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LIGHT EMITTERS BASED ON GERMANIUM-TIN ALLOYS

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Abstract

With a direct energy bandgap and compatibility with commercial circuit processing, germanium-tin semiconductors are attractive for high performance, integrated optoelectronics at middle-infrared wavelengths. Using molecular beam epitaxy and Clean Room processing, GeSn optoelectronic devices were fabricated, and measured to determine their characteristics and limitations. By reducing the substrate temperature to 100°C during growth, the epitaxy was optimized to achieve an unusually high Sn content of 31 atomic %. A variety of substrate wafers were used, including silicon, germanium, and gallium arsenide. The GeSn layers had excellent crystal structure as measured by x-ray diffraction, with smooth surfaces as measured by atomic force microscopy. Novel doping sources were studied, including boron and gallium acceptors for p-type doping, and arsenic and phosphorus donors for n-type doping. The fabricated optoelectronic devices included p-n junctions, heterojunctions, and photoconductors, which had excellent electrical and optical properties, measured using infrared spectroscopy. These results showed that GeSn alloys are suitable for device applications in the field of infrared silicon photonics.

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Objectives:
The objectives of this project were to investigate light emission from optoelectronic devices based on germanium-tin (GeSn) alloys, which have a direct energy gap for efficient operation, and to optimize the GeSn light emitters for applications in the important middle-infrared (mid-IR) spectral region at wavelengths from 2-5 μm.

Approach:
The technical approach was to: (1) optimize the molecular beam epitaxy (MBE) growth of GeSn alloys with sufficiently high Sn contents to achieve mid-IR operation; (2) explore the structural, electronic, and optical properties of high Sn content alloys; and (3) fabricate doped p-n junction optoelectronic devices, and measure their characteristics and limitations using state of the art instrumentation.

Motivation:

Germanium-tin is an interesting semiconductor alloy for optoelectronic applications because it is compatible with silicon CMOS circuit processing, and the alloys have a direct energy bandgap for Sn contents above about 7 atomic %. With the promise of efficient light emission, these alloys have been under active investigation, but there were technical challenges that were poorly understood, including the effects of lattice mismatch strain on the energy band structure, the thermal stability [5] during device fabrication, and the maximum Sn content without precipitation. The published reports of Sn contents above about 15 % were few, but our group has produced Sn contents up to 31 atomic % [15]. Several types of GeSn devices have been reported including field effect transistors, photodetectors, light emitting diodes, and lasers. Only *optically pumped* lasers have been reported, however, and an electrical current injection laser has yet to be realized. To achieve efficient light emitters and *electrically* pumped lasers, this project has focused on the fabrication and characterization of GeSn p-n junctions of high quality with high Sn contents.

Accomplishment Highlights:

The specific research tasks of this project included: the growth of germanium-tin (GeSn) alloys by solid source molecular beam epitaxy (MBE); the growth of GeSn by chemical vapor deposition (CVD) using novel precursors (Si_4H_{10}, Ge_2H_6, and $SnCl_4$); and the fabrication of GeSn doped p-n junction devices and heterostructures. The GeSn materials and devices were characterized using a variety of analytical techniques including: atomic force microscopy (AFM) for surface morphology; Fourier transform infrared spectroscopy (FTIR) for optical absorption, emission, and the extraction of the bandgap energy; current versus voltage (I-V) characterization for the electrical properties; secondary ion mass spectrometry (SIMS) for composition and impurity concentrations; x-ray diffraction (XRD) for the structure, lattice constant, and strain; and electron microscopy (TEM) for lattice imaging and morphology. Collaborations with other groups included Prof. Stefan Zollner (NMSU) for spectroscopic ellipsometry for the optical properties and energy band structure [1,10,11,13].

Highlights of recent achievements since the last year's report include:

1. Achieving the extremely high Sn content of 31 atomic % in a 99.9% relaxed GeSn layer that was 191 nm thick on a Ge substrate. The bandgap is expected to be direct and near, or below zero (- 94.4 meV).
2. Added new dopant sources for MBE, including arsenic donors for n-type, and gallium acceptors for p-type conductivity, because these doping cells operate at lower temperatures than for other dopants, with less heating of the substrate and therefore better GeSn quality.
3. Fabricated a strain engineered GeSn diode, using a partially relaxed buffer layer of n-GeSn with 18% Sn, overgrown by an active p-n homojunction of GeSn (10% Sn) that was fully relaxed, so that the bandgap of the active region will be direct for efficient light emission.

4. Measured the photoconductive response of GeSn detectors on Ge substrates. An 18 % Sn device had response to a wavelength of about 5 μm, and a 21 % Sn device had response to 7 μm.
5. Verified optical emission from p-N GeSn/Ge heterojunction diodes, by using an infrared camera.
6. A grad student, Dominic Imbrenda, visited Prof. Stefan Zollner's group at New Mexico State University (NMSU) for infrared spectroscopic ellipsometry, and determined the optical absorption coefficients of a series of GeSn alloys.
7. Grew several GeSn layers on undoped (semi-insulating) gallium arsenide, so that the electrical measurements will not be disturbed by electrical conduction in the substrate.
8. Measured the Hall effect mobility of GeSn alloys, and found that the electrical conduction was by holes, with somewhat low mobility values (< 100 cm^2/V-S), which is still be analyzed.

Project Significance:

This project was significant because it demonstrated that molecular beam epitaxy (MBE) is a practical method to produce GeSn with Sn contents up to 31%, with excellent structural, electronic, and optical properties [15]. Using MBE, the GeSn was doped p-type and n-type to form junction diodes and heterojunctions, which we have demonstrated to emit and detect infrared light. The GeSn devices were fabricated using processing that was compatible with silicon CMOS technology. The GeSn electrical devices had good characteristics and operated in accord with conventional junction diode principles. The GeSn optical devices produced infrared light emission at room temperature, and had photoresponse in the mid-IR region up to a wavelength of 7 μm for a 21 % Sn device. These results demonstrated that GeSn is a viable new material for IR devices that can be integrated with silicon-based photonics.

Scientific Achievements:

This research project produced several significant achievements. A GeSn layer was grown by MBE with 31 atomic % Sn (rarely achieved previously) and was 191 nm thick and 99.9% relaxed. The key to producing this relatively high Sn content was to use an electron-beam evaporator source for Ge, which reduced the heat load that illuminated the substrate, compared to a conventional thermal (Knudsen) effusion cell. Based on pseudopotential theory, the bandgap of this sample was direct and negative: -94.4 meV, indicating that this alloy was a semimetal. Fig. 1 shows an x-ray rocking curve that was used to determine the structure, lattice constant, and degree of strain. X-ray measurements, including reciprocal space maps (Fig. 1, right panel), indicated the degree of relaxation of the GeSn samples. Although the 31 % Sn sample has not yet been characterized optically, the small bandgaps of high Sn samples suggest that the operation of emitters may extend into the far-IR; a new realm for Si-photonics.

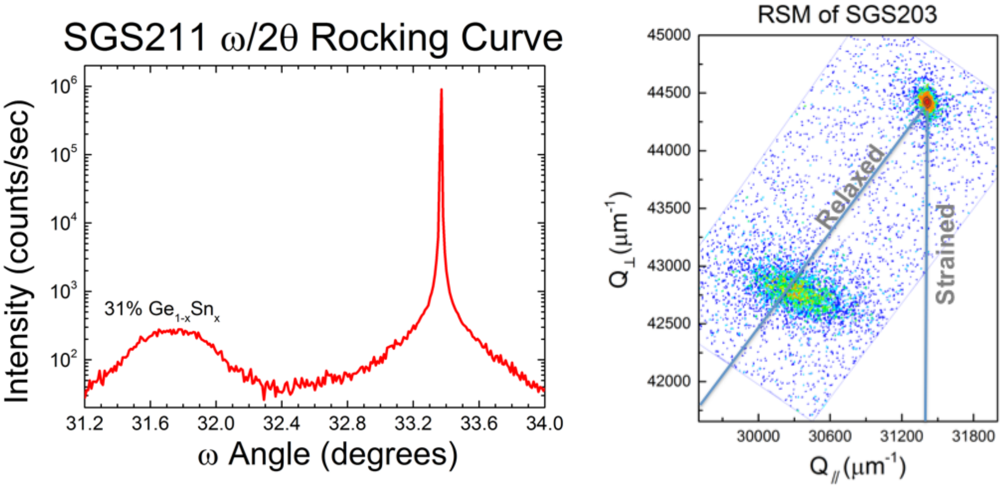

Figure 1. Left panel: x-ray rocking curve for GeSn sample (SGS211) with 31% Sn. Compared to the narrow Ge substrate peak near the diffraction angle of 33.4°, the wider GeSn peak near 31.75°, and the absence of interference (Pendellösung) fringes, was attributed to the presence of misfit dislocations that propagate from the Ge substrate interface into the GeSn layer, which has a larger lattice constant than Ge. Right panel: reciprocal space map (RSM) of sample SGS203 with 26 % Sn, showing intensity contours plotted with respect to the vertical reciprocal lattice vector $Q_\perp$ and the in-plane ([110] direction) reciprocal lattice vector $Q_{||}$. The broader GeSn peak on the left side of the RSM lies along the diagonal relaxation line, indicating nearly complete relaxation.

Table I. Germanium-tin samples with high tin contents grown using an e-beam source for Ge. Layer thickness was from x-ray reflectivity or inferred from growth rates. Sn concentration and layer relaxation were calculated from reciprocal space maps. The RMS surface roughness was from atomic force microscopy.

Sample	Temperature (°C)	Thickness (nm)	Sn (%)	Relaxation (%)	Roughness (nm)
SGS215	120	129	20	91	1.49
SGS205	100	151	24	90	5.70
SGS208	150	155	24	94	1.31
SGS203	100	89	26	> 99	1.84
SGS211	110	191	31	> 99	6.59

Table I shows a series of MBE-grown high Sn layers with good crystal structures (sharp x-ray peaks), reasonably smooth surfaces (<7 nm rms) as shown in Fig. 2, and high yields without Sn precipitation (>90% of the wafer surface), which are important properties for commercialization. Generally, high-Sn epitaxy requires lowering the substrate temperatures, but note that for two samples with similar Sn contents (SGS205 and 208) and similar thickness, that the higher temperature sample (SGS208) was smoother. In conclusion, the growth temperature must be carefully controlled. The key to achieving high yields of good quality GeSn material across the full substrate surface was to carefully clean the Ge wafer using repeated steps of H_2O_2 for thirty seconds to grow an oxide, and then HCl:H_2O (1:4) to strip the oxide. In the vacuum chamber, it was necessary to desorb the surface GeO, which was otherwise difficult to remove, by heating the substrate to 650°C for one hour and then flash heating to 850°C for 5 minutes.

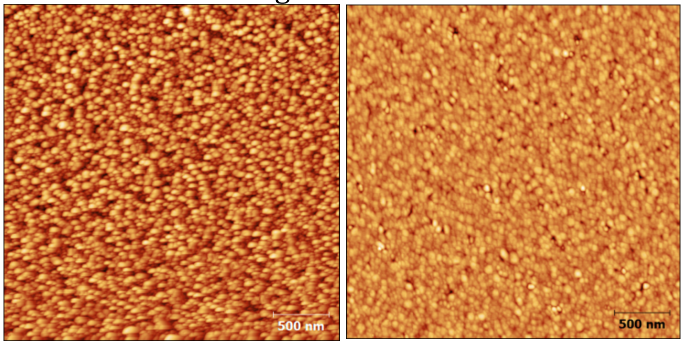

Figure 2. Atomic force microscopy (AFM) scans of surface height versus lateral position showing smooth GeSn over 3x3μm^2 areas. The samples are SGS205 (left) and SGS208 (right), with RMS roughness of 5.7 nm and 1.31 nm, respectively, and both have relatively high Sn contents (24%). The smoother layer at right was grown at a higher temperature, as per Table I.

To accurately control the substrate temperature during MBE growth, without excessive unintentional heating by the effusive cells, a new gallium p-type doping source was installed, which operated at lower temperatures than the prior boron source. A secondary ion mass spectrometry measurement (SIMS) [from: Charles Evans/EAG Laboratories] was used for calibrating the dopant flux versus cell temperature as shown in Fig. 3.

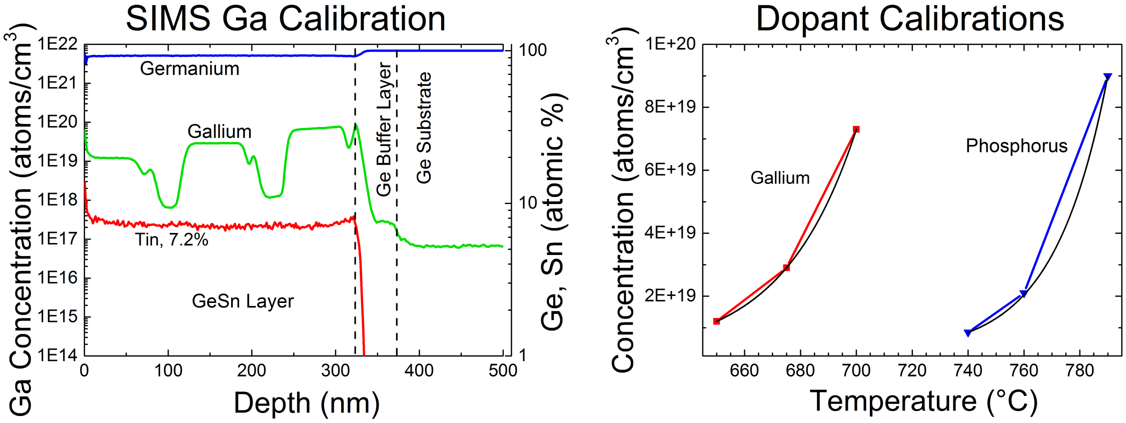

Figure 3. Left panel: secondary ion mass spectrometry (SIMS) plot of gallium concentration in atoms/cm^3 (left y axis), and tin concentration in percent (right y axis) versus material depth. For this stepped calibration sample, the dopant cell was opened for a growth of 75 nm, then closed for 25 nm while the Ge cell was ramped to a lower temperature. Right panel: phosphorus (right, blue) and gallium (left, red) concentrations in the grown layer versus effusion cell temperature. The exponential fitting for each cell flux is shown as overlaid black lines, for a GeSn growth rate of 1 nm/min. For different GeSn growth rates, the net doping concentrations can be easily scaled.

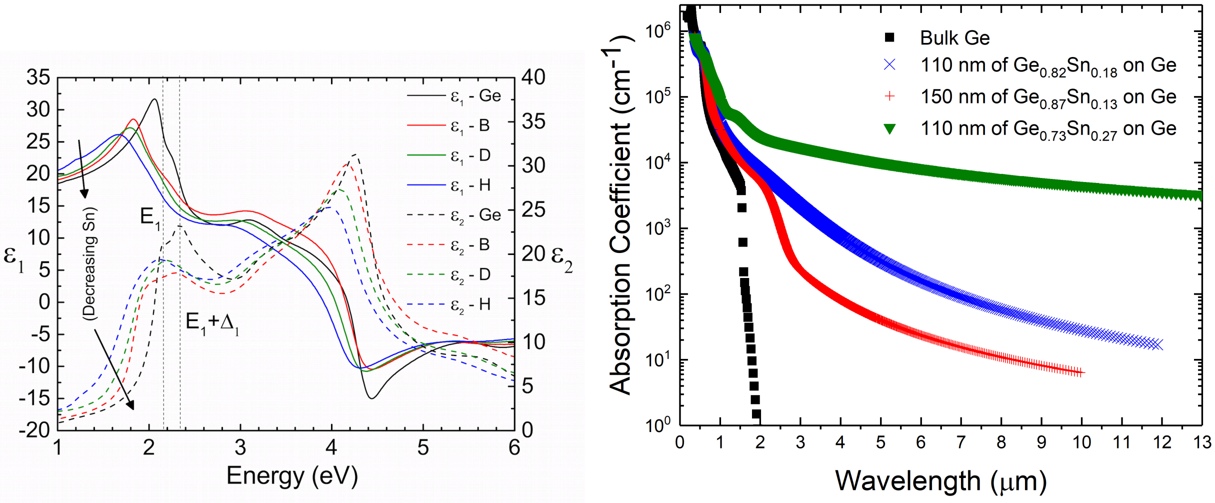

Figure 4. Left panel shows Real (solid) and Imaginary (dashed) parts of the complex dielectric function of GeSn samples B (8.4% Sn), D (12.5% Sn), H (18.3% Sn), and bulk Ge, from spectroscopic ellipsometry. Right panel shows the corresponding optical absorption coefficients versus wavelength of the 12.5%, 18.3%, and 27% Sn samples [16].

To accurately predict the operating wavelength of optoelectronic devices, a knowledge of the energy bandgap is crucial. Optical measurements of the complex dielectric function of GeSn alloys were performed using spectroscopic ellipsometry in collaboration with Prof. Stefan Zollner of New Mexico State Univ. (NMSU). A typical measurement is given in Fig. 4, showing red shifted critical point energies with increasing Sn content. From the imaginary part of the complex refractive index, the optical absorption coefficient was calculated ($4\pi\kappa/\lambda$), plotted versus photon wavelength in the right panel of Fig. 4 for several GeSn compositions up to 27 % Sn, as well as pure Ge. The bandgap energy of these samples can be extracted using Tauc plots, which is planned [16].

Interestingly, both theory and experiment suggest that the compressive strain normally encountered with GeSn grown on Ge should induce an energy bandgap that is *indirect*, even for higher Sn contents. Therefore, for efficient direct bandgap optical devices, the GeSn should be either unstrained (relaxed) or *tensile* strained (grown on a larger lattice constant). To achieve a tensile strained GeSn active region, the device structure shown in Fig. 5 was designed and fabricated. Onto a Ge substrate, stepped GeSn buffer layers were grown including an 18 % Sn region, 40 nm thick, which exceeded the expected 15 nm critical thickness for relaxation based on the Peoples-Bean criterion. Following the buffer layers, the 200 nm p-n active region was grown, with 10 % Sn. X-ray measurements indicated that this 10 % Sn region was indeed tensile strained, and optical measurements yielded a bandgap of about 0.5 eV, as in Fig. 5 (right panel). To make electrical contacts to p-type GeSn, aluminum metal was used; for n-type GeSn and Ge, a stack of titanium/palladium/silver can be used.

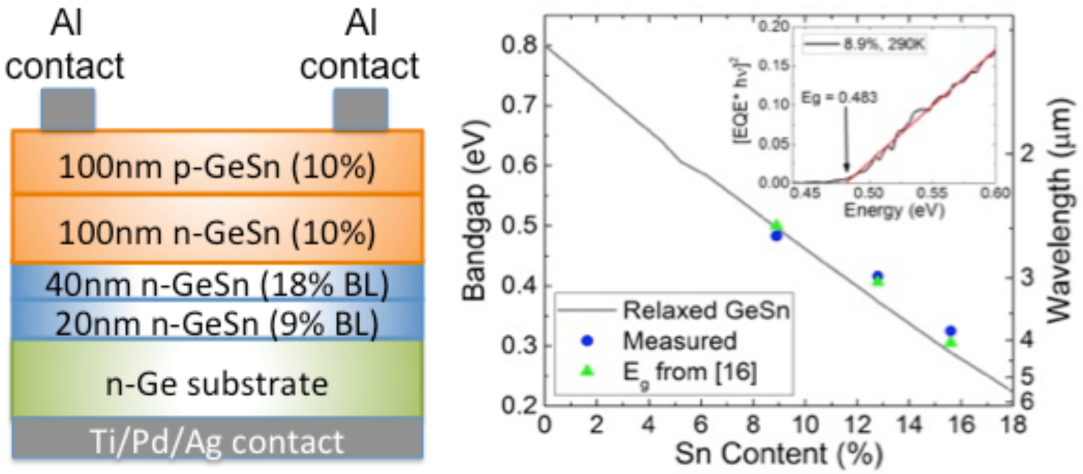

Figure 5. Left panel shows side view layer schematic for tensile-strained p-n junction diode with 10 % Sn, which should have a *direct* energy gap because it was grown on a relaxed GeSn buffer with a *larger* Sn content. Right panel shows the measured bandgap energies for several tensile-strained GeSn homojunction diodes with 9, 12, and 15.5% Sn.

In order to study their properties, several types of GeSn optoelectronic devices were fabricated, including strained junctions as shown in Fig. 5, as well as heterojunctions and photoconductive devices. For example, some interdigitated fingers of Al metal were deposited on a GeSn layer with 18.3 % Sn, which showed photoconductivity out to a wavelength of 5 μm, and a GeSn layer with 21 % Sn showed photoconductivity out to a wavelength of 7 μm [14].

To demonstrate infrared emission, GeSn/Ge n-P heterojunction diodes were fabricated, similar to that shown in Fig. 6. The diodes were forward biased and measured with an infrared camera, with the emission results in Fig. 7. The left panel shows an image of a device in the off-state with no applied current. The right panel of Fig. 7 shows a bright "hot-spot" indicating IR emission at room temperature. Due to a spectrometer malfunction that was only recently repaired, no emission spectra were obtained yet, but these measurements are planned. These results demonstrate that GeSn is suitable for mid-IR applications.

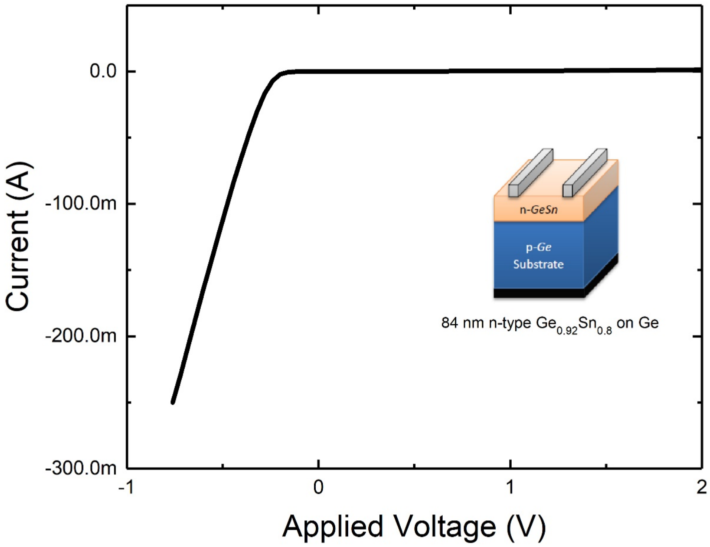

Figure 6. Current-voltage characteristics of GeSn p-n junction light emitting diode. Bias convention is with respect to the n-type top electrode, so that forward bias occurs in the lower-left region, with the applied voltage and current both negative. Note the relatively low reverse leakage current (from 0 to +2 Volts). The diode comprises 84 nm of n-type $Ge_{0.92}Sn_{0.08}$ on a p-type Ge substrate. Doping concentration of GeSn was $1.3x10^{20}$ with phosphorus donors. Top electrodes were lithographically patterned Ti/Pd/Ag, and bottom electrode was Al. This device was mesa etched, and the active area was 0.25 mm^2.

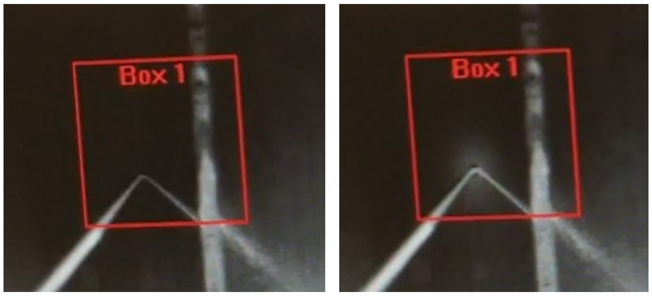

Figure 7. Video capture of light emission from the GeSn/Ge heterojunction light emitting diode of Fig. 6 with 8% Sn, with zero bias (left), and forward bias (right) of 200 mA current at room temperature. The straight gray lines are the electrode wires. The red-outlined “Box 1” regions highlight the light emitting active area, showing a glowing spot at the apex of the gray wires during forward bias. These images were taken with an FLIR microbolometer camera with infrared response.

We explored chemical vapor deposition (CVD) for GeSn epitaxy, using tin tetrachloride ($SnCl_4$) and digermane (10 % in H_2) as the Sn and Ge source precursors, respectively in an ultra-high vacuum (UHV) CVD system [2,3]. Fig. 8 shows the effects of the $SnCl_4$ co-flow on the Ge deposition rate. As the relative flow of $SnCl_4$ increased, the film became smoother, but the deposition rate decreased. Higher CVD temperatures (near 500°C) worsened the surface morphology. Although we successfully grew SiGe films (without Sn) in this CVD system, we found that under the relatively low pressures (≈ µBar) used, the layers contained almost no Sn, and sufficiently high flows of $SnCl_4$ *etched* the surface. We explored the deposition conditions with the goal of producing GeSn layers, but we have concluded that this UHV-CVD system using $SnCl_4$ cannot operate at the higher pressures (milliBar) that are necessary to deposit GeSn, so we ceased this sub-project at the end of 2016.

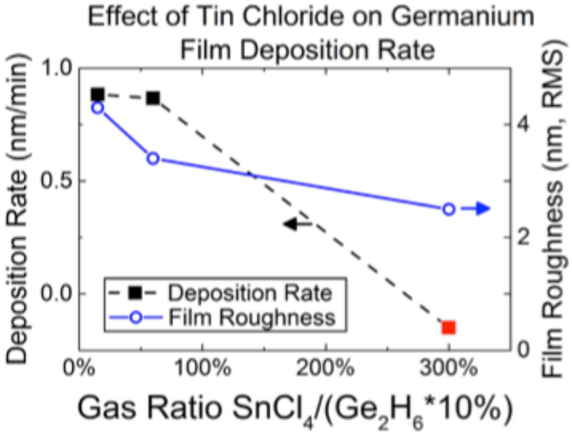

Figure 8. CVD Deposition with $SnCl_4$ vapor and digermane, showing the effect of $SnCl_4$ co-flow on the Ge deposition rate under ultra high vacuum (UHV) conditions. As the relative $SnCl_4$ flow increased, the films became smoother with no Sn incorporation, but the deposition rate decreased to below zero (i.e. etching). All growths were performed at a temperature of 285 °C and a pressure of ~1 µbar.

Technology Transitions:

GeSn samples were sent to Prof. Yung-Kee Yeo of the Air Force Institute of Technology (AFIT) for photoluminescence (PL) measurements. PL had been observed in our previous GeSn layers. Recent GeSn samples with high-Sn contents produced electroluminescence at wavelengths slightly longer than 2 µm, which is a wavelength region that is challenging for conventional PL detectors made from Ge and InGaAs. The current series of PL measurements were not yet conclusive.

In July 2016, discussions (at a conference [9]) were begun with Dr. B. (Chip) Claflin and Dr. A. Kiefer of the Air Force Research Lab (AFRL Dayton) for collaboration on GeSn characterization, including Hall Effect measurements for carrier concentration and mobility. No samples have yet been exchanged.

GeSn samples grown by MBE and SiGe samples grown by CVD were sent to Prof. Stefan Zollner of New Mexico State Univ. (NMSU) for spectroscopic ellipsometry, which measures the optical critical points and band structure. This research provided useful information to improve the growth parameters, and for fundamental knowledge. In July 2017, my student Dominic Imbrenda visited Prof. Zollner's lab for optical measurements. This collaboration resulted in several joint publications and conference presentations; a journal paper was published [11], a paper is in-press [13], and another manuscript is in progress [16].

In collaboration with Dr. G. Katulka (Army CERDEC, Aberdeen Proving Ground), experiments on see-through imaging were performed for the purpose of locating objects and for navigation in obscured environments. Measurements demonstrated that the optimal observability, under the full range of visible, dark, and obscured conditions, was achieved in the 2-5 μm wavelength regime, which is also the operating region for GeSn. For example, the near-IR (1-2 μm) does not give sufficient penetration through smoke, and the far-IR (5-15 μm) does not offer a familiar appearance of objects, which is useful for visual orientation. The best infrared region for both smoke penetration and familiarization is the mid-IR range (2-5 μm) of GeSn. Arrays of GeSn detectors were recently fabricated, and the spectral responses are currently being measured.

GeSn samples grown by CVD were received from Applied Materials (Sunnyvale), and photoconductivity measurements were performed. The results indicated longer wavelength response, and significantly higher responsivity at $\lambda = 1550$ nm for the GeSn devices than for the Ge detectors with similar structure, and this was published [4].

GeSn samples were sent to D. Beatson of Thorlabs (Maryland) for measurements, and for the fabrication of detector arrays. Thorlabs donated $10 K to help fund our new FTIR system (Thermo Nicolet iS50R), and has also donated equipment and optical components.

A series of several GeSn samples with differing compositions were sent to Drs. Charles Magee and Jeff Mayer of Charles Evans/EAG Laboratories to serve as calibration standards for their secondary ion mass spectrometry (SIMS) services. In return, EAG Laboratories agreed to perform, at our request, several SIMS measurements of our future samples for compositional analysis including the concentrations of dopants, and the possible presence of impurities.

Project Relevance:

GeSn alloys are promising for silicon-based photonics at wavelengths from 1 to 15 μm, spanning the near-, mid-, and long-wave infrared (IR). Depending on the Sn content, the energy bandgap can vary from 0.66 eV (pure Ge) to nearly 0 eV (about 30 % Sn). For sufficient Sn content above about 7 atomic %, depending on the strain, the bandgap of GeSn alloys becomes *direct* in *k*-space, for efficient optical emission and detection. GeSn devices may become useful for IR applications in: materials identification; medical diagnostics; navigation imaging; penetration imaging thru fog, smoke, and darkness; chemical sensing; air pollution monitoring; and infrared countermeasures. GeSn has produced light emitters and optically pumped lasers, and offers compatibility with silicon integrated circuit processing. Few other LEDs, however, including those based on the III-V compound semiconductors, can operate in the 2-5 μm range. For example, the Quantum Cascade Lasers can operate in the 3–25 μm range, but they require thousands of precision (and expensive) epitaxial layers, and they do not operate at wavelengths shorter than about 3 µm. GeSn optoelectronics is suitable for co-integration with electronic circuitry, which may enable commercial applications.

Project Importance:

The germanium-tin alloys have nearly ideal properties for optoelectronic applications, particularly in the near- and mid-infrared. With increasing Sn content, the energy bandgap of GeSn decreases, for emitting and detecting applications at wavelengths longer than about 1800 nm, which is the limit of unalloyed germanium. Furthermore, for Sn contents above about 7 atomic %, the bandgap becomes direct in k-space, for efficient infrared emitters, and which is unique among Group-IV semiconductors. As a low-bandgap semiconductor, GeSn offers lower voltage operation than either silicon or germanium, and may have higher mobilities of charge carriers for low power dissipation circuits and systems. Finally, the processing of GeSn is compatible with silicon-based CMOS circuits for conveniently integrated silicon photonics. For these reasons, it is important to improve our knowledge about the properties of GeSn materials and devices, which can enable the future development of optoelectronic devices with even higher performance.

Project Novelty:

Most other research groups have studied the materials properties, but this unique research project has investigated the operating principles of GeSn *devices* for practical applications. We achieved a near world-record content of Sn: 31 atomic percent, in a layer 190 nm thick, which is a combination of composition and thickness that is unmatched by any other research group.

Fundamental Principles:

To improve any technology, a clear and deep understanding of fundamental principles is pivotal. This GeSn project produced several fundamental findings. First, to achieve high Sn contents without precipitation or segregation, the MBE crystal growth temperature was lower than for many other semiconductors such as SiGe. Samples were grown at about 110 °C, using an electron-beam evaporator source for Ge to reduce the heat load on the substrate compared to a conventional thermal effusion source. The fundamental key to achieving high yields of good quality GeSn was to carefully clean the Ge substrate and then to remove the surface oxide in the vacuum chamber using high temperature desorption steps as described in the Accomplishments Section. For device fabrication, it was found that GeSn could be doped with conventional Group IV donors and acceptors, similarly to SiGe doping – not very surprising, but fundamentally important. We explored fundamental electrical and optical properties of GeSn infrared devices that produced both emission and detection. Thanks to this research, the fundamental properties of GeSn became better understood.

Project Publications (submitted, accepted, published) and Presentations:

1. N. Fernando, J. Moya, S. Zollner, J. Hart, D. Zhang, R. Hickey, R. Hazbun, and J. Kolodzey, "Strain dependence of the band structure and critical points of pseudomorphic GeSn alloys on Ge," American Physical Society 4 Corners Meeting, Arizona State University, Tempe, October 16-17, 2015.

2. J. Hart, R. Hazbun; D. Eldridge; R. Hickey; N. Fernando; T. Adam; S. Zollner; and J. Kolodzey, "Tetrasilane and Digermane for the ultra-high vacuum chemical vapor deposition of SiGe alloys," Thin Solid Films, v. 604, pp. 23–27, 1 April 2016, http://dx.doi:10.1016/j.tsf.2016.03.010.

3. R. Hazbun, J. Hart, R. Hickey, A. Ghosh, N. Fernando, S. Zollner, T.N Adam, J. Kolodzey, "Silicon epitaxy using tetrasilane at low temperatures in ultra high vacuum chemical vapor deposition," J. Crystal Growth, v. 444, pp. 21-27, 15 June 2016, http://dx.doi.org/10.1016/j.jcrysgro.2016.03.018.

4. John Hart, Thomas Adam, Yihwan Kim, Yi-Chiau Huang, Alexander Reznicek, Ramsey Hazbun, Jay Gupta, and James Kolodzey, "Temperature varying photoconductivity of GeSn alloys Grown by CVD with Sn concentrations from 4% to 11%," J. Appl. Phys., v. 119, 093105, 2016; http://dx.doi.org/10.1063/1.4942851.

5. N. Bhargava, J.P. Gupta, N. Faleev, L. Wielunski, and J. Kolodzey, "Thermal stability of annealed germanium-tin alloys grown by molecular beam epitaxy," J. Electronic Materials, vol. 46 (3), pp. 1620-1627, 2017, [DOI: 10.1007/s11664-016-5205-y].

6. N. Bhargava, J. Gupta, N. Faleev, L. Wielunski, and J. Kolodzey, "Thermal stability of annealed germanium-tin alloys grown by molecular beam epitaxy," 58th Electronic Materials Conference, University of Delaware, Newark, 22-24 June 2016, presentation I4.

7. J. Hart, R. Hickey, R. Hazbun, T. Adam, and J. Kolodzey, "Annealing characteristics of high Sn content GeSn p-n junction didoes grown by MBE," 58th Electronic Materials Conference, University of Delaware, Newark, 22-24 June 2016, poster PS42.

8. R. Hickey, J. Hart, R. Hazbun, and J. Kolodzey, "Electrical contacts on germanium tin grown by molecular beam epitaxy," 58th Electronic Materials Conference, University of Delaware, Newark, 22-24 June 2016, poster PS43.

9. J. Kolodzey, R. Hazbun, J. Hart, R. Hickey, D. Zhang and D. Eldridge, "The Characteristics of GeSn p-n junction devices fabricated by molecular beam epitaxy," 2016 IEEE Summer Topical Meeting on "Emerging Technology for Integrated Photonics", July 11-13, 2016, Newport Beach, CA, invited talk.

10. N. Fernando, R. Hickey, J. Hart, R. Hazbun, D. Zhang, J. Kolodzey, and S. Zollner, “Effects of composition and strain on band gaps of pseudomorphic GeSiSn on Ge,” AVS 63rd International Symposium, Nashville, TN, 6-11 November 2016.

11. R. Hickey, N. Fernando, J. Hart, R. Hazbun, S. Zollner and J. Kolodzey, “Properties of pseudomorphic and relaxed germanium-tin alloys ($x < 0.185$) grown by MBE,” J. Vacuum Science & Technology B: Nano, v. 35 (2), 021205, 2017; doi: http://dx.doi.org/10.1116/1.4975149.

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13. N.S. Fernando, R.A. Carrasco, R. Hickey, J. Hart, R. Hazbun, S. Schoeche, J.N. Hilfiker, J. Kolodzey, and S. Zollner, “Band gap and strain engineering of pseudomorphic GeSiSn alloys on Ge and GaAs for photonic applications,” J. Vacuum Science & Technology B: Nano, 2017, in press.

14. Ryan Hickey, Dominic Imbrenda, Rigo Carraso, Stefan Zollner, and James Kolodzey, "Photoconductivity of germanium tin alloys with up to 22% tin grown by molecular beam epitaxy," 2017, manuscript in progress.

15. Ryan Hickey, Dominic Imbrenda, and James Kolodzey, “Electrical characteristics of germanium tin alloys with up to 31% tin grown by low-temperature molecular beam epitaxy,” 2017, manuscript in progress.

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James Kolodzey

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Abstract

With a direct energy bandgap and compatibility with commercial circuit processing, germanium-tin semiconductors are attractive for high performance, integrated optoelectronics at middle-infrared wavelengths. Using molecular beam epitaxy and Clean Room processing, GeSn optoelectronic devices were fabricated, and measured to determine their characteristics and limitations. By reducing the substrate temperature to 100°C during growth, the epitaxy was optimized to achieve an unusually high Sn content of 31 atomic %. A variety of substrate wafers were used, including silicon, germanium, and gallium arsenide. The GeSn layers had excellent crystal structure as measured by x-ray diffraction, with smooth surfaces as measured by atomic force microscopy. Novel doping sources were studied, including boron and gallium acceptors for p-type doping, and arsenic and phosphorus donors for n-type doping. The fabricated optoelectronic devices included p-n junctions, heterojunctions, and photoconductors, which had excellent electrical and optical properties, measured using infrared spectroscopy. These results showed that GeSn alloys are suitable for device applications in the field of infrared silicon photonics.

Highlights of recent achievements since the last year's report include:

1. Achieving the extremely high Sn content of 31 atomic % in a 99.9% relaxed GeSn layer that was 191 nm

thick on a Ge substrate. The bandgap is expected to be direct and near, or below zero (- 94.4 meV).
2. Added new dopant sources for MBE, including arsenic donors for n-type, and gallium acceptors for p-type conductivity, because these doping cells operate at lower temperatures than for other dopants, with less heating of the substrate and therefore better GeSn quality.
3. Fabricated a strain engineered GeSn diode, using a partially relaxed buffer layer of n-GeSn with 18% Sn, overgrown by an active p-n homojunction of GeSn (10% Sn) that was fully relaxed, so that the bandgap of the active region will be direct for efficient light emission.
4. Measured the photoconductive response of GeSn detectors on Ge substrates. An 18 % Sn device had response to a wavelength of about 5 µm, and a 21 % Sn device had response to 7 µm.
5. Verified optical emission from p-N GeSn/Ge heterojunction diodes, by using an infrared camera.
6. A grad student, Dominic Imbrenda, visited Prof. Stefan Zollner's group at New Mexico State University (NMSU) for infrared spectroscopic ellipsometry, and determined the optical absorption coefficients of a series of GeSn alloys.
7. Grew several GeSn layers on undoped (semi-insulating) gallium arsenide, so that the electrical measurements will not be disturbed by electrical conduction in the substrate.
8. Measured the Hall effect mobility of GeSn alloys, and found that the electrical conduction was by holes, with somewhat low mobility values (< 100 cm2/V-S), which is still be analyzed.

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Archival Publications (published) during reporting period:

1. J. Hart, R. Hazbun; D. Eldridge; R. Hickey; N. Fernando; T. Adam; S. Zollner; and J. Kolodzey, "Tetrasilane and Digermane for the ultra-high vacuum chemical vapor deposition of SiGe alloys," Thin Solid Films, v. 604, pp. 23–27, 1 April 2016, http://dx.doi:10.1016/j.tsf.2016.03.010.

2. R. Hazbun, J. Hart, R. Hickey, A. Ghosh, N. Fernando, S. Zollner, T.N Adam, J. Kolodzey, "Silicon epitaxy using tetrasilane at low temperatures in ultra high vacuum chemical vapor deposition," J. Crystal Growth, v. 444, pp. 21-27, 15 June 2016, http://dx.doi.org/10.1016/j.jcrysgro.2016.03.018.

3. John Hart, Thomas Adam, Yihwan Kim, Yi-Chiau Huang, Alexander Reznicek, Ramsey Hazbun, Jay Gupta, and James Kolodzey, "Temperature varying photoconductivity of GeSn alloys Grown by CVD with Sn concentrations from 4% to 11%," J. Appl. Phys., v. 119, 093105, 2016; http://dx.doi.org/10.1063/1.4942851.

4. N. Bhargava, J.P. Gupta, N. Faleev, L. Wielunski, and J. Kolodzey, "Thermal stability of annealed germanium-tin alloys grown by molecular beam epitaxy," J. Electronic Materials, vol. 46 (3), pp. 1620-1627, 2017, [DOI: 10.1007/s11664-016-5205-y].

5. R. Hickey, N. Fernando, J. Hart, R. Hazbun, S. Zollner and J. Kolodzey, "Properties of pseudomorphic

and relaxed germanium-tin alloys (x < 0.185) grown by MBE," J. Vacuum Science & Technology B: Nano, v. 35 (2), 021205, 2017; doi: http://dx.doi.org/10.1116/1.4975149.

6. N.S. Fernando, R.A. Carrasco, R. Hickey, J. Hart, R. Hazbun, S. Schoeche, J.N. Hilfiker, J. Kolodzey, and S. Zollner, "Band gap and strain engineering of pseudomorphic GeSiSn alloys on Ge and GaAs for photonic applications," J. Vacuum Science & Technology B: Nano, 2017, in press.

New discoveries, inventions, or patent disclosures:

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No

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none

Change in AFOSR Program Officer, if any:

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Extensions granted or milestones slipped, if any:

none

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

	Starting FY	FY+1	FY+2
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Equipment/Facilities			
Supplies			
Total			

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