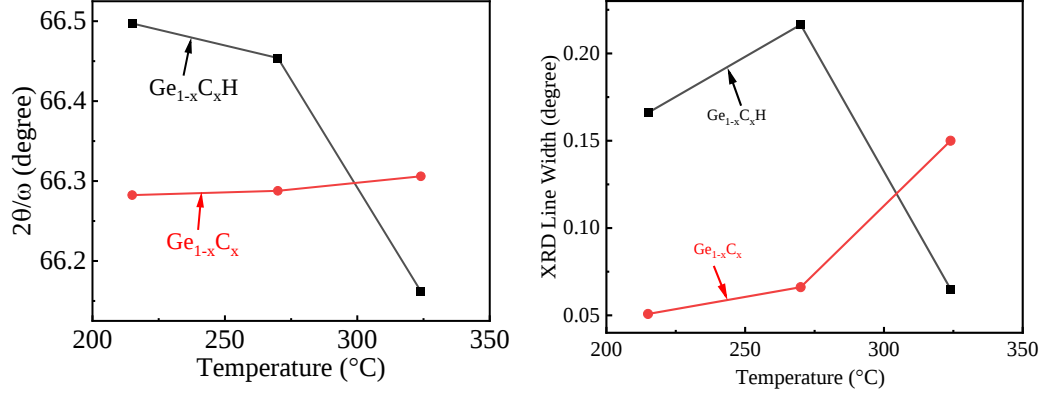


Figure 4.4: XRD of $Ge_{1-x}C_x$ with and without H for various growth temperatures. (a) $2\theta/\omega$ peak position (b) FWHM

All $Ge_{1-x}C_x$ layers were completely coherent with their substrates as determined from High-Resolution Reciprocal Space Mapping (HR-RSM) analysis. Representative RSM around asymmetric (115) reflections is presented in Figure 4.5. The HR-RSM was obtained from a 150 nm thick $Ge_{1-x}C_x$ alloy grown at $T_{sub} = 215$ °C. This result rules out strain relaxation as a cause for the roughening or peak shifts observed in AFM, RHEED, or XRD.

The dramatic shift of the $Ge_{1-x}C_x$ peak to larger angles in XRD might be caused by significantly more C in the alloy, or a larger fraction of the C being substitutional instead of interstitial. However, it is worth asking if the shift to tensile strain could also be caused by vacancies: missing atoms in the lattice. Dr. Wistey used the Vienna Ab-initio Software Package (VASP) to calculate the lattice constants of fully relaxed 128 atom supercells of pure Ge_{128} , Ge_{127} plus 1 C atom, and Ge_{127} plus 1 vacancy: 5.783 Å,

5.765 Å (-0.31%), and 5.7665 Å (-0.29%), respectively, using PBE methods. Since the lattice constants of both $\text{Ge}_{127}\text{C}_1$ and $\text{Ge}_{127}\text{V}_1$ are so similar, shifting the XRD peak twice as far as the original $\text{Ge}_{1-x}\text{C}_x$ by adding vacancies would require as many vacancies as C atoms, which is extremely unlikely.

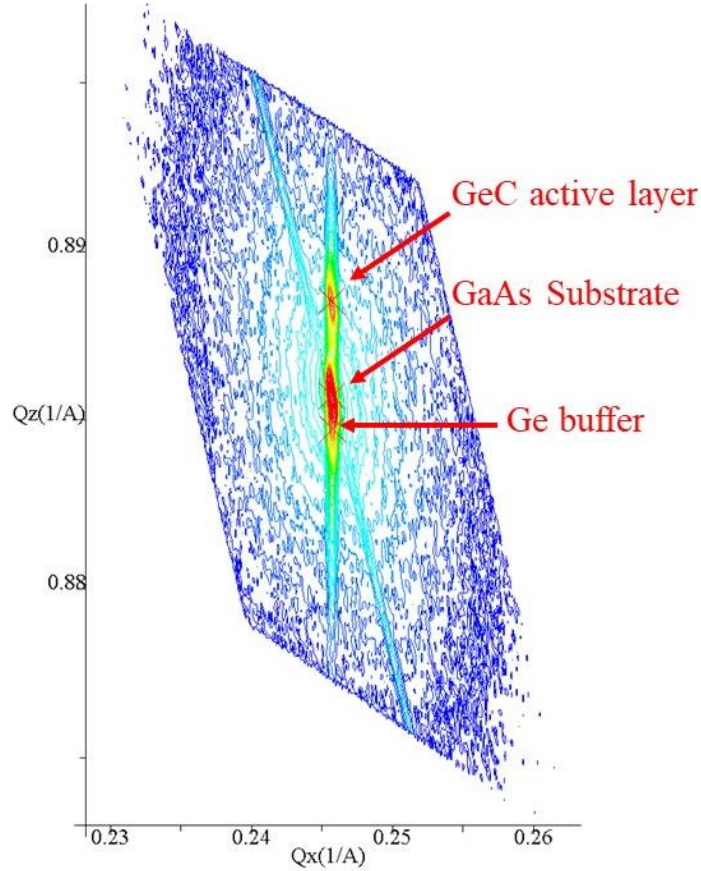


Figure 4.5: RSM showing strained $\text{Ge}_{1-x}\text{C}_x$ layer

Conversely, it might be that instead of the H adding C and tensile strain, perhaps the hydrogen-free $\text{Ge}_{1-x}\text{C}_x$ samples are instead *losing* tensile strain through self-compensation: tensile strain from C partly compensated by compressive strain from defects. Resolving this question would require techniques to measure interstitial C, such as RBS, or else defects in the lattice, such as DLTS. Both are underway, but neither has finished as of this writing.

In the meantime, the simplest explanation for the shifts in XRD, the RHEED, and the AFM for the atomic H samples is that H causes a much larger fraction of C to be incorporated substitutionally, perhaps twice as much.

4.4.3 Raman Spectroscopy Measurements

The Raman spectroscopy was carried out to study whether C atoms were incorporating substitutionally in the Ge lattice and to validate the results from other characterization tools. As I mentioned in Chapter 3, the substitutional C atoms in the Ge lattice give rise to a local vibrational mode near 530 cm^{-1} [79], [81], [103]. Figure 4.6 shows the Raman spectrum over the Stokes shift range between 270 and 650 cm^{-1} , along with the spectrum from bulk Ge is also presented in that figure as a reference to identify the local mode. We attribute the peak at 595 cm^{-1} to two-phonon intensity close to the Brillouin zone center [104]. The peak at 575 cm^{-1} is a second-order band from the Ge optical branch due to a high transverse optical (TO) phonon density of states near the X point in the Ge phonon dispersion curve [104], while the shoulder at 550 cm^{-1} is related to a two-phonon process involving one longitudinal optical (LO) and transverse optical (TO) phonon mode [103]. The shift near 467 cm^{-1} corresponds to a convolution of the Ge two-phonon longitudinal optical and acoustic (LA) modes [103], [104]. All other Raman peaks in this spectrum, except the narrow line at 530 cm^{-1} , are also present in the spectrum from a pure Ge (100) wafer. The 530 cm^{-1} line is absent from the Ge wafer spectrum, consistent with its interpretation as the Ge-C local mode. All Raman spectra had the baseline removed using local minima, and they were normalized based on the second-order Ge peak at 570 cm^{-1} . The Ge-C local mode-related peaks were fit using a Lorentz function centered at 530 cm^{-1} and presented separately (Figure 4.7b).

The samples grown at $T_{sub} = 215$ and 270 °C showed a blue shift toward higher frequencies (cm^{-1}) in the first-order Ge peak, along with a blue shift in the Ge-C local mode to 531 and 534 cm^{-1} for the same samples (Fig 4.7 and Fig 4.9c). This shift might be explained by excess H incorporating in the Ge; further investigation is necessary to understand this phenomenon fully. In contrast, corresponding samples grown without atomic H showed little to no blue shift.

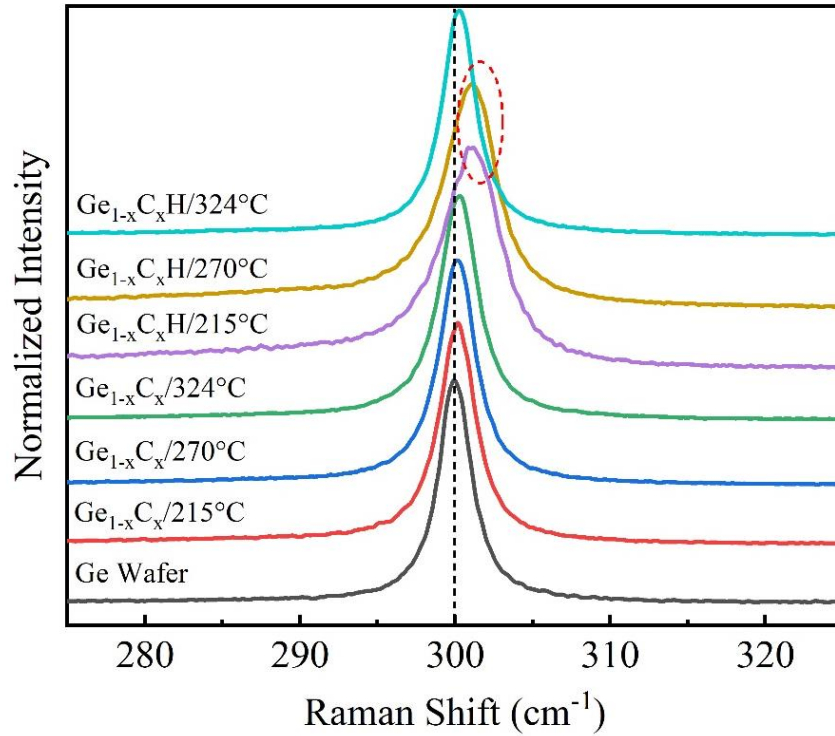


Figure 4.6: Raman shift for 1st order Ge peak of $\text{Ge}_{1-x}\text{C}_x$ with and without H_2 . Circled area highlights blueshift in two samples.

Figure 4.7(b) and 4.9(d) show the intensity difference in the 530 cm^{-1} Ge-C local mode between the samples grown with and without H. Introducing atomic H has significantly increased the intensity of this peak, suggesting a significant increase in substitutional C incorporation [68], [69], [74], [79]–[81]. Further measurement of these samples using nuclear reaction analysis Rutherford backscattering (NRARBS) to quantify

the fraction of substitutional and total C is currently underway by Dr. Rachel Goldman's group at the University of Michigan.

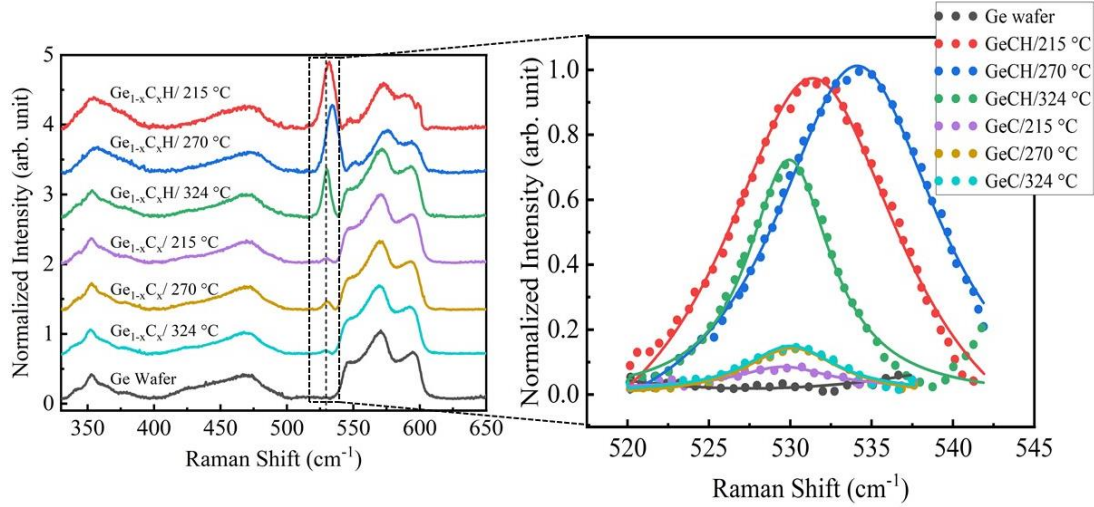


Figure 4.7: Raman spectra of Ge and $\text{Ge}_{1-x}\text{C}_x$. Inset shows region near Ge-C local mode at 530 cm^{-1} .

The full-width half maxima (FWHM) of the 530 cm^{-1} Ge-C peak for samples grown with H at $T_{\text{sub}} = 215$ and $270 \text{ }^\circ\text{C}$ are relatively high: $\sim 14 \text{ cm}^{-1}$ and $\sim 13 \text{ cm}^{-1}$, respectively. However, the FWHM drops to $\sim 6 \text{ cm}^{-1}$ for the sample grown at $T_{\text{sub}} = 324 \text{ }^\circ\text{C}$. By comparison, all three samples grown without H had a FWHM of 6 cm^{-1} (Fig 4.8). There was also a strong correlation between the narrowness of both Raman and XRD line width and temperature, as shown in Figs. 4.8 and 4.9(b), but only for samples grown with H. These suggest higher T_{sub} is important for the best crystal quality at high at.%C. Without H, the Raman line width was consistently near 7 cm^{-1} at all T_{sub} , although the XRD line width increased with T_{sub} . This suggests the overall crystal quality was degrading at higher temperatures, but the local C bond environments were similar, i.e. Ge-C bonds remained despite degradation of the crystal.

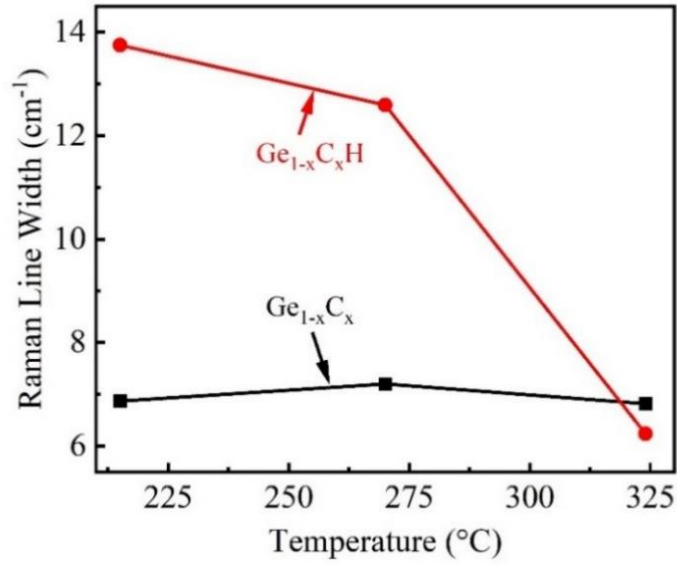


Figure 4.8: Change in Raman line width with growth temperature

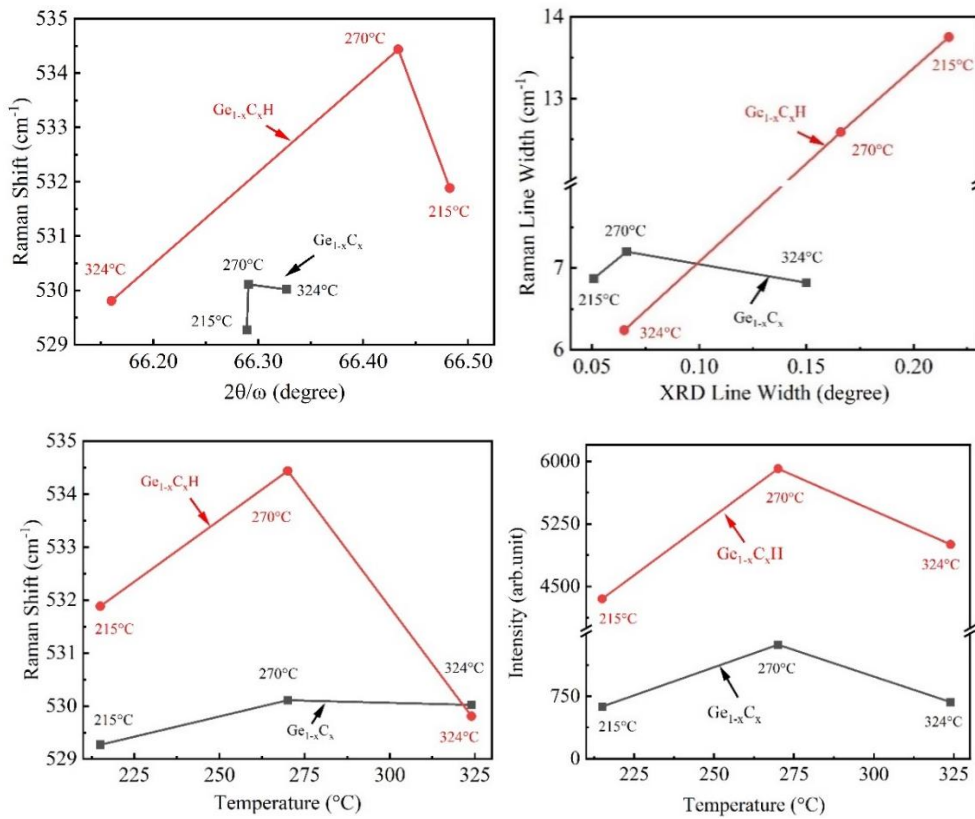


Figure 4.9: Raman spectra of the Ge-C local mode. (a) Correlation between the Raman shift and XRD 2θ/ω; (b) Correlation between the Raman and XRD line width; (c) Change in Raman shift with the growth temperature; and (d) Raman intensity comparison between samples grown with and without atomic H

Raman spectra were also measured from 1270 cm^{-1} to 1650 cm^{-1} to look for graphitic C. Figure 4.10 shows no sign of graphitic C in any of the six $\text{Ge}_{1-x}\text{C}_x$ films, which is a milestone in terms of avoiding C clusters during $\text{Ge}_{1-x}\text{C}_x$ growth. This validates our choice of CBr_4 as a novel precursor for growth of $\text{Ge}_{1-x}\text{C}_x$.

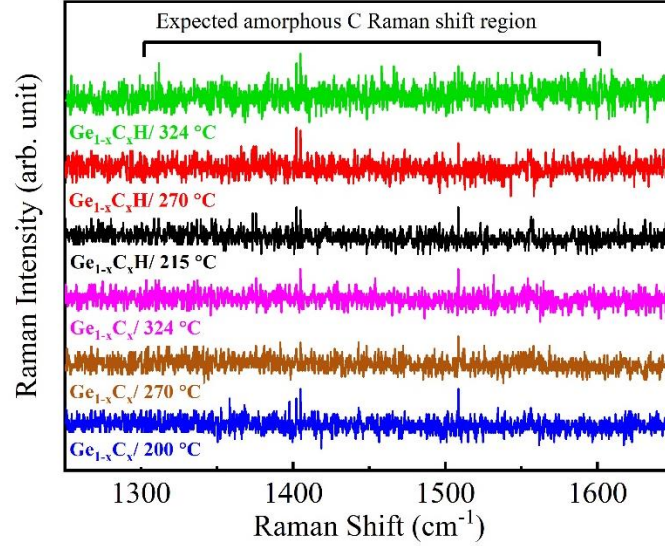


Figure 4.10: Expected graphitic C Raman shift on $\text{Ge}_{1-x}\text{C}_x$ (with and without H)

4.4.4 Photoluminescence

The driving goal of this work was to produce light emitting materials, so we performed 83K photoluminescence on all six samples, as shown in Figure 4.11. Except for the samples grown at 270 °C with H and 215 °C without H, all remaining samples showed PL near 0.61 eV . The PL peaks at 0.74 eV and 0.82 eV come from the indirect and direct valleys of the Ge buffer layer [105]. These are shifted from the room temperature bandgaps (0.65 and 0.80 , respectively) due to the low temperature.

From the computational modeling, adding $\sim 1\%$ of substitutional C to the Ge should reduce the overall bandgap of $\text{Ge}_{1-x}\text{C}_x$ film by $170 \pm 50\text{ meV}$ [28]. The PL emission near 0.61 eV is the first reported result that agrees with band anticrossing theory and our numerical modeling in VASP [28]. As mentioned in the XRD analysis section,

growth temperatures below 400 °C are likely to produce Ge vacancies, which would lead to rapid recombination of electrons and holes. That might be the possible reason for not seeing PL from the sample grown at 215 °C without H. In the case of a sample grown with H at the same temperature, we assume atomic H could help fill those Ge vacancies and generate PL, but further investigation is necessary. We believe the reason for the very weak emission from the sample grown at 324 °C with H is the very low percent of C present in $\text{Ge}_{1-x}\text{C}_x$ film. We had only $0.45 \pm 0.02\%$ of substitutional C on that sample, according to HR-XRD, which was likely not enough to reduce the direct bandgap below or even near the indirect bandgap. Further study can be done with a high C percentage to verify this claim.

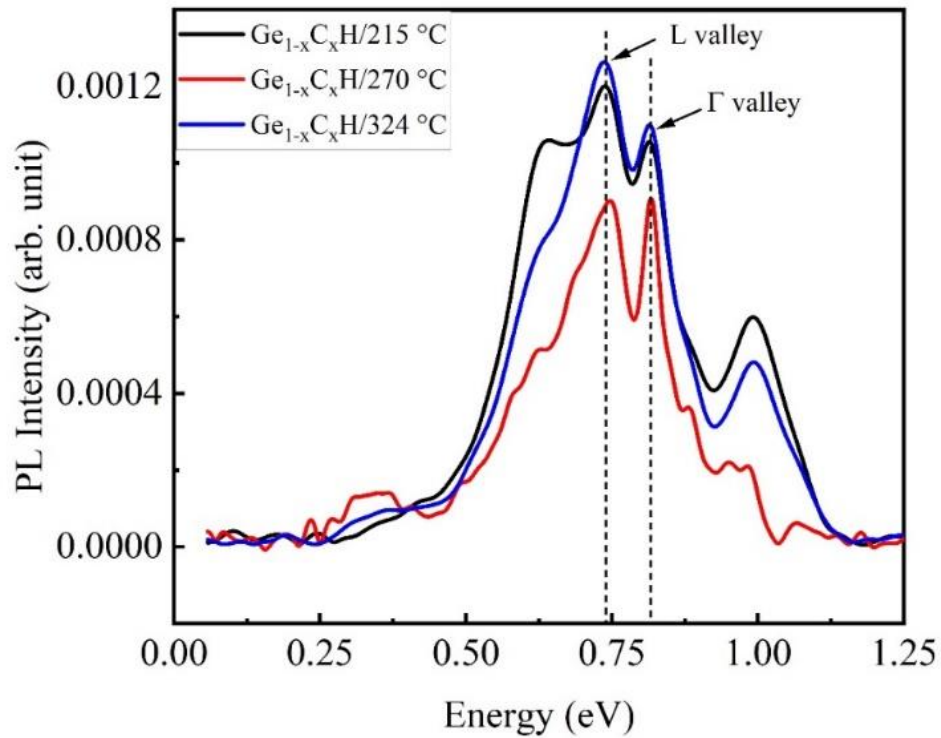


Figure 4.11: PL spectrum from $\text{Ge}_{1-x}\text{C}_x\text{H}$

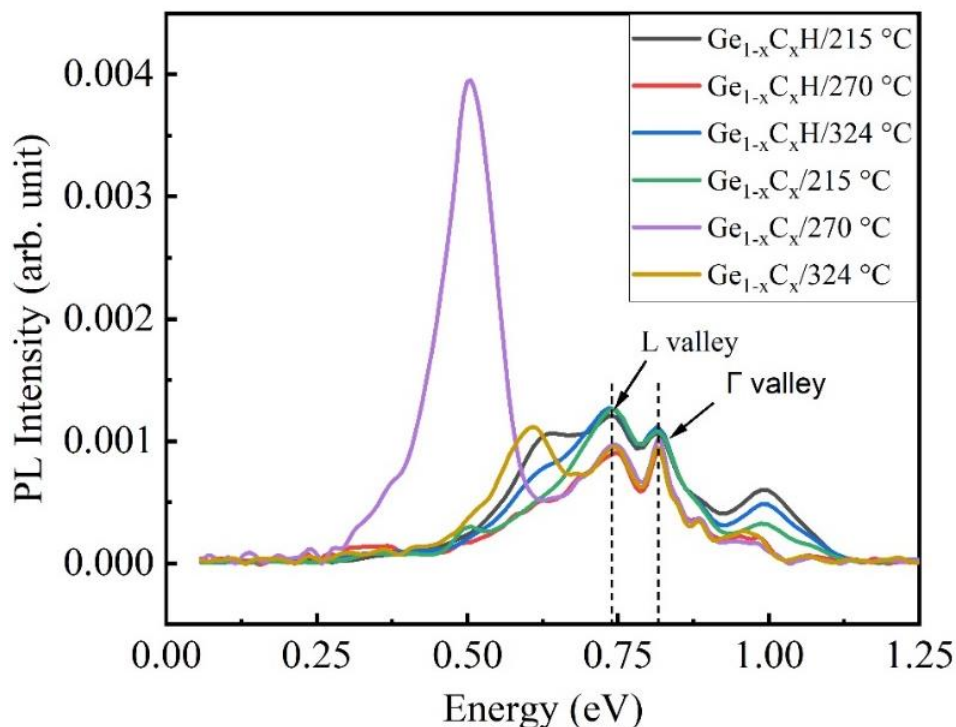


Figure 4.12: PL Spectrum from the $\text{Ge}_{1-x}\text{C}_x$ and $\text{Ge}_{1-x}\text{C}_x\text{H}$

Table 4.1: Data from the characterization of $\text{Ge}_{1-x}\text{C}_x$ with and without H_2

T_{sub} °C	H/ No H	RMS Roughne ss (nm)	RHEED Pattern	XRD Peak (degree)	XRD FWHM (degree)	%C	Raman Peak (cm^{-1})		PL (eV)
							Ge	$\text{Ge}_{1-x}\text{C}_x$	
215	H	1.40	Spotty	66.50	0.167	1.15	300.99	531.88	0.60
270	H	4.76	Spotty	66.45	0.216	1.10	300.95	534.43	0.60
324	H	0.11	Streaky	66.16	0.065	0.49	300.25	529.81	No PL
215	No H	0.63	Streaky	66.28	0.051	0.71	300.14	529.27	No PL
270	No H	8.56	Spotty	66.29	0.067	0.74	300.13	530.11	0.50
324	No H	7.53	Spotty	66.31	0.155	0.79	300.21	530.02	0.61

4.5 Summary and Conclusion

We demonstrated the first growth of $\text{Ge}_{1-x}\text{C}_x$ using a flux of atomic H to reduce undesirable C-C bonding and similar C clusters on the growth surface. Growths with and without H showed several opposing trends: smooth surfaces only resulted from low temperature growth without H, or high temperature growth with H. HR-XRD showed all

$\text{Ge}_{1-x}\text{C}_x$ layers were fully strained to the GaAs substrate, and the smooth samples also showed the clearest Pendellösung fringes. At higher T_{sub} , H may have reduced the fraction of C in the sample, since the XRD peak shifted back toward that of pure Ge. However, lower temperature growth with H actually shifted the $\text{Ge}_{1-x}\text{C}_x$ peak almost 2x farther toward tensile strain (larger angles) compared with samples grown without H, which cannot be explained by vacancies alone, so it appears H increases the fraction of C incorporated substitutionally in Ge. Raman spectroscopy showed a clear Ge-C local vibration mode near 530 cm^{-1} for all samples with or without H, though a blue shift happens for the samples grown at $215\text{ }^{\circ}\text{C}$ and $270\text{ }^{\circ}\text{C}$ in the presence of H, which we attribute to H incorporation in Ge. Most significantly, this work successfully demonstrated the first photoluminescence at 0.61 eV and 0.62 eV from $\text{Ge}_{1-x}\text{C}_x$ thin films grown at $324\text{ }^{\circ}\text{C}$ without H and $215\text{ }^{\circ}\text{C}$ with H, respectively. This research is a significant step forward toward achieving an efficient, room temperature Group IV laser on silicon.

5. TENSILE STRAINED GERMANIUM WAVEGUIDE LASER SIMULATIONS

5.1 *State of the Art*

Mechanical effects play an essential role in semiconductor physics. Mechanical strain affects semiconductor electronics structure, including the band edges, energy levels, density of states, mobilities, etc. Tensile strain in Ge has drawn attention among the scientific community for the past decade because strain may convert Ge from an indirect to a direct bandgap for strong light emission. However, few research groups have shown that Ge can be turned into a direct bandgap material applying sufficient tensile strain [14], [16], [17], [106], [107]. Others have used a smaller amounts of strain with very heavy n-type doping to achieve lasing [15], [17], [108]–[111].

A traditional approach to achieve significant tensile strain in Ge has been to grow it on a relaxed InGaAs buffer layer [18], [56], [112]. Significant strain as high as 2.33% has been reported [112], but the InGaAs is a poor barrier material for carrier confinement and is not CMOS compatible. Some groups tried Si₃N₄ stressor on top of the Ge layer grown on the GaAs [55], [113] substrate or silicon-on-insulator (SOI), which is a step closer to CMOS compatibility because it allows etching under the Ge waveguide [114]. De Kersauson et al. achieved optical gain in their Ge nanowire grown on top of the GaAs substrate with a Si₃N₄ stressor [113].

Another approach to achieve tensile strain on Ge is using the thermal expansion coefficient mismatch. Relaxed Ge grown directly on Si at high temperature. Because Ge shrinks faster than Si as they cool together, due to a larger thermal expansion coefficient, the Ge layer becomes tensile strained at low temperature.

However, none of these experimental methods showed evidence of direct bandgap Ge. Since the tensile strain was insufficient to achieve direct bandgap Ge, some groups have tried n-type doping alongside tensile strain. Sun, Liu, and Cheng et al. used this technique in conjunction with high n-doping to fill the L valley [15], [32]; thus, the quasi-Fermi level of the electrons already lies in the Γ valleys even without carrier injection due to n-type doping. This technique successfully demonstrated electroluminescence in a light-emitting diode device fabricated with these strained structures.

Furthermore, Camacho-Aguilera *et al.* recently demonstrated an electrically pumped Ge laser using strain and n-doping [111]. However, their efficiencies were very low, which they attributed to high losses due to free-carrier absorption loss. A direct bandgap material without significant doping is not expected to suffer from these issues. Liu et al. calculated a minimum threshold current density of 5.6 kA/cm^2 for an optically pumped Ge laser. In contrast to my work below, they performed their calculations assuming a single, uniform, isotropic strain within the waveguide, which is not physically realistic. That is probably one of the reasons for the discrepancy between their computational and experimental results. Petykiewicz et al. reported direct bandgap light emission from strained Ge nanowires coupled with high-Q nano-photonics. They were able to tune the emission wavelength over 400 nm with a single lithography step. They also found that the optical cavities formed with highly strained ($>2.3\%$ tensile strain) Ge show reduced optical loss [26]. Bao et al. has recently demonstrated optical pumped lasing at liquid N_2 temperature in highly strained Ge nanowires using 1.6% uniaxial tensile strain [25]. They also mentioned that the amplified material gain in strained Ge

could sufficiently overcome optical losses at 83 K; thus, they observed multimode lasing with an optical pumping threshold density of $\sim 3.0 \text{ kWcm}^{-2}$ [25].

This research aims to design a Ge ridge waveguide laser using a SiN_x stress liner to induce strong tensile strain in the Ge. In practice, SiN_x is deposited with 1-2 GPa of compressive strain using dual frequency plasma vapor deposition. The compressive SiN_x expands slightly when wrapped around a ridge, pulling the underlying semiconductor outward with it. A dual-frequency plasma-enhanced chemical vapor deposition (DFPECVD) can deposit compressively stressed SiN_x . Our group previously demonstrated that $>2\%$ tensile strain was achievable using SiN_x stress liners [37]. We simulated anisotropic and nonuniform strain, gain and refractive index across the waveguide for the first time, for higher accuracy than in previous reports. The optical gain and threshold current density calculations include mirror loss, free carrier absorption (FCA) loss including inter-valance band absorption (IVBA) loss. We showed that lasing from SiN_x strained Ge waveguides should be possible though threshold current density remains high.

5.2 COMSOL Strain Models

COMSOL is a well-developed software package for multi-physics simulation. It is particularly well suited to structural and stress/strain calculations such as the strained Ge waveguides used here. Using COMSOL, I calculated the strain profile across the entire Ge waveguide for given distribution of compressive stress in the SiN_x stress liner. To perform the stress-strain simulation, the SiN_x layer was initially defined as having a strong compressive stress, then the structure was allowed to relax. As mentioned previously, when the SiN_x layer relaxes, it expands and pulls the Ge waveguide

underneath, resulting in biaxial tensile strain within the waveguide. To achieve $\sim 2.4\%$ tensile strain, we had to apply 10 GPa of initial compressive stress. The induced tensile strain could result in a negligible amount of wafer bowing. I simulated many variations of the waveguide, as shown in (Figures 5.1-5.6), to find the aspect ratios that would induce strong tensile strain near the top of the waveguide and compressive strain on the bottom part. In this work, we ignored the wafer bowing, which would cause only a small change in strain.

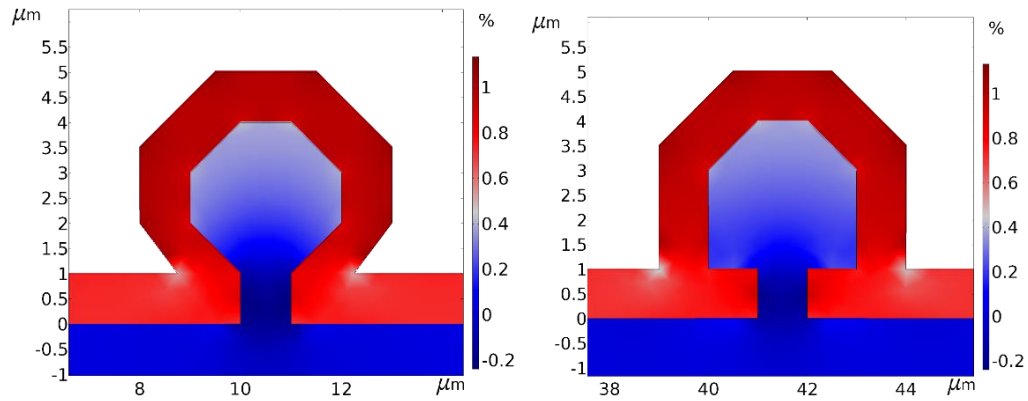


Figure 5.1: Volumetric strain in waveguides wrapped with 1 μm thick SiN_x stress liner: (a) polygon shape waveguide (b) dom shape waveguide.

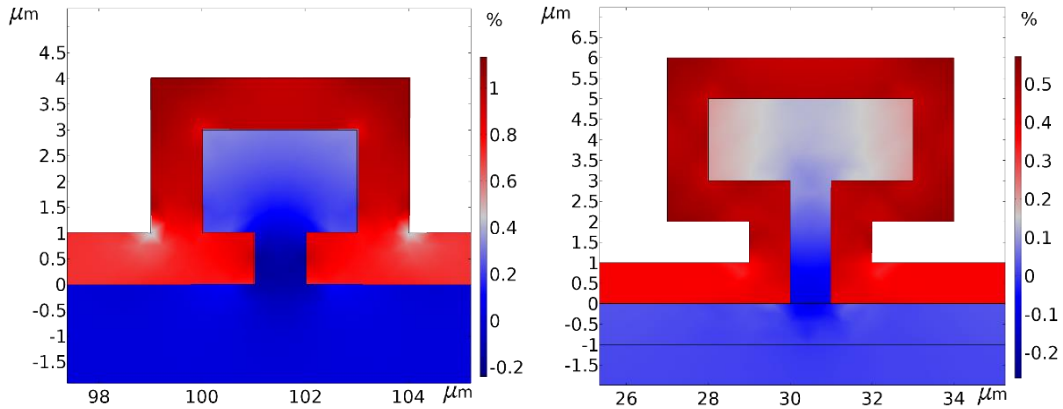


Figure 5.2: Volumetric strain in waveguides wrapped with 1 μm thick SiN_x stress liner: (a) undercut rectangular waveguide (b) undercut rectangular long neck waveguide.

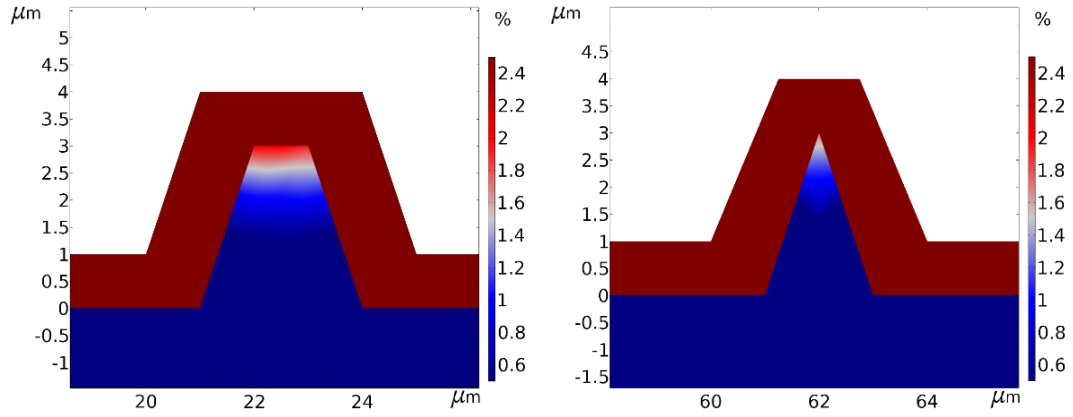


Figure 5.3: Volumetric strain in waveguides wrapped with 1 μm thick SiN_x stress liner: (a) trapezoidal waveguide (b) triangular waveguide.

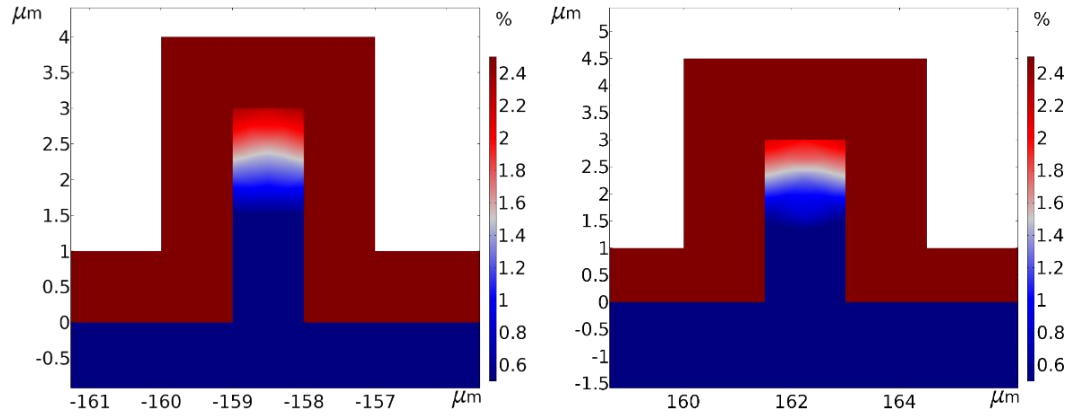


Figure 5.4: Volumetric strain rectangular ridge waveguides: (a) 1 μm wide, 3 μm tall, with 1 μm thick SiN_x stress liner, (b) 1.5 μm wide, 3 μm tall, wrapped with 1.5 μm thick SiN_x.

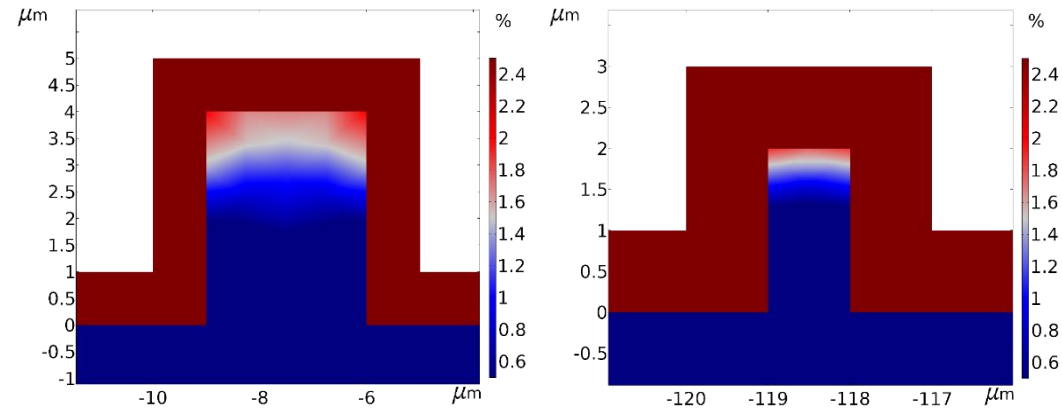


Figure 5.5: Volumetric strain in rectangular ridge waveguides: (a) 3 μm wide, 3 μm tall, 1 μm SiN_x, (b) 1 μm wide, 2 μm tall, 1 μm SiN_x.

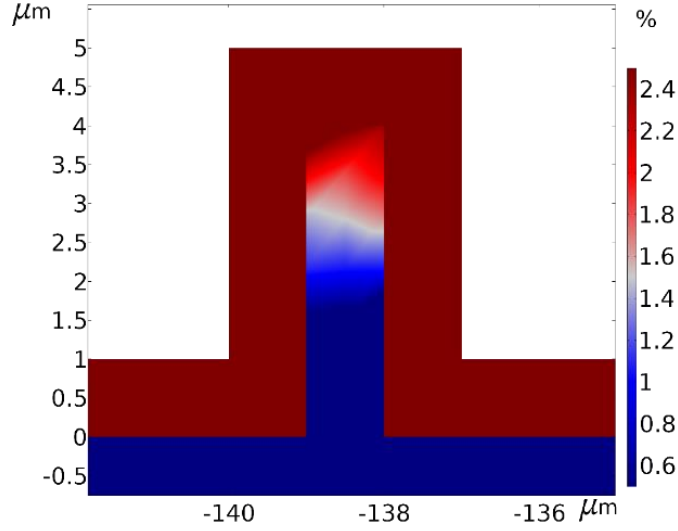


Figure 5.6: Volumetric strain of a rectangular ridge waveguide 1 μm wide and 4 μm tall, 1 μm SiN_x .

A rectangular ridge waveguide with 3 μm height and 1 μm width showed the desired combination of tensile and compressive strains, as shown in Figure 5.4(a).

From the strain profile across the waveguide, we next needed to calculate the refractive index profile.

5.3 VASP Simulation and Optical Mode

VASP allows calculation of the band structure and optical properties of a material from first principles (at least nominally). For this research, VASP was used to calculate the direct and indirect bandgaps and complex refractive index for Ge under a variety of strains (ϵ_{xx} , ϵ_{yy}), including mixtures of compressive and tensile anisotropic strains. Computations were performed for a two-atom Ge primitive cell using the HSE06 hybrid functional and spin orbit coupling for high accuracy. Maps of direct bandgap, indirect bandgap, and complex refractive index across the space of (ϵ_{xx} , ϵ_{yy}), and these maps were applied to the strain results from COMSOL to give the 2D profiles across the waveguide cross section for direct bandgap $E_{g,\Gamma}(x,y)$, indirect bandgap $E_{g,L}(x,y)$, absorption $\alpha(x,y)$, and refractive index $n(x,y)$.

5.4 MATLAB Mode Solver

With the refractive index profile at hand, we then needed to calculate the optical mode profile in the waveguide. This was done using a MATLAB based mode solver originally written by Dr. Vijit Sabnis for his Ph.D. at Stanford University.

Using the lowest order optical mode, I calculated the optical confinement factor (OCF or Γ) or overlap integral between the optical mode and a given quantum well (QW) in the waveguide:

$$\text{OCF or } \Gamma = \frac{\int \int_{z_1}^{z_2} |E_{op}(x,z)|^2 dz dx}{\int \int_{-\infty}^{\infty} |E_{op}(x,z)|^2 dz dx} \quad (5.1)$$

where Γ , E_{op} , z_1 , and z_2 are the optical confinement factor, electric field, and the start and end of the QW active region, respectively. The numerator is the overlap integral of the optical mode with only the active or gain region (QW), and the denominator is the integral over the entire waveguide.

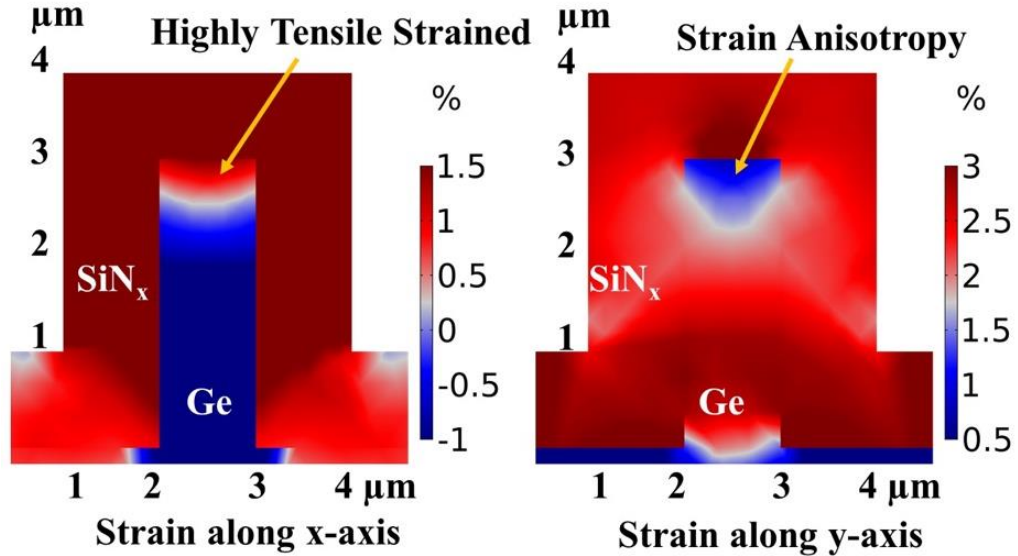


Figure 5.7: Vertical and the horizontal component of the tensile strain

The calculated refractive index and absorption for Ge are shown in Figure 5.8, as a function of strains in both x and y . Calculated refractive index data were used to map the refractive index profile within the waveguide as shown in Figure 5.9.

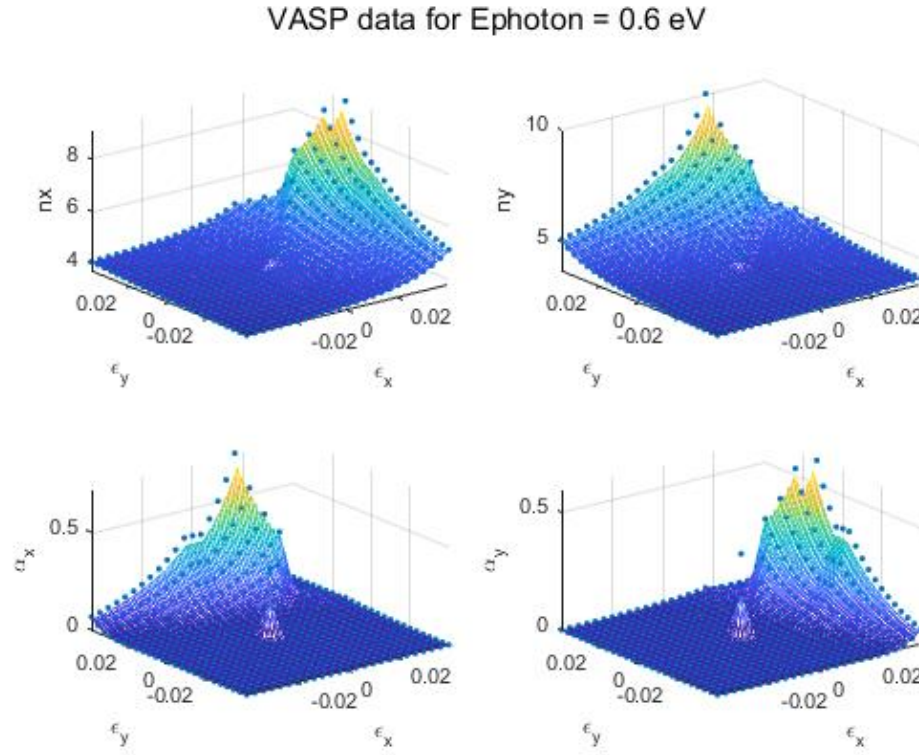


Figure 5.8: Optical properties of Ge with x and y strains from -2% to +2% for photon energy 0.6 eV. (a) Refractive polarized along x -axis, (b) Refractive index polarized along y -axis, (c) Absorption polarized along x -axis, and (d) Absorption polarized along y -axis.

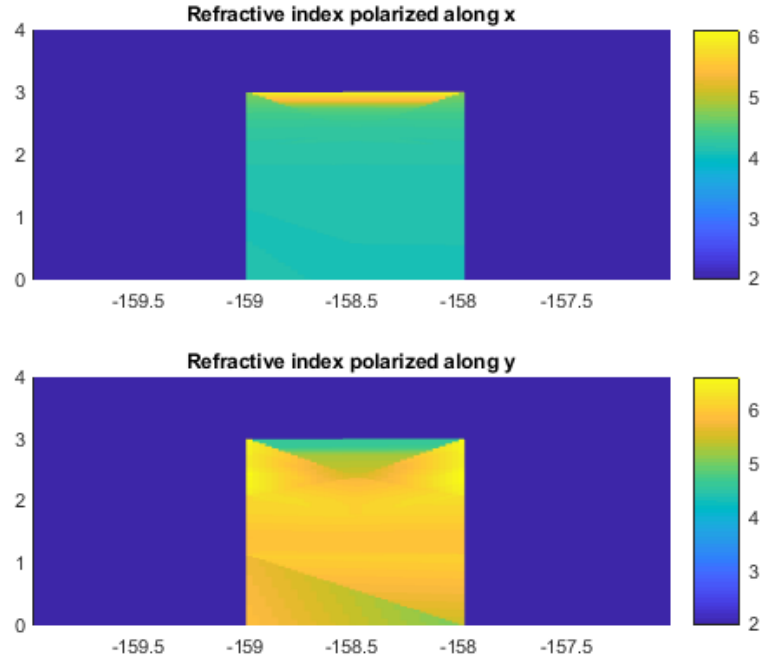


Figure 5.9: Refractive index map within the waveguide at 0.6 eV photon energy. (a) Polarized along the x-axis, and (b) Polarized along the y-axis. Horizontal and vertical axes are position in μm .

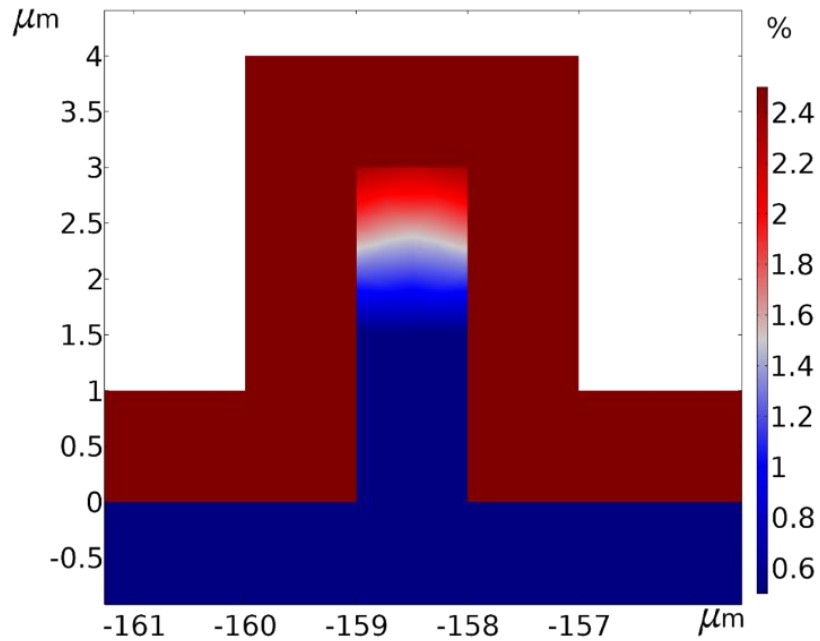


Figure 5.10: Volumetric strain on a rectangular ridge waveguide. The net tensile strain at the top part and compressive strain at the bottom part of the waveguide.

Due to the horizontal components of the strain, a significant horizontal compressive strain occurs along the bottom of the waveguide, and strong tensile strain in the top portion of the waveguide. This resulted in tight electronic and optical confinement on a tiny region near the top of the waveguide. However, the vertical component of the strain does the opposite, which tends to push the optical mode down toward the substrate. Fortunately, the horizontal component of the tensile strain at the top part is much stronger than the vertical compressive strain. Hence, we noticed a net tensile strain at the top part of the waveguide (Figure 5.10) and a strong optical confinement. The overall process is shown in Figure 5.11.

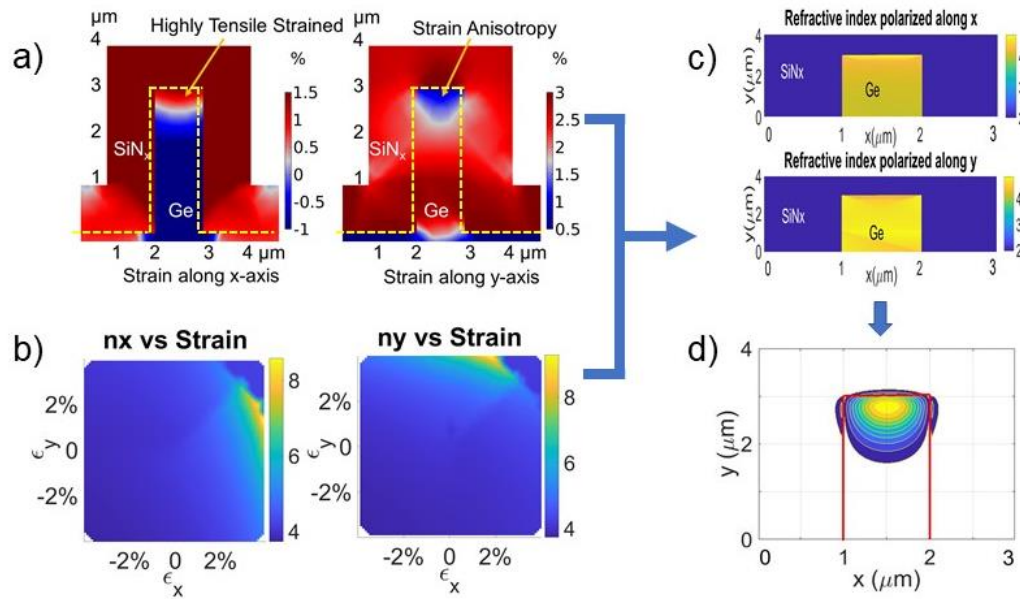


Figure 5.11: Process flow: (a) Horizontal and vertical component of tensile strain, (b) Change in refractive index with strain from VASP, (c) Refractive index profile within the waveguide, (d) Optical confinement.

5.5 Gain Calculations

The gain coefficient at a given photon energy is expressed in terms of absorption coefficient involving band to band transition and electron f_e and hole f_h distribution functions using –

$$g(hv) = |\alpha(hv)| (1 - f_e - f_h) \quad (5.2)$$

where

$$\alpha(hv) = A(hv - E_g^\Gamma)^{\frac{1}{2}}/hv \quad (5.3)$$

and

$$A \approx e^2 (2((m_h^* m_e^* / (m_h^* + m_e^*))^{3/2} / n_r c h^2 m_e^*)$$

where A is a constant related to the effective mass and momentum matrix elements. For bulk Ge with an index of $n_r = 4.1$, $A \approx 1.9 \times 10^4 \text{ eV}^{1/2} \text{ cm}^{-1}$ and strained Ge with an index of ~ 4.5 , $A \approx 2.01 \times 10^4 \text{ eV}^{1/2} \text{ cm}^{-1}$. Biaxial tensile strain breaks the degeneracy of the valence band, so absorption and gain from light and heavy holes were treated accordingly, and Equation (3) was modified as follows -

$$\alpha(hv) = A((hv - E_g^\Gamma(lh))^{1/2} + (hv - E_g^\Gamma(hh))^{1/2})/hv \quad (5.4)$$

where $E_g^\Gamma(lh)$ and $E_g^\Gamma(hh)$ are the energy difference between the top of the light and heavy hole bands to the Γ valley, respectively. To calculate the threshold gain, we used the equation

$$g_{th} = \alpha_m + \alpha_{FCA} + IVBA \quad (5.5)$$

where α_m is the mirror loss:

$$\alpha_m = (1/L) \log \left(1 / (R_1 R_2)^{\frac{1}{2}} \right) \quad (5.6)$$

with L as the length of the waveguide, and R_1 and R_2 are the reflectivity of the cleaved and coated side, respectively, which we assumed to be $R_1 = 35\%$ and $R_2 = 95\%$. Finally, the α_{FCA} in equation (5.5) is the free carrier absorption loss within the waveguide in the

conduction band, which has been obtained by using the following equation reported in Ref. [15]:

$$\alpha_{FCA} = -3.4 \times 10^{-25} N \lambda^{2.25} \quad (5.7)$$

where N is the electron density in cm^{-3} , λ is the wavelength in nm. From total gain and loss, we calculated the net gain at every point in the waveguide based on the strains at that point. The net gain was then multiplied by the optical mode strength and summed over the entire waveguide to calculate the total gain.

We plotted carrier injection vs. net gain for a particular photon energy at a constant dopant to calculate the threshold carrier density. We calculated the carrier injection for which the effective net gain was zero, which is the threshold carrier density. Finally, the threshold current was calculated using the following equation-

$$\frac{\eta_i I_{th}}{q V_a} \approx A n_{th} + B_{\Gamma} n_{th}^2 + B_L \left(n_{th} e^{-\frac{(E_L - E_{\Gamma})}{kT}} \right)^2 + C_n n_{th}^3 + C_p n_{th}^3 \quad (5.8)$$

where I_{th} , η_i , V_a , n_{th} , A , B , and C are threshold current, current injection efficiency, the volume of the active region, threshold carrier density, Shockley-Reed-Hall (SRH) recombination coefficient, radiative recombination coefficient, and Auger recombination coefficient, respectively. SRH recombination was assumed to be negligible in comparison with Auger and radiative recombination. The threshold current density was determined by dividing the threshold current by the total area of the waveguide.

5.6 Results

The initial compressive stress of 10 GPa on SiNx stress results in a maximum 2.4% tensile strain at the top of the Ge waveguide. However, the experimental setup only requires 2 GPa of compressive stress on SiNx to achieve ~2.4% tensile strain. For this

work, the goal was to achieve 2.4% tensile strain; hence we applied 10 Gpa of initial compressive stress on SiNx to accomplish that. The discrepancy between simulation and experimental values is likely due to the way SiNx is actually fabricated, using proton bombardment, and is outside of the scope of this work.

As mentioned above, the tensile strained region at the top of the waveguide has a higher refractive index, up to $n = 4.8$, and the compressive strain region along the bottom has a relatively low refractive index. As expected, the mode solver showed most of the light confined within that tiny portion (higher index region) at the top part of the waveguide. This is helpful for making small devices, as it allows miniaturization of the waveguide. Indeed, the mode was 88% confined within the Ge, with the rest in the SiNx cladding, and $<0.01\%$ in the substrate.

As expected, the maximum OCF for a 10 nm QW was when the QW was placed near the top of the waveguide was $\sim 7\%$ where the refractive index was highest. Similarly, bandgap mapping (Figure 5.12) showed that the bandgap is a minimum at the same location, for the best carrier confinement and highest gain. This QW was therefore used for the subsequent gain and threshold calculations.

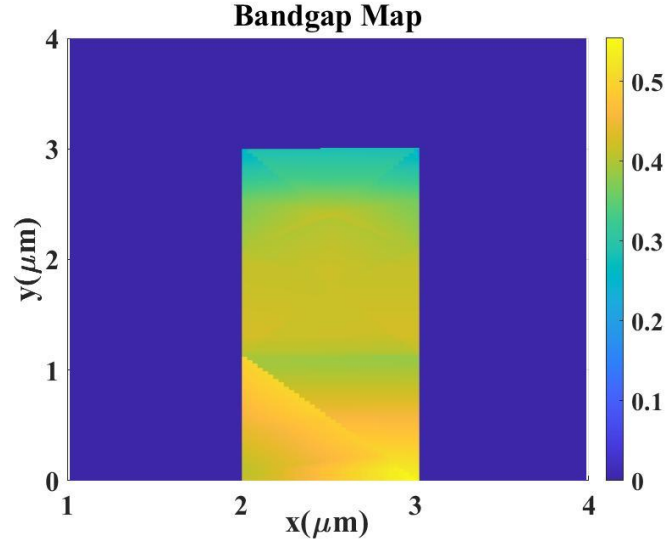


Figure 5.12: Bandgap (eV) within the waveguide for non-uniform bi-axial tensile strain. Note smallest bandgap along top edge.

The optical band to band absorption $\alpha(h\nu)$ was calculated using Equation 5.4 at various carrier injections and operating photon energy. Figure 5.13 shows the optical gain and intervalence band absorption (IVBA) map for every pixel within the waveguide at $1.25 \times 10^{19} \text{ cm}^{-3}$ carrier injection for an operating photon energy of 0.5 eV. For this work, the electron concentrations were assumed to be evenly distributed throughout the waveguide; followup work will include nonuniform population distributions.

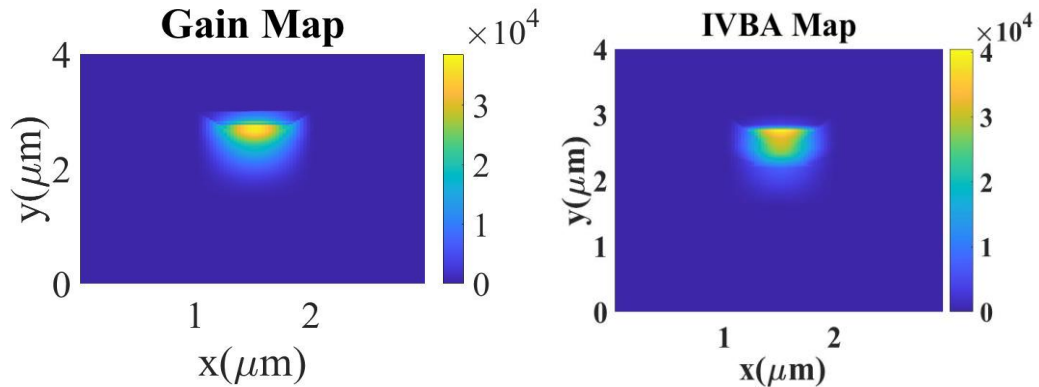


Figure 5.13: (a) Gain within the waveguide for non-uniform bi-axial tensile strain. (b) IVBA within the waveguide for non-uniform bi-axial tensile strain.

5.6.1 Gain

The gain was calculated using Equation 5.2 for a different carrier injection in the presence of a constant dopant concentration (N_d) of $1 \times 10^{19} \text{ cm}^{-3}$. Figure 5.14 shows the change in gain with operating photon energy and carrier injection. At lower carrier injection (N_e) of $4.28 \times 10^{18} \text{ cm}^{-3}$ the maximum gain was 2000 cm^{-1} at 0.6 eV operating photon energy. With the increasing N_e the maximum gain also increases, but after a particular N_e the gain remains constant. For a certain N_e , the total optical increases with increasing photon energy, but it does not increase linearly; after certain photon energy depending on N_e the gain starts to drop and becomes negative. We noticed that the total optical gain has a local maximum, which agrees with ref [115]. To have optical gain, the device must have to follow the population inversion conditions $(E_{fc} - E_{fv}) > E_g > h\nu$, here E_{fc} and E_{fv} are the quasi-fermi energy in the conduction band and valence band respectively, E_g is the bandgap and $h\nu$ is the photon energy. The value of E_{fc} and E_{fv} are directly related to the N_e through the Fermi-Golden rule. As N_e increase, the separation between E_{fc} and E_{fv} also increases, so does the total gain. Now, if the N_e is small enough that $E_{fc} - E_{fv} < h\nu$, there will be no gain due to the violation of the population inversion condition. Figure 5.15 showed that for $N_e = 4.28 \times 10^{18} \text{ cm}^{-3}$ the gain became negative after the photon energy of 0.6 eV and if we increase N_e to $2.62 \times 10^{19} \text{ cm}^{-3}$ the gain stays positive until the operating photon energy pass 0.8 eV. Now the question arises that, if we keep increasing N_e , is gain going raise as well? The answer is no; after a certain N_e the quasi-fermi energy separation became constant hence the gain. Figure 5.14 shows that the gain curve for $N_e = 3.18 \times 10^{19} \text{ cm}^{-3}$ and $N_e = 3.32 \times 10^{19} \text{ cm}^{-3}$ almost overlap each at all operating photon energy. This also explains, injecting too much carrier does not help

achieve gain, and they are not related linearly. In this research, the maximum reported gain was 6326 cm^{-1} for $N_e = 3.32 \times 10^{19} \text{ cm}^{-3}$ at an operating photon energy of 0.8 eV.

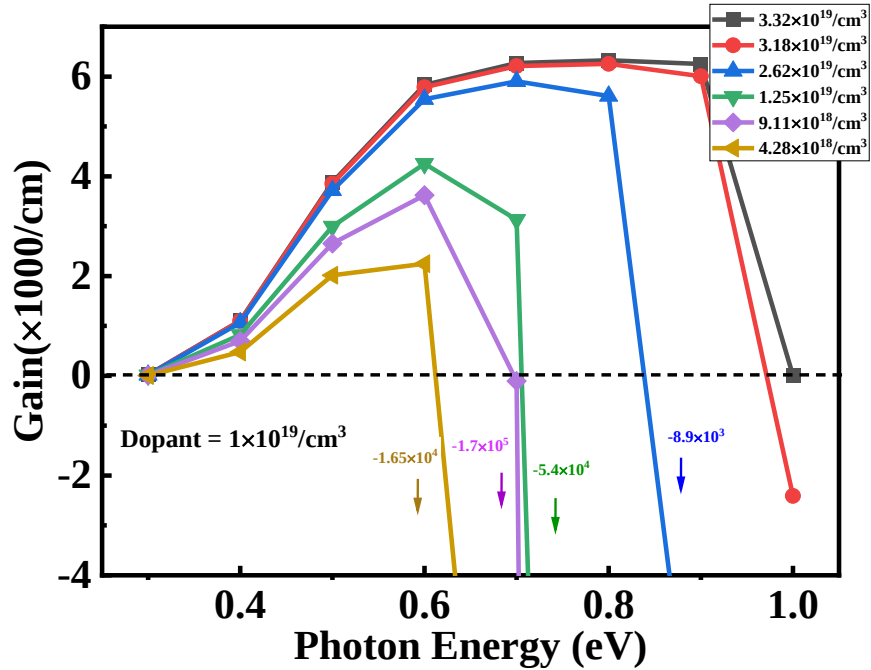


Figure 5.14: Optical gain calculations at different carrier injection.

5.6.2: Intervalence band absorption and free carrier absorption loss

The intervalence band absorption loss (IVBA) is a kind of loss in the valence band, and it was calculated using the same Equation 5.2. Applying tensile strain pushes the light hole (LH) band above the heavy hole (HH) due to the breaks in degeneracy. It contributes to three different kinds of absorption in the valence band: LH-HH, LH-SO, and HH-SO. This work included all three kinds of losses during the total loss calculation to achieve better accuracy. In the case of strained Ge, the energy separation between the light hole and the band's split (SO) is comparable with the light hole and conduction band (CB). When photon energy is applied, some photons excite electrons to the CB, and some push holes to the SO band. Because of that, in tensile strained Ge, the IBVA is very comparable to the total gain. Figure 5.15 shows IVBA changes with the operating photon

energy. Just like gain, it also does not change linearly; rather, IVBA has a local maximum. With the increasing number of carrier injections, IVBA increases significantly, but it saturates after a certain injection level. We noticed that the IVBA is the most significant loss in tensile strained Ge waveguide laser. We calculated maximum IVBA of 4836 cm^{-1} for $N_e = 3.32 \times 10^{19} \text{ cm}^{-3}$ at an operating photon energy of 0.6 eV. Besides IVBA, we also included free carrier absorption loss during the calculations.

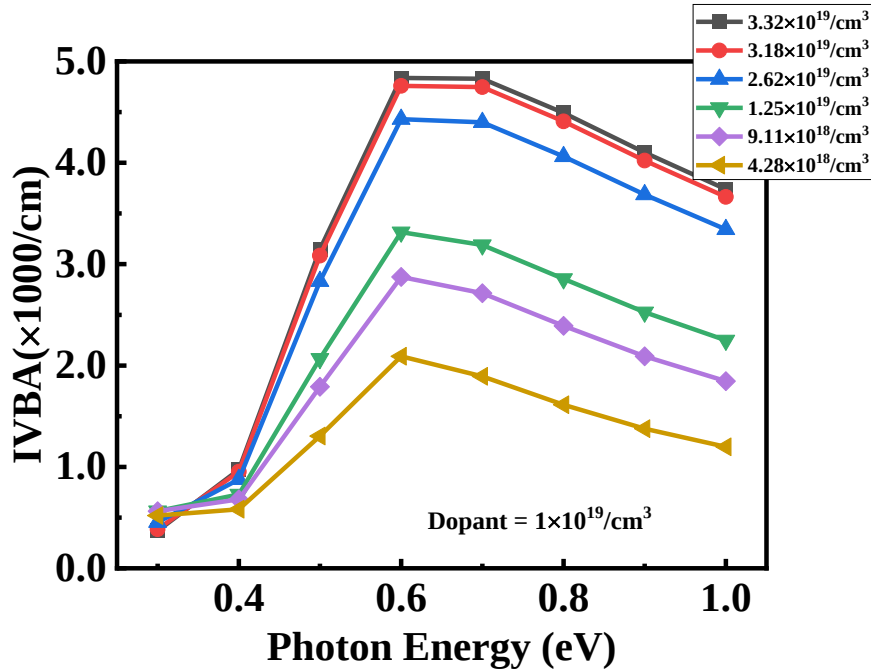


Figure 5.15: Change in intervalence band absorption loss with photon energy and carrier injection.

Free carrier absorption (FCA) is a kind of absorption that takes place in the conduction band. Most of the excited electrons in the CB return to the VB during the recombination process and emit light, but some of the electrons, instead of recombining they absorb the second photon and jump to the next conduction band, start to roam freely as free electrons. We used the Equation 5.7 from Ref. [15] to calculate FCA. Figure 5.16 shows, with increasing photon energy FCA decreases due to the reduction in second-order photon absorption. But FCA increases with increasing carrier injection; in this

work, the maximum reported FCA is 2010 cm^{-1} for $3.32 \times 10^{19} \text{ cm}^{-3}$ at 0.3 eV photon energy. We also observed that the increase in tensile strain increases gain, but it is negligible to significantly higher intervalence band loss; hence, the net gain became even smaller. This explains that a significant increase in strain does not help get lasing from strained Ge.

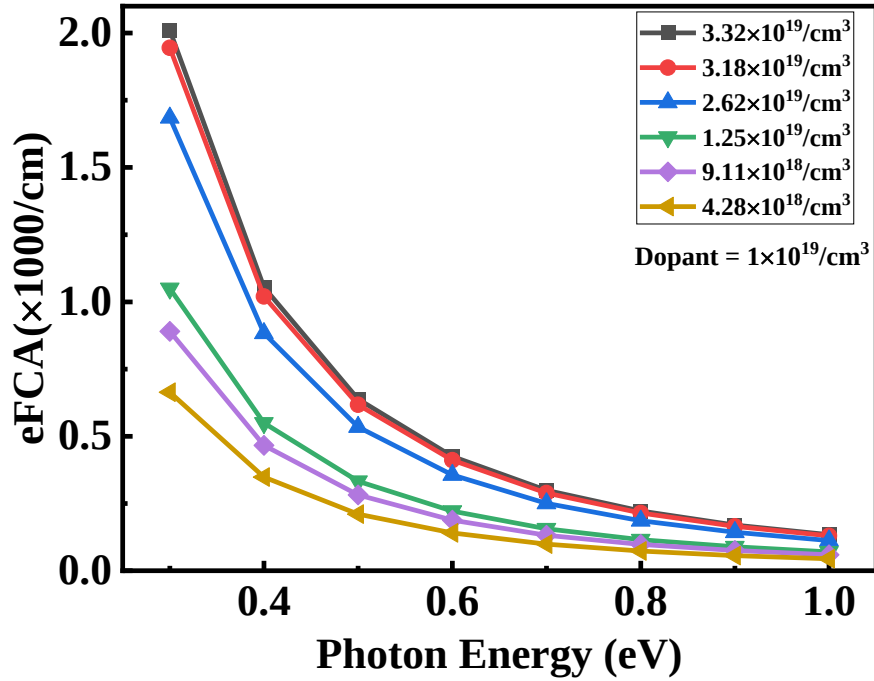


Figure 5.16: Change in free carrier absorption loss with photon energy and carrier injection.

5.6.3 Net Gain and threshold carrier density

Net gain was calculated by subtracting all losses from the total gain. Figure 5.17 shows the net gain changes with operating photon energy at different injection levels. A maximum net gain of 1936 cm^{-1} was reported in this work at 0.9 eV for $N_e = 3.32 \times 10^{19} \text{ cm}^{-3}$. We noticed that the net gain was higher at a higher injection level, and it started to saturate at very high carrier injection just like gain and IVBA.

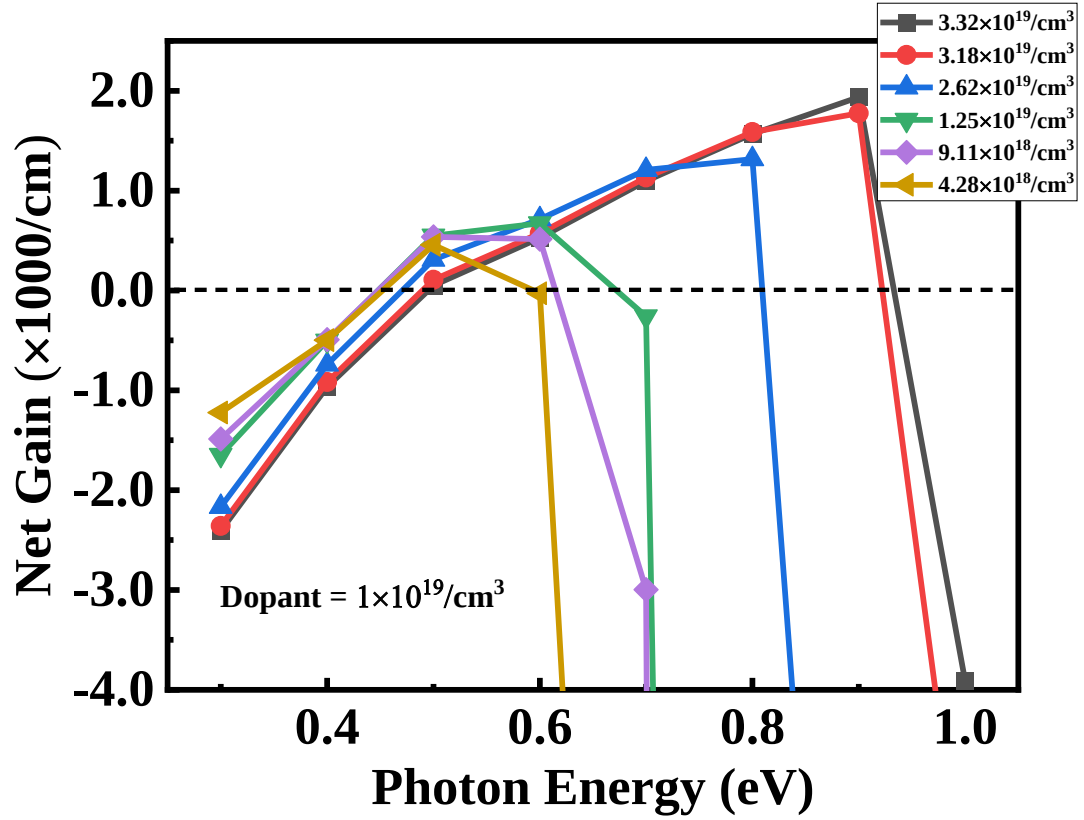


Figure 5.17: Net gain calculation at various photon energy and carrier injections.

The next step was to calculate the threshold carrier density using net gain vs. carrier injection for particular photon energy at constant dopant concentration (Figure 5.18). Threshold carrier density is the number of carriers for which the device overcame all the losses, and net gain became zero. Figure 5.19 showed how net gain varied at different levels of carrier injections for constant operating photon energy and dopant constant. From Figure 5.18, we found calculated threshold carrier density $N_{th} = 4.5 \times 10^{18} \text{ cm}^{-3}$.

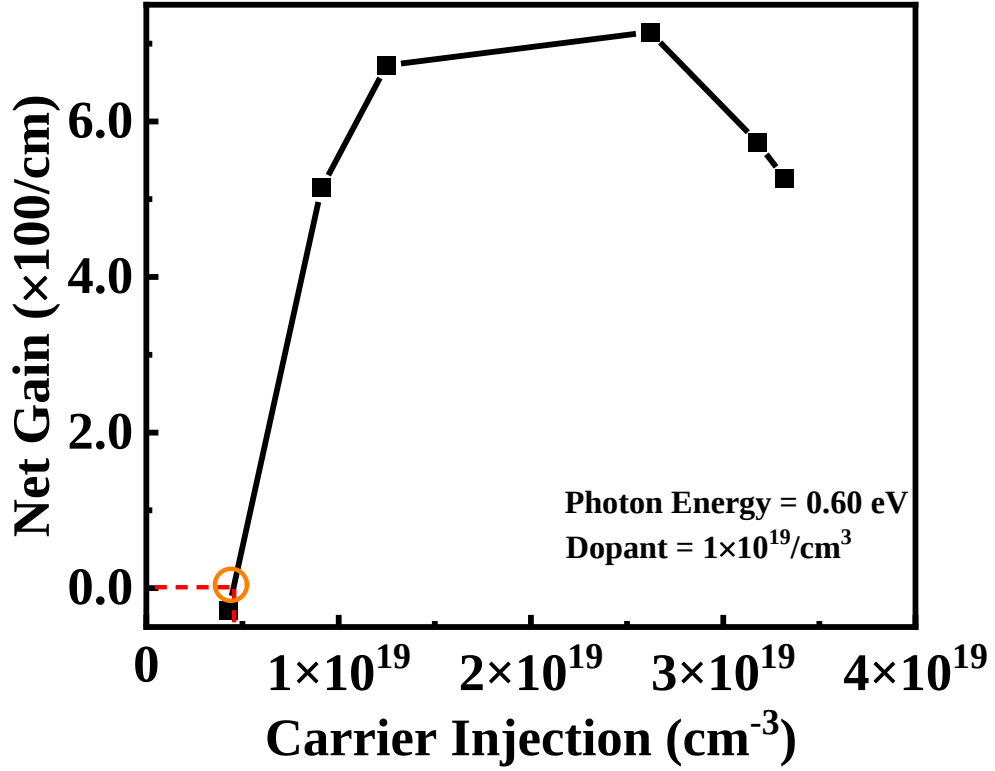


Figure 5.18: Net gain calculation for various carrier injections at constant dopant concentration and photon energy.

Using the value of threshold carrier density; threshold current was calculated following the Equation 5.8-

$$\frac{\eta_i I_{th}}{qV_a} \approx An_{th} + B_{\Gamma}n_{th}^2 + B_L \left(n_{th} e^{-\frac{(E_L - E_{\Gamma})}{KT}} \right)^2 + C_n n_{th}^3 + C_p n_{th}^3 \dots \dots \dots (5.8)$$

The Auger recombination and non-radiative recombination constants were calculated using the equation following Ref. [15]. A threshold current density of 1.4 kA/cm² was calculated by dividing the threshold current by the waveguide area.

Threshold carrier density is directly related to the threshold current and current density; hence, if threshold carrier density increases, threshold current and current density both rise. Figure 5.19 shows the relation between the photon energy, threshold carrier density

and threshold current density. We found that at higher photon energy, both threshold carrier density and current density are higher in the presence of a constant dopant.

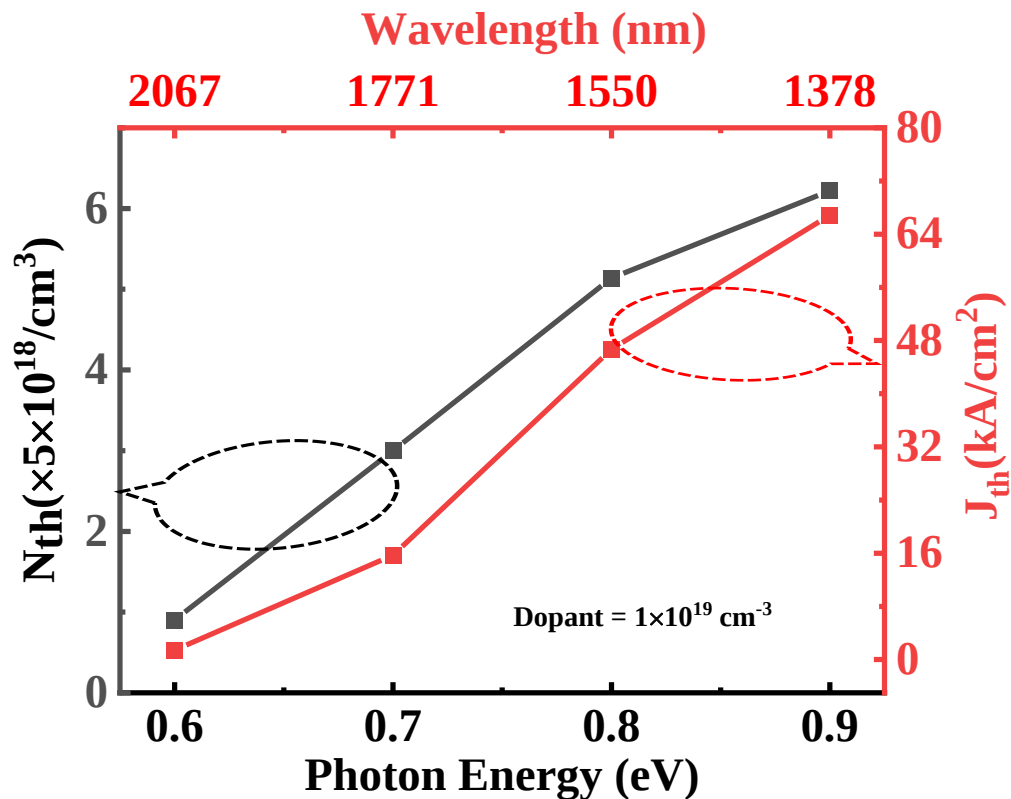


Figure 5.19: Relations between threshold carrier density, photon energy, and threshold current density at constant dopant concentration.

5.7 Summary

The performance of tensile strained Ge waveguide lasers was investigated in this chapter. I designed various sizes and shapes of strained Ge waveguides using COMSOL Multiphysics to optimize the strain profile within the waveguide. The electrical and optical properties of the strained Ge were calculated using Vienna Ab Initio Simulation Package (VASP). COMSOL and VASP results were combined to calculate the optical mode. SiNx stress liners were found to induce a direct bandgap in Ge ridge waveguides, offering optical gain and strong optical confinement in the same location. This study

shows applying a maximum of 2.5% anisotropic tensile strained Ge can be used as a CMOS compatible laser device. The predicted optical gain as high as 4120 cm^{-1} at an injection level of $8 \times 10^{18} \text{ cm}^{-3}$ in the presence of heavy n-type doping $= 1 \times 10^{19} \text{ cm}^{-1}$. However, the threshold current density was quite high, 1.4 kA/cm^{-1} was calculated for a 100 nm wide DH laser. Finally, we conclude at higher biaxial tensile strain and n^{++} doping, it should be possible to achieve lasing. However, further reducing the direct bandgap by adding Sn or C would vastly reduce threshold currents by separating the direct and indirect valleys, so fewer total electrons were needed to reach inversion.

6. CONCLUSION AND FUTURE WORK

The growth of $\text{Ge}_{1-x}\text{C}_x$ and associated characterizations demonstrated in this dissertation is proof of the successful growth of crystalline $\text{Ge}_{1-x}\text{C}_x$ on GaAs substrate using CBr_4 as a precursor for C. It also proves another concept; the substitutional incorporation of C in Ge reduces the overall bandgap of the alloy. Finally, this dissertation addresses the challenges associated with the current state-of-the-art $\text{Ge}_{1-x}\text{C}_x$ growth process. The current state of the $\text{Ge}_{1-x}\text{C}_x$ growth uses high-energy techniques like pyrolytic graphite filaments and rod-fed e-beam as C source materials. However, sourcing C through a high energy process often time supply C clusters; sometimes, it also contributes to surface damage. The most challenging part associated with the growth of $\text{Ge}_{1-x}\text{C}_x$ is to incorporate C substitutionally with Ge. Two effective solutions have been presented in this dissertation using novel approaches that have never been reported before. The Raman spectroscopy and HRXRD showed successful substitutional incorporation of C in Ge. The RSM measurements showed pseudomorphic growth, and the film was fully strained with the substrate. The PL measurements showed optical emission from $\text{Ge}_{1-x}\text{C}_x$ film at a bandgap smaller than bulk Ge for the first time, which is a significant step forward toward Group IV based direct bandgap semiconductor. As I stated in Chapter 1, growing $\text{Ge}_{1-x}\text{C}_x$ thin film with substitutional C incorporation has the following advantages:

- i. This is a significant step forward to achieve direct bandgap and optical emissions from Group IV materials and their alloy. In addition, this will enable monolithic integration of optical devices on existing Si CMOS.

- ii. The Group IV-based laser integration will enable the optical data transfer between chip to chip and cores to the core, which will make the data transfer rate much faster, as light travels much quicker than the electron in long-distance communications. Besides that, a large volume of data can be transferred simultaneously through the waveguide using the WDM technology.
- iii. The monolithic integration of III-V on Si CMOS requires multiple cost-sensitive complex process steps with a very thick buffer layer to prevent the diffusion of III-V materials, which takes a larger area within the chip. Besides that, III-V behaves as contamination in Si foundry. Having a Group IV laser will help overcome these challenges. This dissertation is one step forward in that direction.

6.1 Contribution of this work

a. In this dissertation, I demonstrated the successful growth of $\text{Ge}_{1-x}\text{C}_x$ at various growth temperatures using CBr_4 as a C precursor. Before this dissertation, CBr_4 was never used to grow $\text{Ge}_{1-x}\text{C}_x$ thin film. The HRXRD couple scan found that the substitutional C percentage varied between 0.72 – 0.75% depending on the growth temperature. In addition, the RSM study on a sample showed pseudomorphic growth. The substitutional C signature was confirmed by G-C local mode at 530 cm^{-1} on Raman study. The significant contribution was to achieve optical emission from $\text{Ge}_{1-x}\text{C}_x$ for the first time.

b. In the second project, I introduced atomic H during the growth of $\text{Ge}_{1-x}\text{C}_x$ for the first time. In the presence of atomic H, the total C percentages were higher at low

temperatures than the samples grown without atomic H at the same CBr₄ flux. However, at a relatively higher growth temperature near 324 °C, the C percentage dropped significantly. We assumed this was happening because atomic H started to etch the surface C and Ge near that temperature. Further study is necessary to understand the selective etching of atomic H. For the same sample, I noticed sub-nanometer scale root means square (RMS) roughness and streaky RHEED pattern, which gave us an idea that atomic enhance the growth quality at the higher growth temperature. As atomic H selectively etch sp² C at a higher rate compared to the sp³ C. Hence, we assumed that atomic H etched the graphitic C cluster at a higher rate than heavier Ge_{1-x}C_x alloy, though we do not have enough data to support this, and further study is necessary. However, no sign of graphitic C in Raman spectroscopy supports our claim. The significant contribution of this project was to understand the impact of atomic H on the growth dynamics of Ge_{1-x}C_x.

c. During the third project, I studied tensile strained Ge and Ge alloy to achieve direct bandgap and optical emission. From the tensile strained Ge project, I was able to identify that the intervalence band absorption (IVBA) is the most significant source of loss in a strained Ge waveguide laser. Furthermore, the valence band degeneracy was contributing to the higher IVBA. The other sources of loss were the free carrier absorption loss and the mirror loss. The calculated threshold current density was 1.43 kA/cm², much higher than the traditional III-V laser. The conclusion was that incorporating tensile strain with Ge alloy might solve the higher threshold current density problem.

6.2 Future work

6.2.1 $\text{Ge}_{1-x}\text{C}_x$ growth at variable CBr_4 flux

In this dissertation, I have shown the successful growth of $\text{Ge}_{1-x}\text{C}_x$ with and without atomic H. In the future study, using the initial growth condition from this research, further growth of $\text{Ge}_{1-x}\text{C}_x$ can be done using variable CBr_4 flux with and without atomic H. This will give an idea about the impact of C percentage on the film's optical and electrical properties. In this research, with 0.72-0.75% of substitutional C, optical emissions were observed near 0.6 eV. The future study with increasing C percentage can give an idea of whether increasing C percentage can further reduce the bandgap toward achieving direct bandgap.

6.2.2 High-temperature growth $\text{Ge}_{1-x}\text{C}_x$ in the presence of atomic H

In this dissertation, I found that, $\text{Ge}_{1-x}\text{C}_x$ grown at 324 °C with atomic H exhibit an exceptionally low RMS roughness. Besides that, the streaky RHEED pattern resembles excellent surface reconstruction during the growth. Furthermore, the C percentage at that high temperature in the presence of H went down to 0.45%, which is much lower than the theoretically expected ~1% C percentage to achieve the direct bandgap on $\text{Ge}_{1-x}\text{C}_x$. Hence, we didn't notice optical emission from the film. However, since the film quality was excellent in terms of crystal quality and substitutional C incorporation, we think further study is necessary using the variable C percentage to understand whether a higher percentage of C will improve the optical emission or not. Besides that, an investigation is essential to calculate etch rate of atomic H at various growth conditions to optimize the flow rate of atomic H.

6.2.3 Extended defect analysis of $\text{Ge}_{1-x}\text{C}_x$ thin film

In this dissertation, the successful incorporation of C in Ge has been demonstrated. The XRD and Raman measurements suggest the substitutional incorporation of C in Ge, yet we do not see strong optical emissions. This might happen due to various kinds of the defect. An electrical characterization on a thick $\text{Ge}_{1-x}\text{C}_x$ film can be done to identify the point defects and vacancies. Besides that, to get a better sense of substitutional and interstitial C, Rutherford backscattering can be done. To determine the unwanted molecules in the film surface (bromine, oxygen, or hydrogen), the time of flight secondary ion mass spectroscopy can be done. All these characterizations together can give a better sense regarding the presence of a defect in the film.

APPENDIX SECTION

APPENDIX A: STABILIZATION OF CBr_4 BEAM EQUIVALENT PRESSURE (BEP)

In this dissertation carbon tetrabromide (CBr_4) was sourced from evaporated solid CBr_4 , which evaporates at room temperature. By nature, it is a sticky gas, and wants to stick to the wall of the metal tubes. Continuous evaporation and the stickiness of CBr_4 results unstable beam equivalent pressure (BEP) during the growth, which could lead to non-uniform growth. To address this issue, we had to implement a few techniques.

To prevent CBr_4 sticking to the wall, we wrapped the entire metal line using heating tape. Using heating tape has some limitations, for example keeping the temperature too high in heating tape might crack the CBr_4 even before enters the growth chamber and deposit graphitic C. Hence, the thermocouple was set to near 100 °C intentionally; it was high enough temperature to prevent stickiness and low enough that CBr_4 will not start cracking.

The second challenge was to stable the BEP. We noticed, after opening CBr_4 to chamber in showed a little spike. From there BEP slowly goes down to a local minimum and again starts to raise slow and steady. We noticed, after 30 minutes of observation the BEP became double of the BEP at local minimum (Figure A.1). To prevent this, we introduced a multi-step BEP stabilization process. Where, we initially opened the needle valve wide to achieve higher BEP than expected and let it flow until the BEP starts to raise from local minimum. In next step, the needle valve was dialed down slowly to atleast 1 turn more than expected needle valve position and let it stable. Again, BEP will raise from local minimum but at a much slower rate. In final step, the needle valve was

dialed down to a position where the CBr₄ BEP was as expected for the growth. This process takes about 1 hour from beginning to the end.

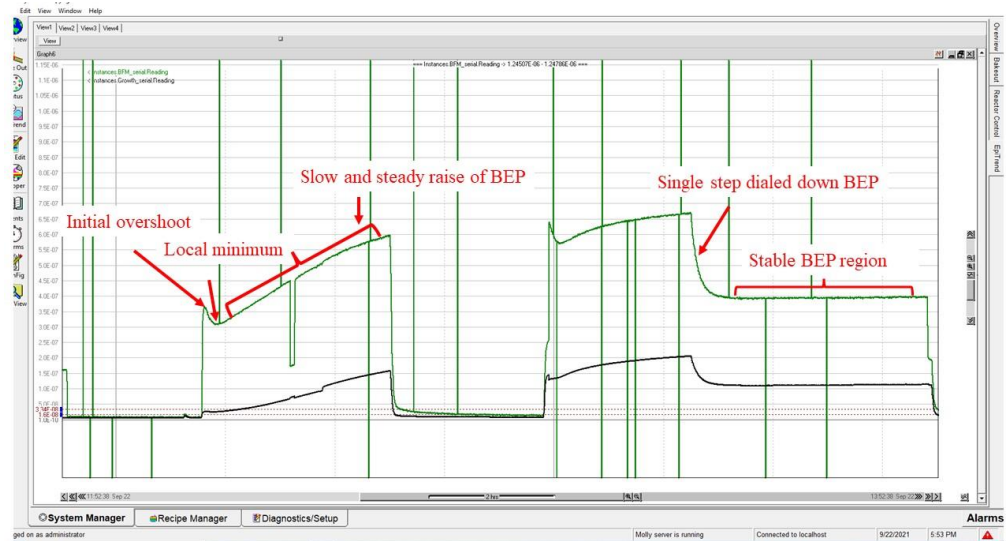


Figure AI.1: Slow and steady increase of beam equivalent pressure after opening CBr₄ to chamber.

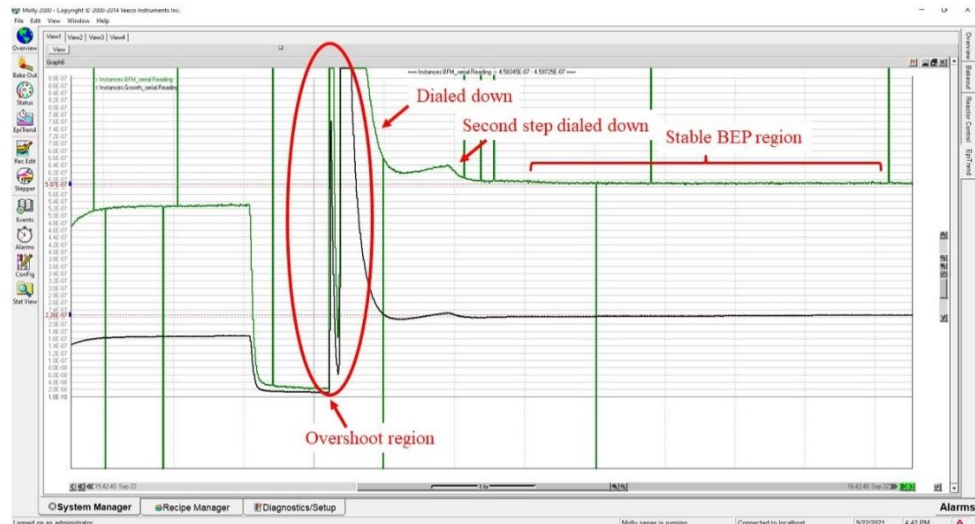


Figure AI.2: Overshooting of CBr₄ BEP and multi-step dialed down of BEP to achieve stabilization

APPENDIX B: POSSIBLE SURFACE REACTION AND BOND DISSOCIATION

ENERGY

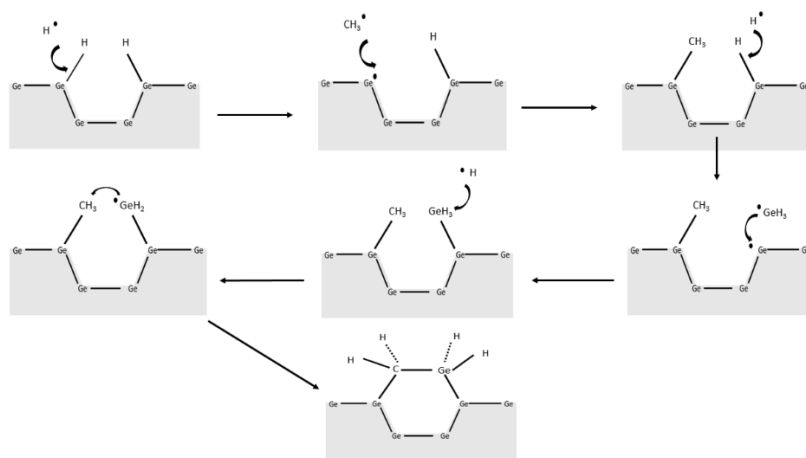


Figure AII.1: Possible surface reaction during the growth GeC

Table AII.1: Bond dissociation energy of possible surface reaction

<u>Chemical bond</u>	<u>Bond dissociation</u>
C-H	411 kJ/mol
Ge-C	238 kJ/mol
H-H	436 kJ/mol
H-Br	366 kJ/mol
Ge-Br	276.1 kJ/mol
Ge-H	263 kJ/mol
Ge-Ge	188 kJ/mol
C-C	347 kJ/mol
C=C	613 kJ/mol
C≡C	839 kJ/mol

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