AFRL-AFOSR-VA-TR-2020-0056

# Group-IV Photonic-Materials by Molecular Beam Epitaxy

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TRUSTEES OF TUFTS COLEGE INC

06/08/2020
Final Report

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Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ RTB1
Arlington, Virginia 22203
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# REPORT DOCUMENTATION PAGE

*Form Approved*
*OMB No. 0704-0188*

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**1. REPORT DATE** *(DD-MM-YYYY)*
19-06-2020

**2. REPORT TYPE**
Final Performance

**3. DATES COVERED** *(From - To)*
30 Sep 2015 to 29 Sep 2019

**4. TITLE AND SUBTITLE**
Group-IV Photonic-Materials by Molecular Beam Epitaxy

**5a. CONTRACT NUMBER**

**5b. GRANT NUMBER**
FA9550-15-1-0417

**5c. PROGRAM ELEMENT NUMBER**
61102F

**6. AUTHOR(S)**
Thomas Vandervelde

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**
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**8. PERFORMING ORGANIZATION REPORT NUMBER**

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**
AF Office of Scientific Research
875 N. Randolph St. Room 3112
Arlington, VA 22203

**10. SPONSOR/MONITOR'S ACRONYM(S)**
AFRL/AFOSR RTB1

**11. SPONSOR/MONITOR'S REPORT NUMBER(S)**
AFRL-AFOSR-VA-TR-2020-0056

**12. DISTRIBUTION/AVAILABILITY STATEMENT**
A DISTRIBUTION UNLIMITED: PB Public Release

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**
The grant was awarded in conjunction with a DURIP grant (FA9550-15-1-0352) and the combined primary objective is to renovate an existing SiGe molecular beam epitaxy (MBE) system and convert it to a state of the art SiGeSn system. The system identified for this project is the dual-chamber VG90 system designed and built by John C. Bean while he was at Bell Labs in the mid-90s before he moved, with the system, to the University of Virginia (UVa). As the PI, Tom Vandervelde, was one of the few graduate students that John Bean ever trained, John willingly donated the system along with the rest of his laboratory equipment to Tom, Figure 1. This donation formed the core of the new Tufts Epitaxial Core (TEC) Facility. The total value of the equipment in this facility is over $27,000,000. The versatility of this MBE system was the of particular interest, with each deposition chamber capable of handling six inch wafers and can use up to three e-gun sources, three effusion cells, and a gas based low energy implantation system. The chambers are also physically large measuring over a meter in diameter: this leaves a lot of room to add characterization and other sensing tools

**15. SUBJECT TERMS**
Molecular Beam Epitaxy, Group-IV materials, CSiGeSn compounds, photonics, optical interconnects

**16. SECURITY CLASSIFICATION OF:**

**17. LIMITATION OF ABSTRACT**

**18. NUMBER OF**



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| a. REPORT | b. ABSTRACT | c. THIS PAGE | | PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| Unclassified | Unclassified | Unclassified | UU | | POMRENKE, GERNOT |
| | | | | | **19b. TELEPHONE NUMBER** *(Include area code)* 703-696-8426 |

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

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Lead organization: Tufts University
Type of Business: Educational


Grant Effective Date: 08/15/15
Award # FA9550-15-1-0417



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The grant was awarded in conjunction with a DURIP grant (FA9550-15-1-0352) and the combined primary objective is to renovate an existing SiGe molecular beam epitaxy (MBE) system and convert it to a state of the art SiGeSn system. The system identified for this project is the dual-chamber VG90 system designed and built by John C. Bean while he was at Bell Labs in the mid-90's before he moved, with the system, to the University of Virginia (UVa). As the PI, Tom Vandervelde, was one of the few graduate students that John Bean ever trained, John willingly donated the system along with the rest of his laboratory equipment to Tom, Figure 1. This donation formed the core of the new Tufts Epitaxial Core (TEC) Facility. The total value of the equipment in this facility is over $27,000,000. The versatility of this MBE system was the of particular interest, with each deposition chamber capable of handling six inch wafers and can use up to three e-gun sources, three effusion cells, and a gas based low energy implantation system. The chambers are also physically large measuring over a meter in diameter: this leaves a lot of room to add characterization and other sensing tools.

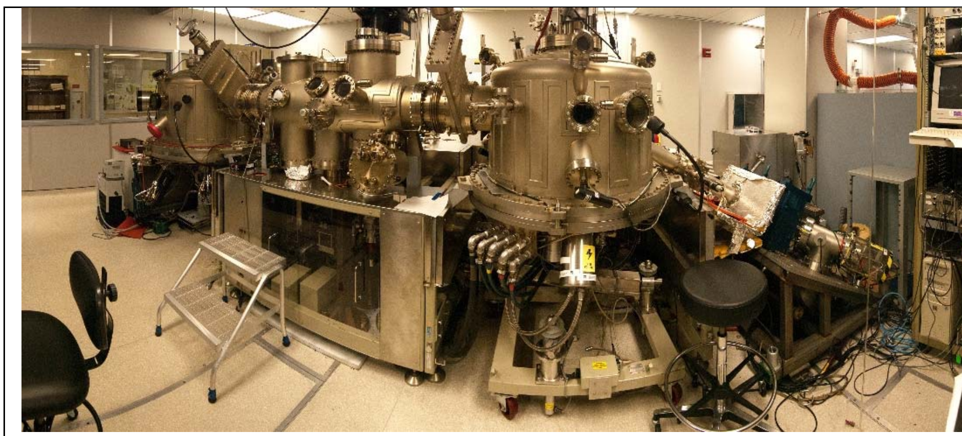

**Figure 1:** The dual-chamber VG90 system at the University of Virginia prior to disassembly.

During 2016 the system had to be dissembled and packed with great care at UVa. Many of the pieces are very fragile or had to be stored under vacuum or in an inert atmosphere. To accomplish this process properly, Professor Vandervelde along with multiple graduate students spent many weeks spread over several months at UVa along with the relevant MBE company Riber USA carefully taking the system apart and packing it up. Some pictures of the disassembly and removal process are shown in Figure 2.


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**Figure 2:** The two growth chambers are separated from the preparation chamber in the upper left picture. The removal and packing process of one of the growth chambers is shown in the other three pictures; moving it out of the building (upper right), crating it (lower left), and lifting it onto the moving truck (lower right).

Due to these awards, this one and the DURIP, Tufts agreed to spend over $5,000,000 to renovate a 12,000 sq-ft suite (Figure 3) containing a large 8,000 sq-ft class 10,000 cleanroom to house the VG90 system. This space is now designated as the Tufts Epitaxial Core (TEC) Facility and is under Professor Vandervelde directorship. The renovations, shown in Figure 4, included adding: a section of raised floor, processed chilled water, house LN2 (6,000 Gal tank), house Dry-N2, compressed air, toxic exhaust, new ventilation, life safety sensing/alarms, UPS back-up , a new back-up generator, and system hoists. The School of Engineering is also providing a full-time Research Professor, Kevin Grossklaus, to run the facility.


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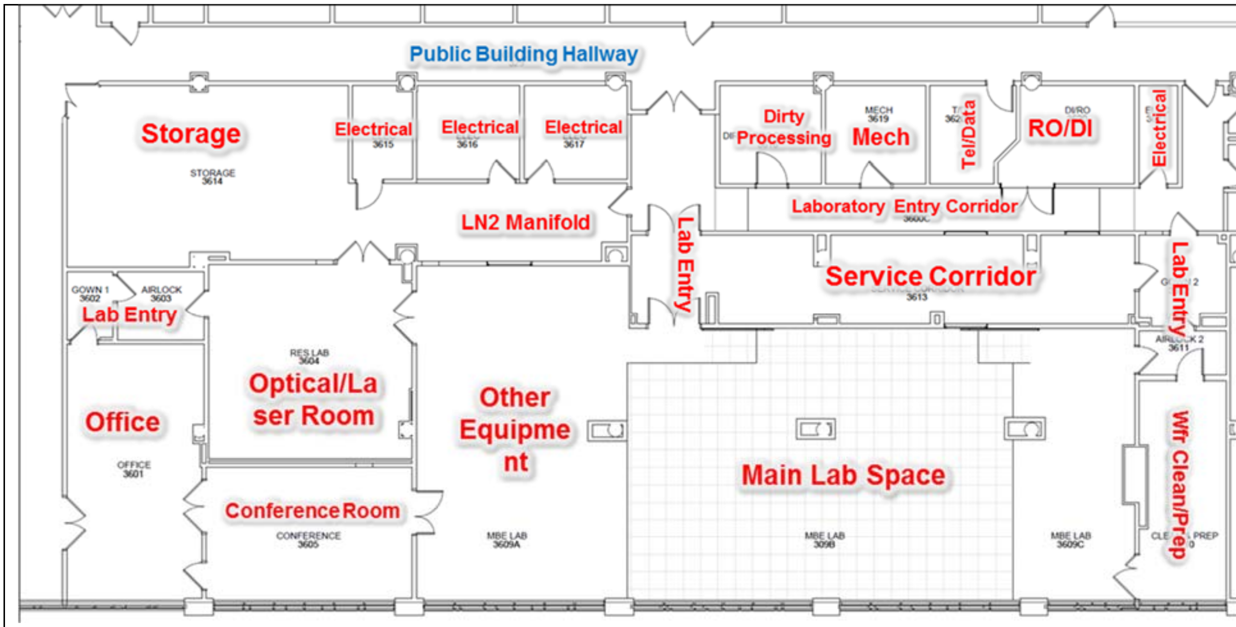
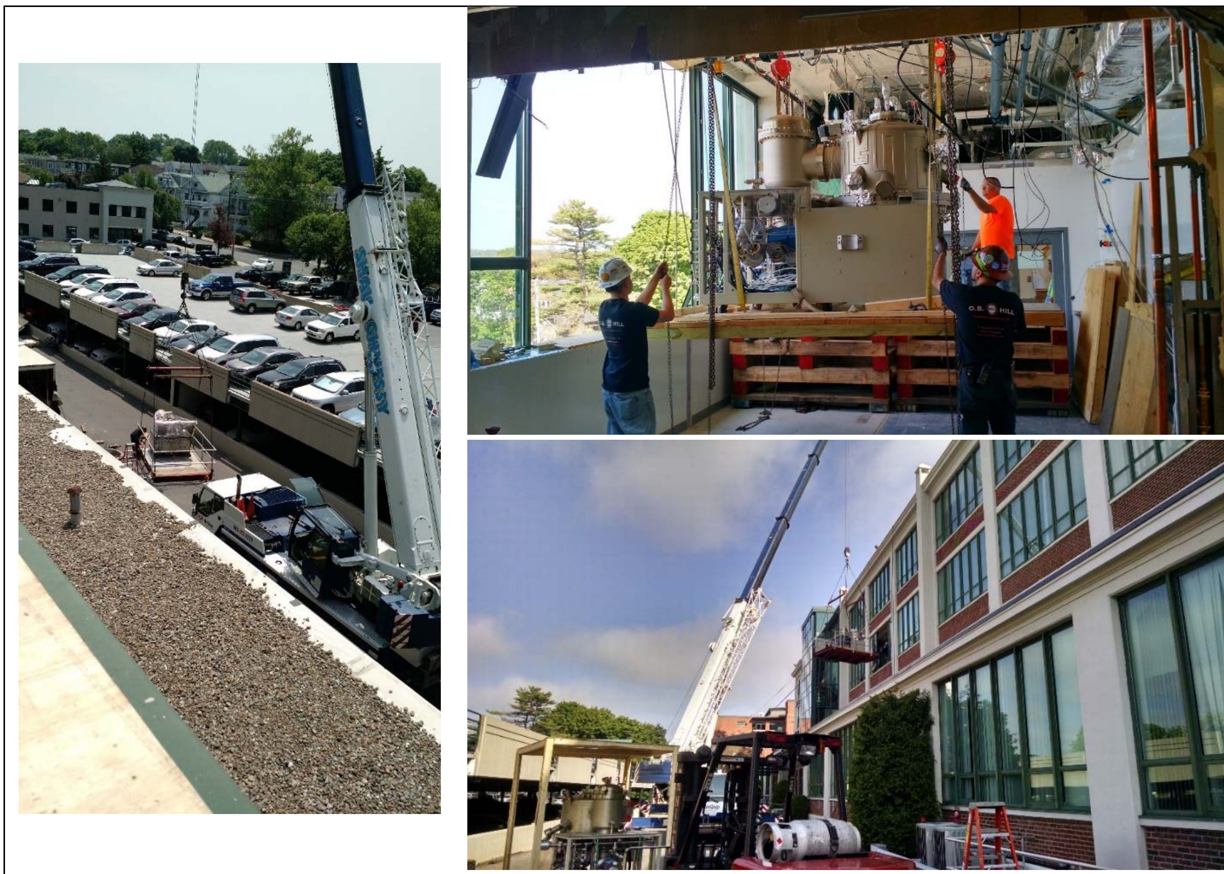



**Figure 3:** A layout of the suite renovated by Tufts for $4.2M to house the Tufts Epitaxial Core (TEC) Facility. The area labeled "Main Lab Space" is where the MBE system is located

**Figure 4:** While the space looked pretty nice before we started (upper left), it needed considerable renovation to bring it up to being capable of housing our research facility. The addition of the raised floor

(right) was critical to safely pass cables and plumbing for the MBE systems. Additional significant upgrades to the electrical system and air handling system had to be made (lower left).

Once the system reached Tufts and the lab space had been made ready, they were craned into the lab space through a 3rd story window, Figure 5. Once in their final position, the facilities connections could be finalized. Re-assembly of the system, Figure 6, was actuated during this time and repairs were made for damage caused during shipping. Riber was called back in at this point to begin to install the new control software and update the electronics of the system, which continued into Year 2.

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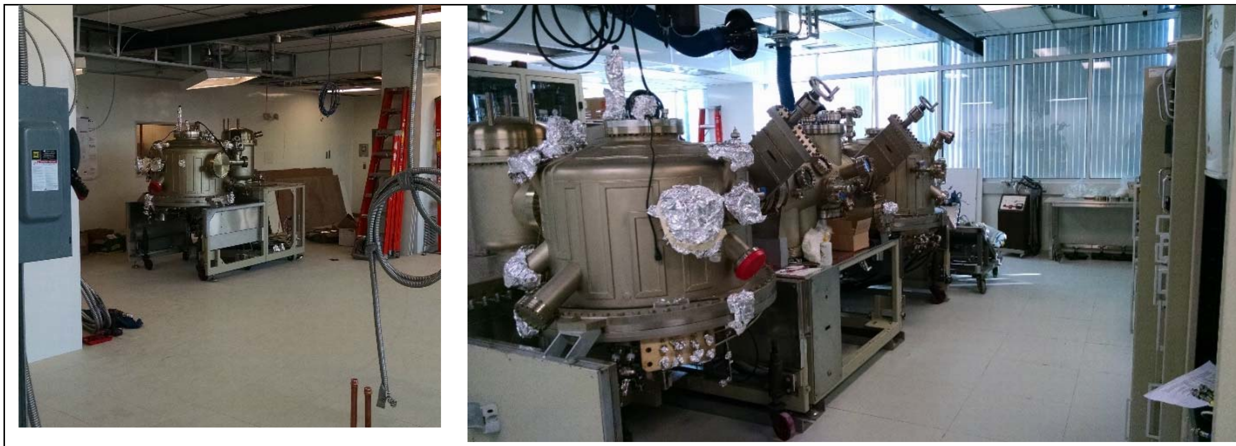

**Figure 5:** The upper pictures show the process of lifting the MBE chambers to the 3rd floor. The system was then placed roughly into position.

**Figure 6:** Left) Two graduate students work to reassembly the ion implantation doping system for the MBE system. Right) Research Professor Kevin Grossklaus scrapes the old epitaxial deposits off of the internal surfaces of the epitaxial growth chamber.

In Year 2, renovation of the space continued. A six-thousand gallon LN2 tank was installed to supply liquid cryogen for system cooling shrouds and house nitrogen to run pneumatics. Additionally, a 450 gallon glycol cooling system was installed to provide non-cryogen liquid cooling. For safety, oxygen depletion sensors were added and then augmented with sensors to detect any leakage of the dopant gases, $BF_3$ and $AsF_5$.


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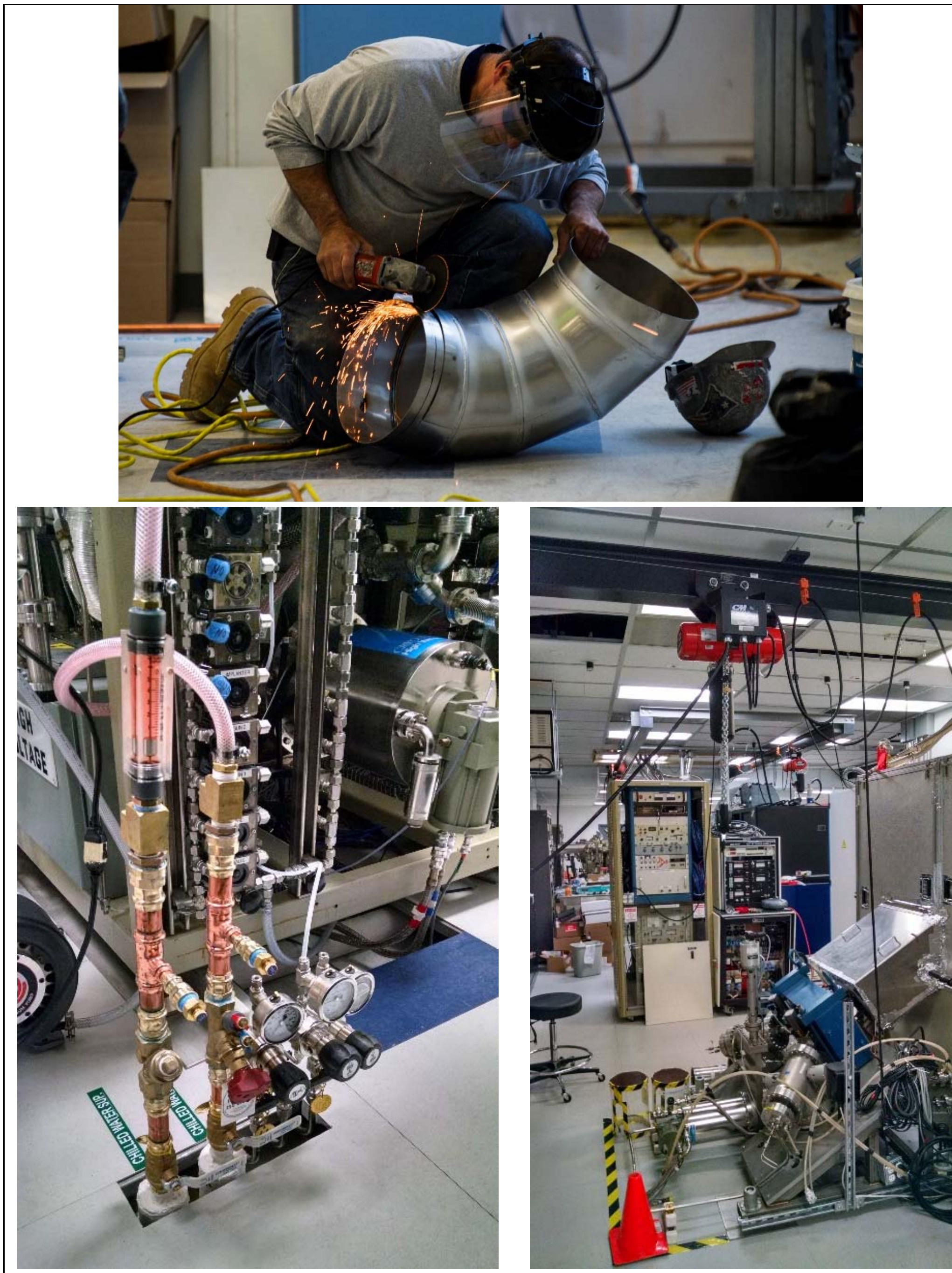

**Figure 7:** The upper picture depicts a welder fabricating new stainless steel ventilation ducts to deal with the HF fumes left over from cleaning Si wafers. Lower left) the glycol cooling lines supply and return along with three gas supplies: house air, house nitrogen, and high purity nitrogen. Lower right) the hoist for moving heavy components positioned over the implantation system.

During the completion of the facility renovation, we proceeded with the followed by upgrading and renovating the MBE system itself with the help of Riber USA. This process included the replacement of the 90s technology, homebrew visual basic control system, with a modern one Figure 8. This replaced eleven outdated electronics racks with one rack and two computers. Additionally, we replaced the aging manipulator/heater on the primary deposition chamber and added three effusion cells to enable the co-deposition of tin and two surfactant materials.

**Figure 8:** Eleven outdated electronics racks were replaced with one rack and two computers, top and center left. The replacement of the primary manipulator, center right, was critical as it was a looming failure point for the system. We also installed three new effusion cells (bottom pictures) to supply epitaxial tin and surfactant materials.

After the installation, we later found out that the Riber technician that was working with us had not sealed one of the internal cooling line connections well enough: the copper gasket shifted and pinched. This led to our flooding the inside of the chamber with glycol when we ran the cooling system the first time, Figure 9. Now the new effusion cells had to be sent back to France to be taken apart and cleaned. It took close to 6 months to get the cleaned cells back. After cleaning the inside of the chamber and baking the system to get rid of any trace of the oil, we were able to get back to business and perform some initial growths.

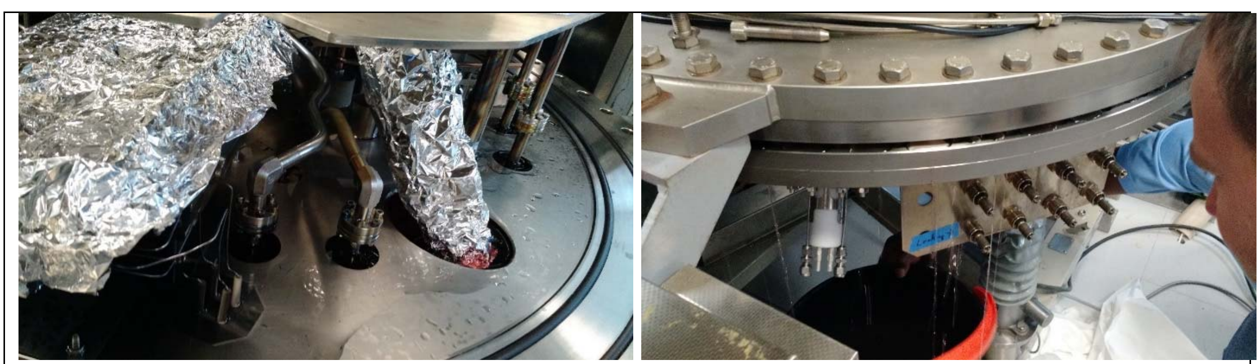

**Figure 9:** Two images of the newly opened chamber with glycol pouring out of the opening (right) and pooled on the inside of the flange (left).


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By Year 3, the renovation was effectively complete, Figure 10, and we were able to perform some initial growths. Figure 11 shows AFM scans of several example growths, where we saw the best results for epitaxial growths at temperatures around 180°C. When we slowed the deposition rate too much, carbon contamination was evidenced by pit formation on the surface. At the edge of the pits, there was some lattice relaxation and GeSn or Sn islands formed around them.  When growth temperature was increased phase separation occurred and Sn Volmer-Webber islands formed. This highlights the critical nature of the growth conditions.

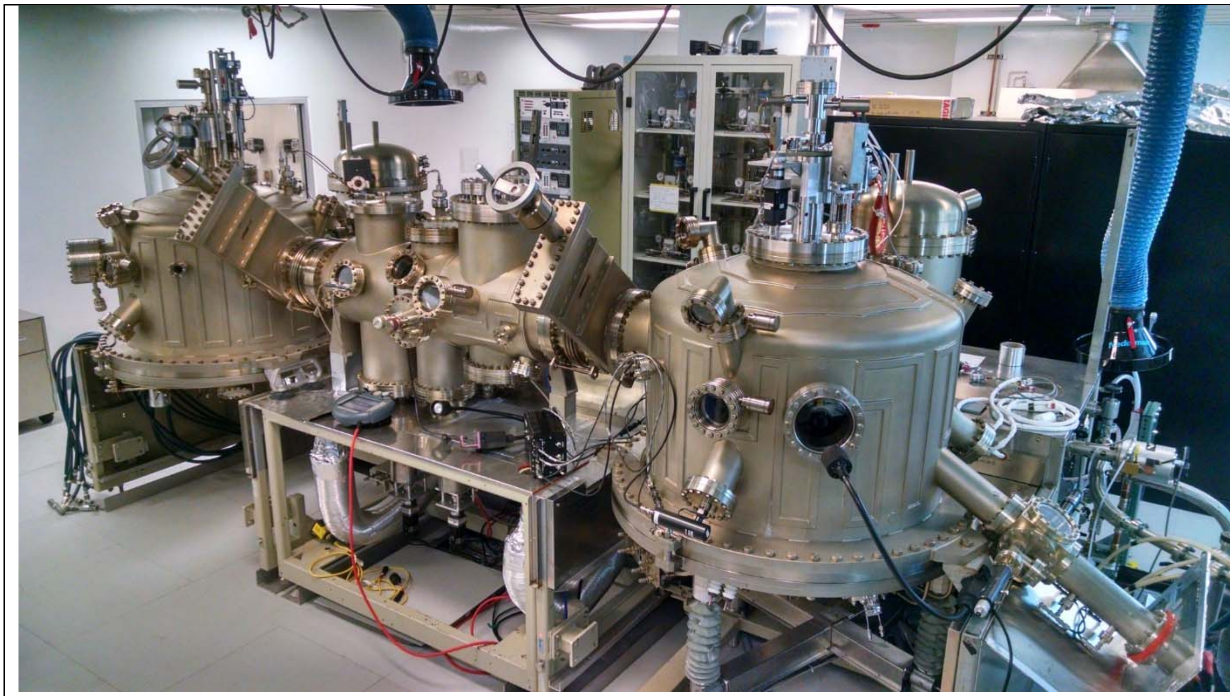

**Figure 10:** The dual-chamber VG90 system after re-assembly at Tufts University. The primary deposition chamber is shown on the right with the ion implantor extending off of the image.  To the left of that chamber are the preparation chamber and the second deposition chamber.

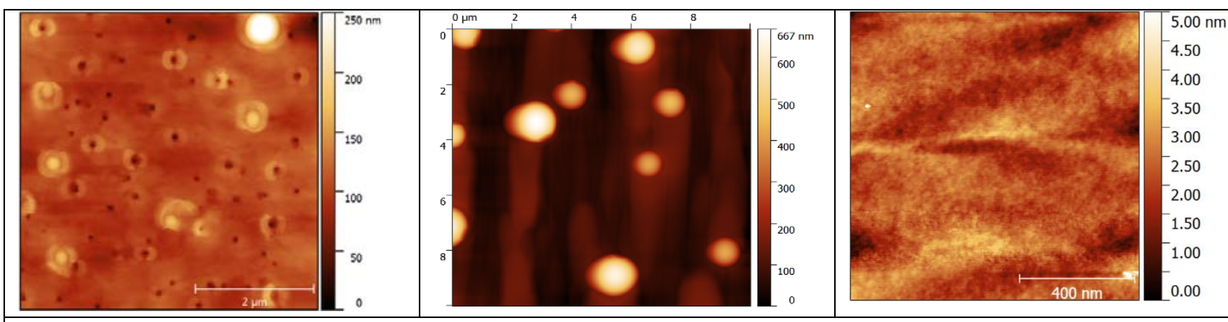


**Figure 11:** Left) When growth is too slow pit formation (black spots) occurs, which is likely evidence of carbon contamination. You can also see evidence of a relaxed lattice around pits, which nucleates GeSn or Sn islands. Center) Higher temperature growths (>250°C) lead to Sn-surfactant effect.  Large Sn-islands form on surface. Right) For cool growth conditions, ~180°C, smooth surfaces are possible and moderate tin incorporation (~4%)


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In our initial growth we discovered additional problems in the equipment that needed to be upgraded/replaced. The existing temperature control system is not well calibrated for the temperatures used, so we ordered a new pyrometer that is better calibrated for these low growth temperatures. Additionally, we needed a beam flux monitor (BFM) to measure the Sn flux accurately, Figure 12. The existing Sentinel system, which is an EIES based sensor, was not replaced in the initial renovation, could not work for the Sn source, and had repeated failures. It was also out of date and could no longer be repaired, so we decided to replace that as well with a Guardian EIES system. Additionally, the CV-14 e-gun power source was suffering failures. It sprung a leak and dumped 450 gallons of coolant on the floor, but the bigger issue was that it was not integrateable with the new control software, so we ordered new e-gun controllers. We received these parts we are installed them into the system in Year 4.

**Figure 12:** Two pictures of the new beam flux monitor that we had to custom design o work in our system. As of the submission of this report, we will have just installed this into the chamber to calibrate the Sn flux rate more accurately

During Year 3 and Year 4, to help guide these studies, we performed initial density functional theory (DFT) studies. DFT can be used to examine the energetics of different atomic arrangements, provide basic mechanical properties, and provide basic band topology. Quantum Espresso is a freely available and widely used DFT modeling package already built and running on the ECE network and the Tufts High Performance Research Computing Cluster. Simulations of different Si+Ge+Sn configuration energies can be used to give us insight into experimental results and help to guide future experiments to achieve stable high Sn materials.


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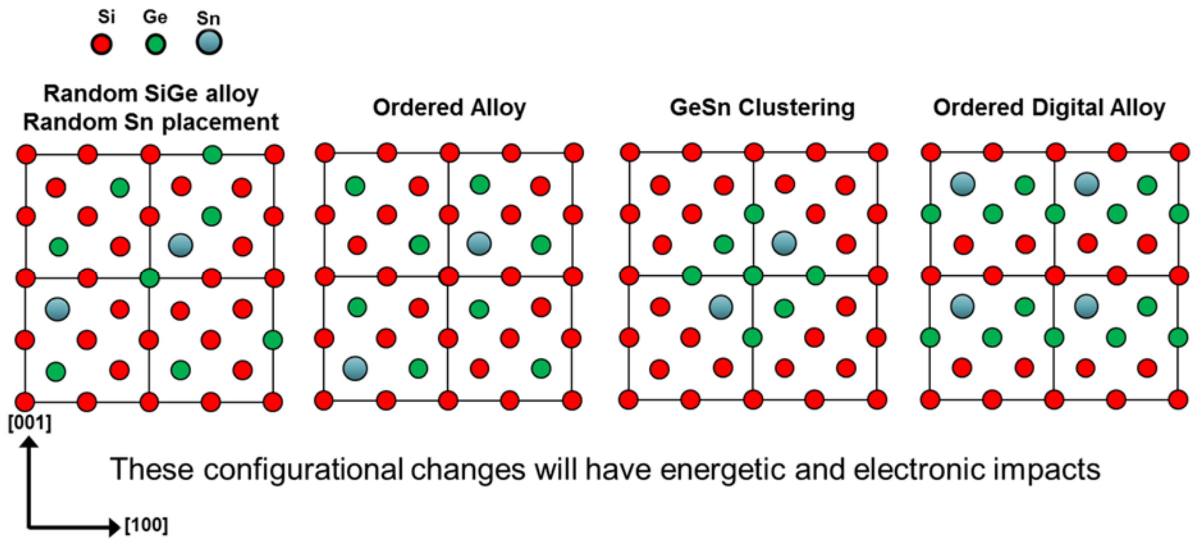


**Figure 13:** In the SiGeSn system we can use DFT to examine the effects of :Sn clustering; GeSn clustering; Ge and Sn alloy ordering in SiGeSn; Digital Alloys

As an example, Figure 14, based on preliminary calculations, shows the strain-free mixing enthalpy and equilibrium lattice parameters of the disordered Si-Ge-Sn solid solution (SGS'ss). This data was generated by parameterizing an alloy Hamiltonian to a training set of 517 first-principles density functional theory calculations. Figure 14(a) shows that there is a high formation enthalpy penalty to form a Sn-rich Ge-Si-Sn solid solution. This indicates that Sn-rich solid solutions will experience a large driving force to phase separate. Our preliminary results are consistent with experiments, which indicate a large miscibility gap in the Si-Ge-Sn ternary composition space and a very low equilibrium solubility limit of Sn in Si-Ge solid solutions. This immiscibility is largely due to the large size difference between Sn on the one hand and Si and Ge on the other. Strain engineering of the type discussed in the epitaxy section is, therefore, a promising route with which to form Sn rich Si-Ge-Sn solid solutions (SGS'ss). Epitaxial strain can potentially suppress a miscibility gap when the end members have very different lattice parameters. The approach is to impose strain constraints through a suitable choice of substrate such that the strain penalty of phase separation is larger than the chemical free energy cost of forming a SGS'ss with a high Sn concentration. Even if strain constraints do not exist where non-dilute SGS'ss are thermodynamically stable, boundary conditions can be found that minimize the thermodynamic driving force for phase separation. This can be achieved by identifying epitaxial substrates that are lattice matched to the desired Ge-Si-Sn alloy lattice parameters. The equilibrium lattice parameter, depicted as a ternary contour plot in Figure 14(b) demonstrates the wide range of lattice parameters realizable over the range of Si-Ge-Sn compositions. Figure 14(b) also indicates which contours of constant lattice parameter coincide with common substrates. For example, InP is lattice matched to equiatomic Ge-Si-Sn solid solutions


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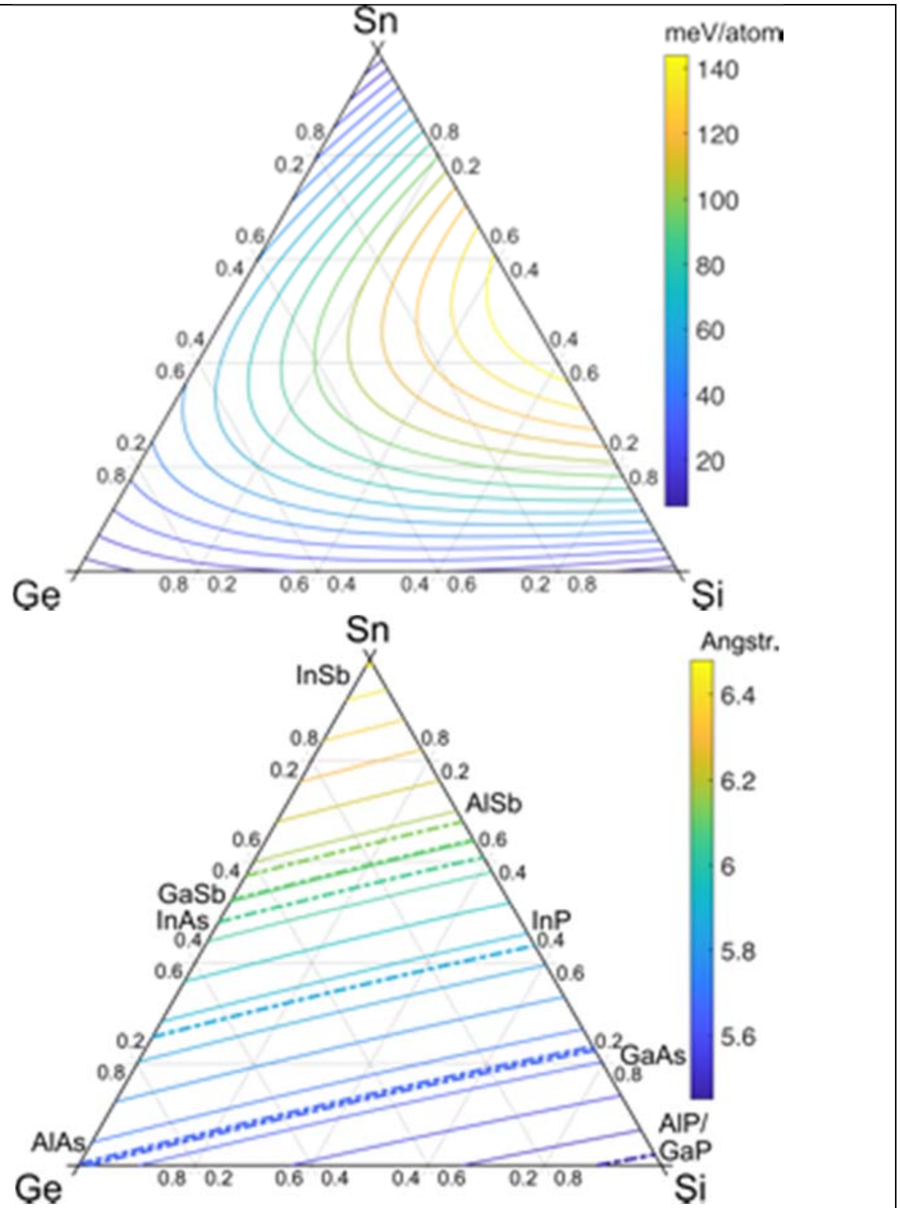


**Figure 14:** Upper) Contour plot of the enthalpy of mixing for a disordered Ge-Si-Sn solid solution as a function of alloy concentration. Lower) Contour plot of the cubic lattice parameter of a disordered Ge-Si-Sn solid solution as a function of concentration. The plot also shows curves of constant lattice parameter that are compatible with different substrates. For example, the aqua blue contour line labeled InP corresponds to concentrations of Ge-Si-Sn solid solutions that can be grown on a (001) InP substrate with zero misfit strain.


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Beyond the simulation results, in Year 4 we were able to push additional experimental results. We continued our study of low temperature of growths to explore the growth space of below CVD accessible temperatures. We studied films grown between 600 to 200 °C and characterized by Ellipsometry, HRXRD, and AFM. We found that we were able to maintain good epitaxial quality without any sign of degradation to 350 °C and moderate growth rate easily, but we found that quality starts to degrade at temperatures below 200 °C.

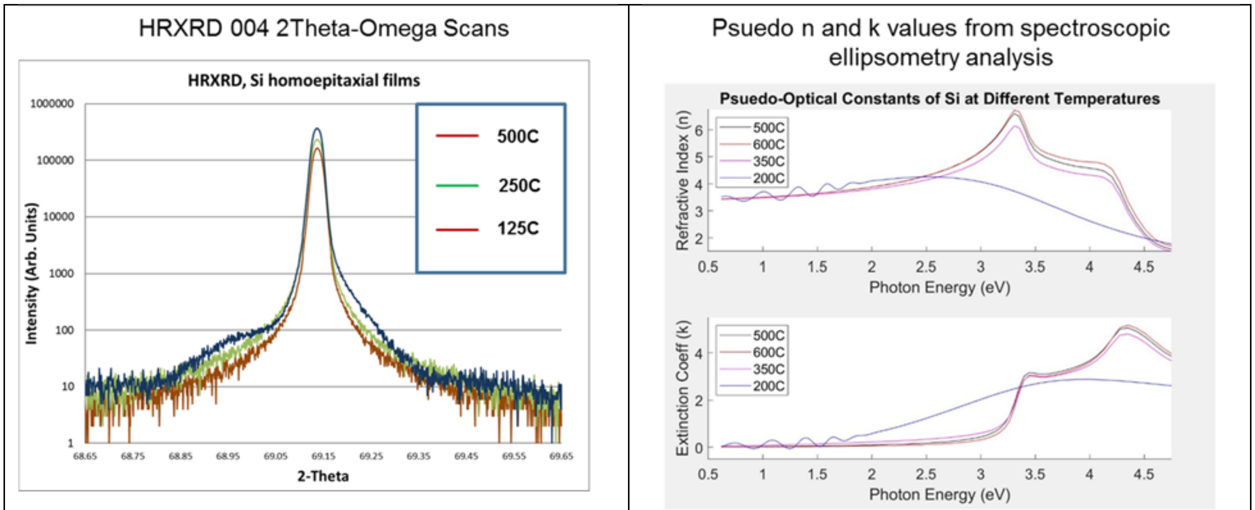


Figure 15: Left) HRXRD of grown samples at various temperatures. Changes in Si 004 peak shape at 200°C likely indicate high defectivity. Right) Dramatic shift in optical properties and loss of sharp interband absorption features in the 200°C film likely indicate degradation of crystalline quality

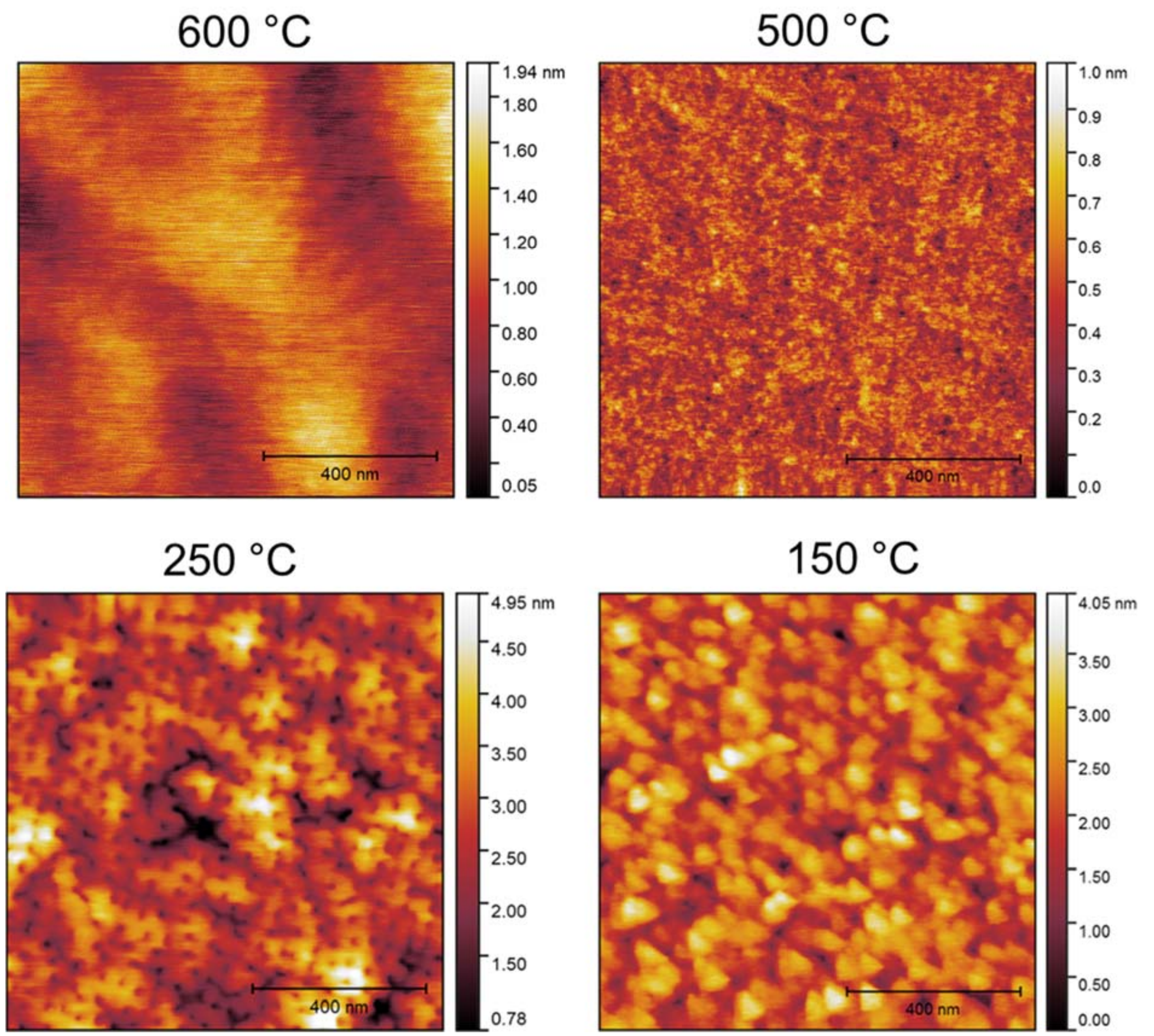


Figure 16: As temperature decreased average surface roughness increased, but even down to 150 °C the surface roughness was not too bad.

Beyond being able to grow high quality material at low temperature, growing **doped** material at low temperature is another challenge. Being able to get dopant to incorporate and be activated can be a significant challenge in the Group-IV system especially at low temperatures. For this study we stated with Ga, since if Ga doesn't incorporate as a dopant, it can be used as a surfactant. As part of this study, we focused on the surfactant effect.


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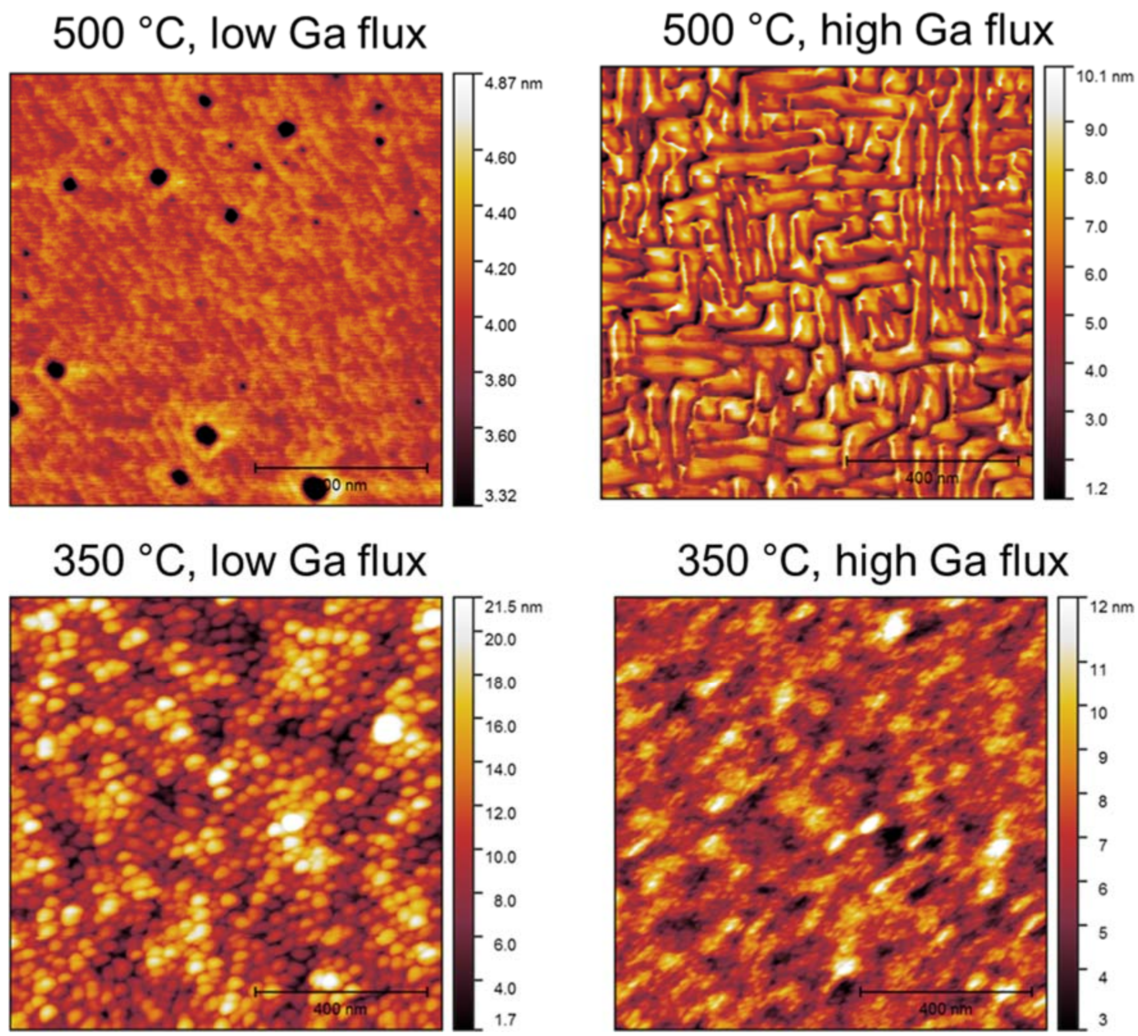


Figure 17: Thus far, all Ga fluxes tried have produced an increase in film roughness, indicating we are still not achieving an improvement from any surfactant effect. Ga use at low temperature roughens the film significantly, similar to growing without Ga at 200 °C.

The system had one final problem to throw at us during this award, the magnetic coupling in the manipulator ate themselves. After replacing the magnets once and having them eat themselves again, we have discovered that Riber used an inferior quality magnet that could not survive the system required bake-out. We have sent back the manipulator to have the new magnets placed within it.  We should have the manipulator back by late 2018 or early 2020.


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## Summary

The primary objective of this project was to renovate the VG90 MBE system for the growth of SiGeSn materials. This work has been completely successful on that front. There were significantly more obstacles and setbacks than expected, but we have successfully created a system with unparalleled capability. We have initial data proving that we can grow SiGeSn down to temperatures as low as 150 °C. With further exploration of this phase space, this offers new opportunities for the successful creation of SiGeSn alloys of great utility.

**This work resulted in two dissertation/thesis defenses:**

- Defended May 2019, Jon Manninen (US Marine Vet) – Improving Group IV Photonics: Examining Material Properties of Epitaxially Grown, Low-Temperature SiGeSn and Gallium-doped SiGeSn Thin Films
- Defended December 2017, John Chivers – Frequency Selective Surfaces for Optoelectric Devices and Molecular Beam Epitaxy of Group IV Photonics

**Conference Papers and Presentations:**

- Low Temperature Epitaxial SiGeSn and the Limits of Global Strain Relief; Amanda Lemire,John Chivers, Kevin Grossklaus, and Thomas Vandervelde;Materials Research Society Fall Meeting 2019 (accepted)
- Doping and Surfactant Behavior of Gallium in Low-Temperature Silicon-Germanium and Silicon-Germanium-Tin Growth; Amanda Lemire, Jon Manninen, John Chivers, Kevin Grossklaus, and Thomas Vandervelde; North American Molecular Beam Epitaxy Conference 2019
- Optical Property Comparison of Epitaxial Low Temperature SiGe and SiGeSn Measured by Variable Angle Spectroscopic Ellipsometry; Jon Manninen, John Chivers, Kevin Grossklaus, and Thomas Vandervelde; APS March Meeting Boston 2019

**Journal papers:**

- Limits of Global Strain Relief in SiGeSn Epitaxy, Journal of Crystal Growth (In process)
- Doping and Surfactant Effect of Gallium in Low Temperature SiGeSn, Journal of Crystal Growth (In process)
- We have the beginnings of data for a bunch more papers, but we need more growths to make it meaningful that were cut short when the manipulator broke.

**National Lab collaborations:**

- We have been working with Michael Yakes and Stephanie Tomaluso at NRL to examine the topic of adatom diffusion. We worked with them on the diffusion of some adatoms in

III-V materials and have been talking about how we can do a similar study for Group-IV materials.

- I have also been talking with Chip Clafin at WPAFB about trying to start a collaboration, but that is still at the stage of bouncing some emails back and forth. I owe him a visit to WP, hopefully once that occurs we can have a solid collaboration going.

**Collaborations with companies:**

- I have not worked with AIMPhotonics, but would be interested in talking with them.
- I have talked with MTPV about using SiGeSn for thermophotovoltiacs and they are interested in testing some diodes once we make them.

**Collaborations with other academics:**

- Collaboration with Van der Ven at UCSB on modeling (DFT+KMC+MD+Continium)
- Nascent collaborations with Soref at Umass-Boston and Aksamija at UMass-Amherst


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