[Title]

A [thesis/dissertation] submitted in partial fulfillment
of the requirements for the degree of
[Doctor of Philosophy/Masters] in [Microelectronics-Photonics / Materials Science / Materials Engineering / Materials Science and Engineering]

by

[student's name]
[University]
Bachelor of Science in [dept], [date]
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Master of Science in [dept/program], [date]
[University]
Doctor of Philosophy in [dept/program], [date]

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University of Arkansas

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Abstract

[Germanium-tin alloys with Sn compositions higher than 8 at. % to 10 at. % have recently attracted significant interest as a group IV semiconductor that is ideal for active photonics on a Si substrate. The interest is due to the fact that while at a few percent of Sn, GeSn is an indirect bandgap semiconductor, at about 8 to 10 at. % Sn, GeSn transitions to a direct bandgap semiconductor.]

Acknowledgements

[First of all, I would like to express my sincere gratitude to my scientific advisor Professor Gregory J. Salamo for his support during the Ph.D. study and whose invaluable critique and advices shaped my scientific approach. I would also like to thank Dr. Rick Wise for accepting me into the Microelectronics-Photonics program, as well as for his guidance that helped to complete this journey.]

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Chapter 1. Introduction

1.1 Background

Silicon (Si), and to a lesser extent germanium (Ge), are the central semiconductors for electronics today. Yet, modern photonic devices are based on a variety of different compound semiconductors, each of which is chosen to provide the ultimate performance for specific applications [1].

1.1.1 Crystal Structure

The atomic arrangement in a crystal is determined by the valence electron configuration of constituent atoms. Group IV elements Si, Ge, and Sn are known as tetrahedral solids since their four valence electrons participate in electron sharing with four adjacent atoms.

1.1.2 Lattice parameter of the GeSn alloy

The substitution of Sn atoms with the larger atomic radius (Table 1.2) into the Ge lattice results in a sufficient increase of the unit cell volume. The equilibrium lattice parameter, a_0, for a binary $Ge_{1-x}Sn_x$ compound is a function of Sn content, x. The value of a_0 can be simply estimated as a linear interpolation (Vegard's law) between the Ge and α-Sn bulk lattice constants with the bowing parameter correction as follows [48],

$$a_0 = a_{Sn}x + a_{Ge}(1-x) + bx(1-x) \qquad \text{(Equation 1.1)}$$

Chapter 2. Experimental and theoretical methods

2.1 X-ray diffraction

The x-ray diffraction (XRD) experiment was carried out by using the Panalytical X'Pert Pro MRD diffractometer. The diffractometer is equipped with a fixed 1.6 kW x-ray tube with Cu anode that produces monochromatic Cu Kα1 radiation with the wavelength λ = 1.5406 Å. The monochromatization of the x-ray beam was achieved with the four-bounce Ge (220).

2.1.1 X-ray diffraction ω/2θ scan

The ω/2θ scan (radial scan) is performed by simultaneously changing the incident beam angle, ω, and the scattering angle, 2θ, so that the change of the detector is rotated with a step size Δ(2θ) that corresponds to twice the step size over the ω axis (Figure 2.2a).

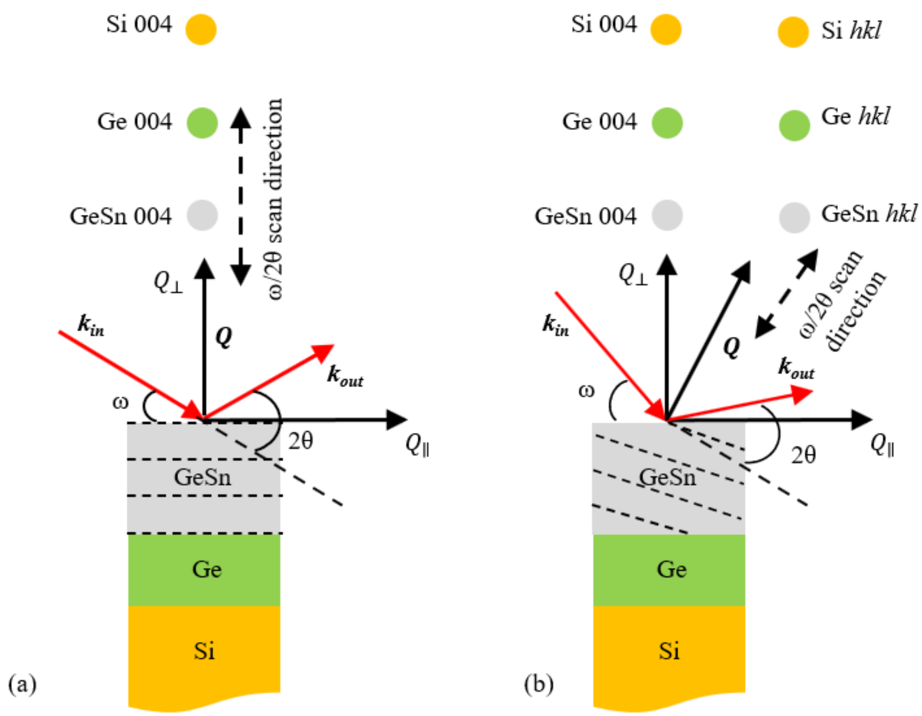


Figure 2.1 The scattering geometry for an ω/2θ scan for the case of symmetrical (a) and asymmetrical (b) reflection.

Chapter 3. The interplay of compressive strain and Sn composition in GeSn/Ge/Si(001) heterostructures

3.1 Introduction

Epitaxial growth of $Ge_{1-x}Sn_x$ layers on Ge is affected by the built-in compressive strain that is the result of large mismatch (15%) between the crystal lattice of Ge and α-Sn. Accordingly, the magnitude of strain in a $Ge_{1-x}Sn_x$ layer is a function of Sn composition and, thus, increases with the Sn content.

For a $Ge_{1-x}Sn_x$ alloy, the lattice parameter, a_0, and the elastic constants vary with Sn composition, x, almost linearly. Therefore, these are approximated using Vegard's law,

$$a_0 = xa_{Sn} + (1-x)a_{Ge} \qquad \text{(Equation 3.15)}$$

$$C_{11} = xC_{Sn}^{11} + (1-x)C_{Ge}^{11} \qquad \text{(Equation 3.16)}$$

$$C_{12} = xC_{Sn}^{12} + (1-x)C_{Ge}^{12} \qquad \text{(Equation 3.17)}$$

Chapter 4. Structural stability of GeSn/Ge heterostructures under thermal annealing

4.1 Introduction

Germanium-tin alloys are exciting semiconductors for CMOS compatible photonic applications due to their direct bandgap at Sn concentrations larger than 8-10 at. % [24]. At the same time, under the equilibrium growth conditions, the solid solubility of Sn in Ge is less than 1.1 at. % and the eutectic temperature is as low as 231.1 °C.

Table 1.1. The measured Sn content and lateral strain in the GeSn layer of samples S1, S2, and S3 using the GeSn peak position on the $\bar{2}\bar{2}4$ RSM.

Sample	Sn content, x (at. %)	Lateral strain, $\varepsilon_{\parallel} \times 10^{-3}$
S1	6.8	-7.4
S2	6.9	-0.4
	7.9	-1.3
S3	6.5	-0.1
	7.3	-0.8

Chapter 5. Conclusion and outlook

In this dissertation, the thermal stability, structural, and optical properties of the GeSn/Ge/Si(001) heterostructures were investigated by XRD, PL, AFM, EDX, SIMS, Raman spectroscopy, and x-ray diffraction simulations.

Simulations of x-ray diffuse scattering from the GeSn layers were exploited for rapid and accurate determination of the Sn composition, strain state, and density of misfit dislocations in each region of the GeSn layer. It was shown that the Sn incorporation during the growth of the GeSn layer is suppressed due to the built-in compressive strain.

References

[1] L. Chrostowski and M. E. Hochberg, *Silicon photonics design*. Cambridge, United Kingdom: Cambridge University Press, 2015, pp. 5–16.

[2] M. J. Deen and P. Kumar Basu, *Silicon Photonics : Fundamentals and Devices*. New York, NY, USA: Wiley, 2012, pp. 1–11.

[3] L. Pavesi, “Will silicon be the photonic material of the third millenium?,” *Journal of Physics Condensed Matter*, vol. 15, no. 26. IOP Publishing, pp. 1169–1196, Jul. 09, 2003, doi: 10.1088/0953-8984/15/26/201.

Appendix A: Description of Research for Popular Publication

Estimation of chemical composition and deformation at nanoscale

At present days, silicon is the key element for most electronic devices, partly owing to its semiconducting properties and the fact that silicon is the second most abundant element on the Earth's crust. Over the years silicon technology was advancing at a fast pace, which ultimately resulted in low-cost manufacturing and affordable electronics. At the same time, silicon exhibits poor optical properties that hinder its prospects for active photonic devices, which include light emitting and sensing applications. There are many other materials with excellent optical properties. For example, such materials as gallium arsenide (GaAs), gallium phosphide (GaP), as well as their alloys, have been extensively used for light-emitting applications. Nonetheless, their integration with silicon electronics is cumbersome since these are chemically dissimilar materials.

Appendix B: Executive Summary of Newly Created Intellectual Property

Germanium-tin alloys with the Sn content above 8 at. % were extensively studied as prospective quasi direct bandgap semiconductors for optoelectronics on Si substrate. The bandgap directness of GeSn was tightly correlated to the alloy composition and the strain state, which has an ultimate effect on the optical properties. The structural stability of GeSn under annealing treatment was correlated with the Sn segregation, strain relaxation, and the density of defects. The major results obtained in the course of this research are summarized below.

1. Experimental and theoretical X-ray diffraction analysis was demonstrated as a precise and non-destructive technique for the rapid assessment of the chemical composition, strain state, and density of defects in GeSn alloys.
2. The suppressed Sn incorporation in the GeSn layers during the epitaxial growth on Ge was quantitatively correlated to the built-in compressive strain.

Appendix C: Potential Patent and Commercialization Aspects of Listed Intellectual Property Items

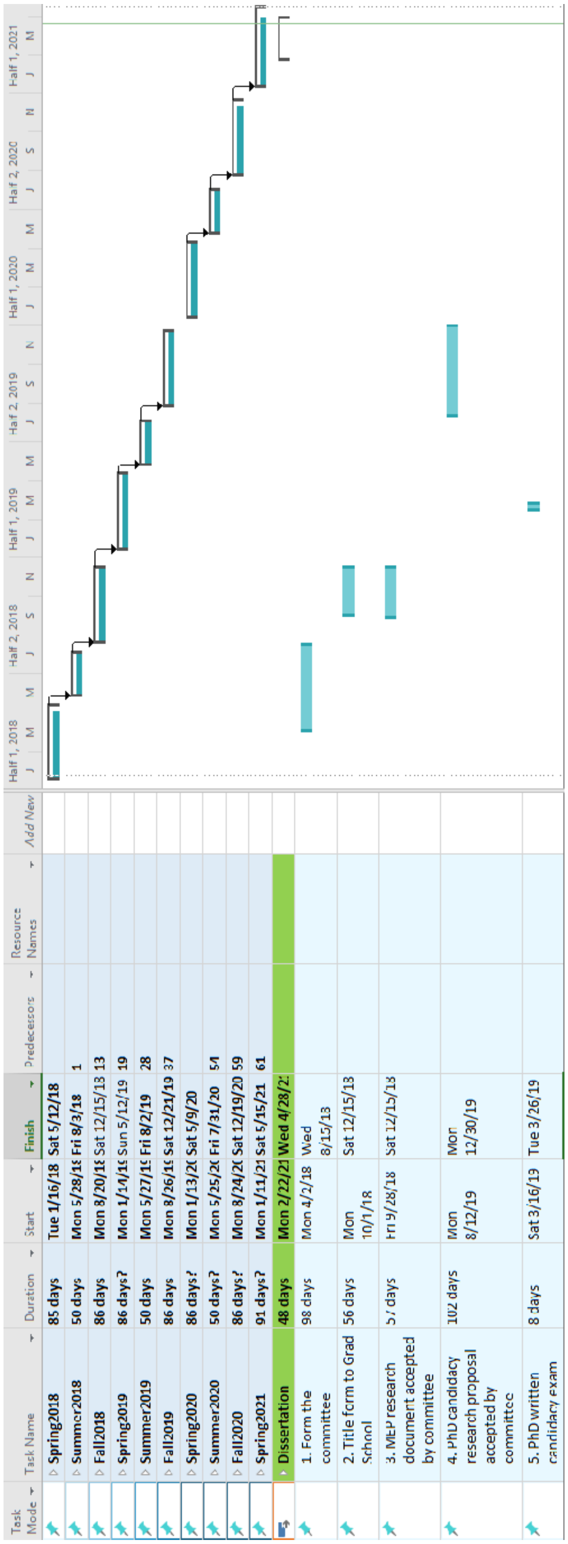
C.1 Patentability of Intellectual Property

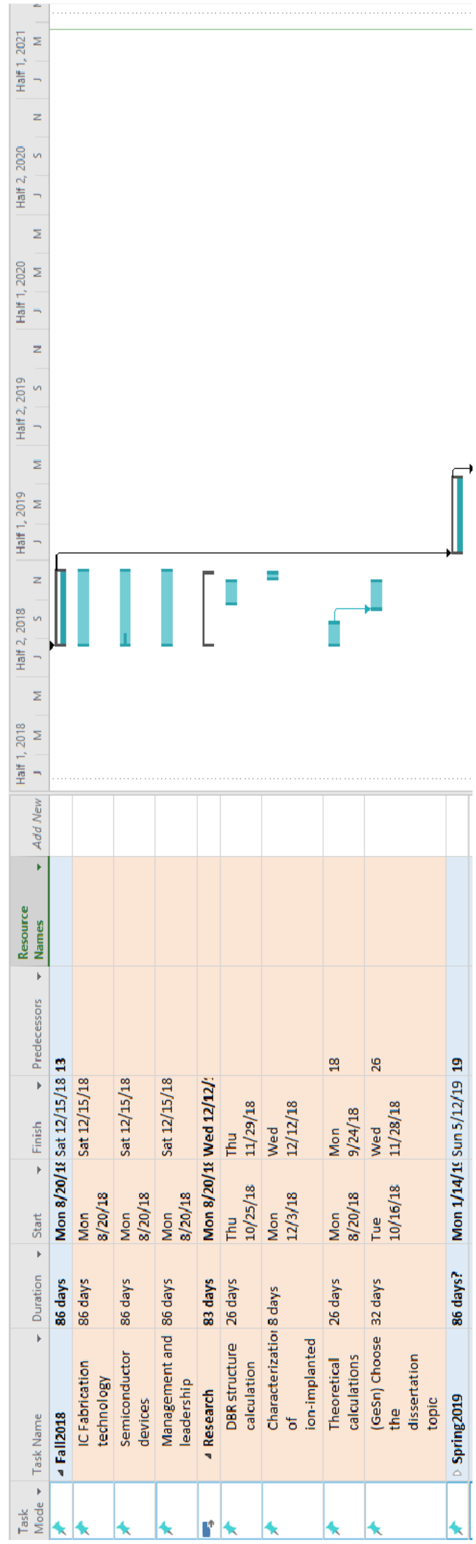
The four items listed were considered first from the perspective of whether or not the item could be patented.

1. The X-ray diffraction method developed in this research to measure the chemical composition, strain state, and density of misfit dislocations in the GeSn/Ge/Si(001) heterostructures cannot be patented since it is well known and extensively used for other material systems.
2. The effect of suppressed Sn incorporation in the GeSn layers during the epitaxial growth cannot be patented because it occurs naturally and is not an invention.

Appendix D: Broader Impact of Research

Appendix E: Microsoft Project for [MS/PhD] [MicroEP/MSEN] Degree Plan





Appendix F: Identification of All Software Used in Research and Dissertation Generation

Computer #1:
- Model Number: Dell Optiplex 9010
- Serial Number: 7038090
- Location: NANO213B
- Owner: Hryhorii Stanchu

Software #1:
- Name: Microsoft Office 365
- Purchased by: University of Arkansas Site License

Software #2:
- Name: Matlab R2018b
- Purchased by: University of Arkansas Site License

Software #3:
- Name: 3ds Max 2019
- Purchased by: University of Arkansas Site License

Software #4:
- Name: Vesta ver. 3.5.2
- Purchased by: free of charge

Software #5:
- Name: Mendeley Desktop ver. 1.19.4
- Purchased by: free of charge

Appendix G: All Publications Published, Submitted and Planned

Published

[1] **H. V Stanchu**, A. V Kuchuk, Y. I. Mazur, K. Pandey, F. M. de Oliveira, M. Benamara, M. D. Teodoro, S.-Q. Yu, and G. J. Salamo, "Quantitative Correlation Study of Dislocation Generation, Strain Relief, and Sn Outdiffusion in Thermally Annealed GeSn Epilayers," *Cryst. Growth Des.*, vol. 21, no. 3, p. 1666-1673, Jan. 2021, doi: 10.1021/acs.cgd.0c01525.

[2] S. V Kondratenko, S. S. Derenko, Y. I. Mazur, **H. Stanchu**, A. V Kuchuk, V. S. Lysenko, P. M. Lytvyn, S.-Q. Yu, and G. J. Salamo, "Impact of defects on photoexcited carrier relaxation dynamics in GeSn thin films," *J. Phys. Condens. Matter*, vol. 33, no. 6, p. 065702, Feb. 2020, doi: 10.1088/1361-648X/abc4ce.

[3] S. K. Saha, R. Kumar, A. Kuchuk, **H. Stanchu**, Y. I. Mazur, S.-Q. Yu, and G. J. Salamo, "GaAs epitaxial growth on R-plane sapphire substrate," *J. Cryst. Growth*, vol. 548, p. 125848, 2020, doi: https://doi.org/10.1016/j.jcrysgro.2020.125848.

Planned

[4] Oluwatobi Olorunsola, **Hryhorii Stanchu**, Solomon Ojo, Krishna Pandey, Joe Margetis, John Tolle, Andrian Kuchuk, Yuriy I. Mazur, Gregory Salamo, and Shui-Qing Yu, "Effects of annealing-induced strain on GeSn indirect-to-direct bandgap optical transition".