



AFRL-AFOSR-VA-TR-2016-0044

Next generation, Si-compatible materials and devices in the Si-Ge-Sn system

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**10/09/2015
Final Report**

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**Air Force Research Laboratory
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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) 09-29-2015		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) July 2012 - June 2015	
4. TITLE AND SUBTITLE Next generation, Si-compatible materials and devices in the Si-Ge-Sn system			5a. CONTRACT NUMBER FA9550-12-1-0208		
			5b. GRANT NUMBER FA9550-12-1-0208		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) J. Kouvetakis J. Menendez			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Arizona State University Tempe Campus Tempe Arizona 85287			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/RTA Air Force Office of Scientific Research 875 North Randolph Street Suite 325, Room 3112 Arlington, Virginia 22203-1768 USA			10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR / RTA		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited					
13. SUPPLEMENTARY NOTES					
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15. SUBJECT TERMS Group IV Semiconductors					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Gemot S. Pomrenke, RSE (Program Manager)
U	U	U	UU		19b. TELEPHONE NUMBER (Include area code)

Final report

Grant Title: FA9550-12-1-0208/ Next generation, Si-compatible materials and devices in the Si-Ge-Sn system

PIs J. Kouvetakis and J. Menendez, Arizona State University

1.0 Abstract:

The program demonstrated synthesis, optical and electrical characterizations, and device fabrication of GeSn and GeSiSn alloys integrated on Si platforms. These materials were produced via next generation deposition chemistries based on industrially viable hydride compounds. Emphasis was placed on the fabrication of direct-gap GeSn binaries grown on Ge buffered Si as well as light-emitting GeSiSn ternaries covering a broad band of tunable wavelengths from 1300 nm to 2500 nm for the first time. First generation GeSiSn LEDs and IR photodetectors were also demonstrated establishing the ternary as a thermally robust alternative to the binary for long wavelength applications. New breakthrough designs of direct-gap GeSn LEDs were introduced and shown to exhibit superior response relative to the state-of-the-art. The latter technology was further advanced via the creation of degenerate pn junctions representing the basic building block of quasi-direct diode lasers. The demonstration of electrically injected devices in this study was made possible by the ability to dope the materials *p*- and *n*-type at levels up to $10^{20}/\text{cm}^3$ using practical *in situ* methods developed under the grant.

2.0 Deliverables :

As of 10/2/2015 35 peer-reviewed papers acknowledging support of the grant have been published and one manuscript is currently under revision. These publications are listed at the end of this report. The students and PIs supported of the grant also gave over 20 invited and contributed presentations in national and international meetings and workshops during the performance period of the project. The grant made significant contributions to the formation of human resources. Four students received Ph.D. degrees with AFOSR support: Richard Beeler (currently at Intel), Liying Jiang (currently at IBM), Gordon Grzybowski (currently at Wright Patterson AFB) and Chi (Seth) Xu (currently at ASU). An additional four Ph.D students at ASU Chemistry and Physics programs received support from the grant: James Gallagher (will defend his thesis in physics Fall of 2015), Patrick Sims and Lasitha Seranratne (will defend their Ph.D theses in chemistry in Spring of 2016) and Patrick Wallace (currently in his second year of his Ph.D. studies).

3.0 DoD collaborations:

The program established collaborations with Prof Yung-Kee Yeo and his group at AFIT ASU to conduct optical and electrical measurements and study the temperature dependent PL, EL and Hall effects. Several publications were produced and a number of talks were given at national APS meetings highlighting the joint work. ASU also collaborated with Dr. Bruce Clafin at AFRL (Wright Patterson AFB)

for structural, optical, and electrical characterizations with emphasis on areas complementary to those available to the ASU team, such as temperature-dependent Hall measurements and *deep-level transient spectroscopy (DLTS)* to investigate electrically active defects and carrier traps in these materials.

4.0 Research accomplishments and highlights:

The main milestones of the project accomplished over the three years performance period are summarized in sections a-f below. The impact of the discoveries on transitioning the Si-Ge-Sn materials technologies into the device arena is also discussed.

(a) Photoluminescence from $Ge_{1-x-y}Si_xSn_y$ ternaries and LEDs: Synthesis of light emitting $Ge_{1-x-y}Si_xSn_y$ materials with tunable wavelengths over a wide range in the mid IR (down to 2500 nm) was conducted on Si(100) and Ge buffered Si(100) platforms. This work represents the first demonstration of PL emission in the ternary system paving the way for possible laser and LED designs. These light emitting $Ge_{1-x-y}Si_xSn_y$ alloys were subsequently utilized to create working LEDs for the first time in this material system.

(b) Fabrication of $Ge_{1-x-y}Si_xSn_y$ photodiodes: Fabrication of the first generation of $Ge_{1-x-y}Si_xSn_y$ photodiodes was demonstrated with absorption edges above and below that of Ge. This pioneering work has sparked a cascade of IP activity by major national and international energy and optoelectronic companies.

(c) Determination of indirect-to-direct gap cross over in $Ge_{1-y}Sn_y$: A comprehensive study of the compositional dependence of both direct and indirect gap of $Ge_{1-y}Sn_y$ alloys using photoluminescence resulted in the first systematic determination of the indirect-to-direct gap cross-over in $Ge_{1-y}Sn_y$ providing guidance for the design and fabrication of light emitting diodes and lasers.

(d) Fabrication of next generation $Ge_{1-y}Sn_y$ LEDs based on homo-structure and hetero-structure *p-i-n geometries*: A comprehensive study was conducted of the compositional dependence of direct and indirect gap electroluminescence including devices with Sn concentrations at direct gap transition and beyond. This was enabled via implementation of an advanced design of lattice engineered pin diodes beyond the state of the art at the time.

(e) LEDs based on $Ge_{1-y}Sn_y$ diodes with degenerate *p-n junctions* as a prelude to electrically-pumped lasers: First-generation LED prototypes with quasi-direct and direct-gap compositions have been grown and measured showing significant electroluminescence efficiency and excellent electrical response.

(f) Development of practical *n-type technologies en route to electrically injected devices and optically pumped waveguides*: CMOS compatible doping strategies were developed for in situ activation of Si-Ge-Sn systems using industrially feasible molecular reagents. The approach has been applied to produce optically pumped $Ge_{1-y}Sn_y$ waveguides and *n-type* $Ge_{1-y}Sn_y$ alloys with enhanced PL emission. To our knowledge the doping work represents the most advanced approach in this technology space. Furthermore the doping work has also attracted the attention of the Ge-on-Si community due to our demonstration of Ge materials and devices with superior electrical properties.

The subsequent sections provide a more detailed account of results and discussion for the various thrusts and milestones listed above, including background information, task objectives, technical approach and methods. In some cases future research directions are proposed focusing on most promising systems identified in this study.

5.0 Results and discussion of representative examples:

(a-b) Light emitting $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ materials and devices

The use of tetragermane (Ge_4H_{10}) and tetrasilane (Si_4H_{10}) as Ge and Si sources, respectively, has led to the growth of $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ alloys for the first time in a single-wafer format under ultra-high purity conditions. This process development improved the control of multilayer structures and enabled the incorporation of higher amounts of Sn, as needed for studies of potential applications in photodetectors, LEDs and potentially lasers. Using this approach high performance *p-i-n* photodiodes were initially fabricated on Ge wafers and Ge-buffered Si wafers with adjustable absorption edges above and below Ge (1300 - 1800 nm). Device structures lattice matched to Ge exhibited defect-free interfaces producing extremely low dark currents compared to conventional group IV analogs. These developments represented the first example of devices based on ternary $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ alloys with $x/y \sim 4$.

Next we fabricated $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ alloy layers with $y > x$ exhibiting direct gap behavior and strong photoluminescence for the first time in this class of materials. The band-gaps determined using PL and photocurrent measurements were found to span the

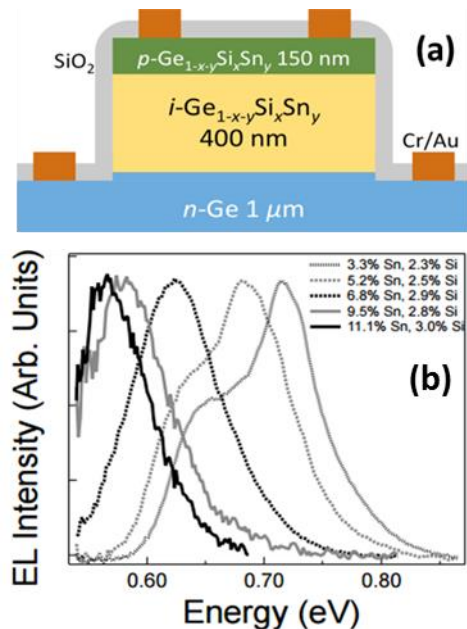


Figure 1: (a) Schematic of first generation $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ LED. (b) Normalized EL spectra of diodes with 3.3-11.1 % Sn illustrating a redshift in both direct and indirect gap peaks with increasing Sn contents. An overlap of the indirect/direct peaks is observed for the 7-11 % Sn devices.

wavelength range down to 2500 nm. The results showed that the separation of the indirect and direct edges in a given sample systematically decreased with increasing Sn, replicating the basic features of the $\text{Ge}_{1-y}\text{Sn}_y$ electronic structure including a transition to direct gap semiconductor. These light emitting $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ alloys were subsequently utilized to create working LEDs for the first time in this material system. Initial-generation prototypes with $x \sim 0.03$ and $y = 0.035-0.11$ were fabricated in hetero-structure *p-i-n* geometry [$n\text{-Ge}/i\text{-Ge}_{1-x-y}\text{Si}_x\text{Sn}_y/p\text{-Ge}(\text{Sn}/\text{Si})$] depicted by the schematic in Figure 1(a) containing a single defected interface. The devices showed absorption edges that systematically red-shift from 1750 to 2200 nm with increasing Sn content, covering all telecom bands and beyond, in analogy to $\text{Ge}_{1-y}\text{Sn}_y$ alloys. Additionally, the devices exhibited strong direct and indirect gap electroluminescence with tunable wavelengths as shown in Figure 1(b). These findings, combined with the enhanced thermal stability of $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ relative to $\text{Ge}_{1-y}\text{Sn}_y$ and the observation that ternary alloy disorder does not adversely affect the

emission properties, indicate that $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ should represent a practical target system for future generations of group-IV light sources on Si. The breakthrough demonstration of $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ LEDs has stimulated further experimental and theoretical studies of the compositional dependence of the direct/indirect band gaps using EL, from which the energies of these transitions can be determined. Predicted giant bowing parameters might lead to direct gap materials with emission near the 1550 nm range of fundamental interest for telecommunications. Fabrication of samples with suitable Si/Sn

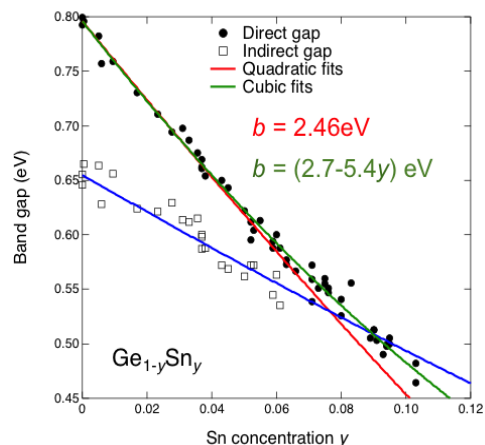


Figure 2 : Plots of E_0 and E_{ind} showing for $\text{Ge}_{1-y}\text{Sn}_y$ a cross over composition $y \sim 9\%$ Sn at the intersection of green and blue lines which represent the best fits of the data. Cubic fits indicate a compositional dependence of the bowing parameter thus providing an accurate determination of direct gap crossover for the first time

concentrations to validate these predictions should be the next step in the pursuit of direct gap $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$.

(c-d) Light emitting $\text{Ge}_{1-y}\text{Sn}_y$ materials, pin diodes, detectors and LEDs

The introduction of the more reactive trigermene (Ge_3H_8) in place of digermene (Ge_2H_6) as the source of Ge under this program has led to the growth of thick $\text{Ge}_{1-y}\text{Sn}_y$ bulk-like films ($> 500\text{nm}$) with lower defectivities than state-of-the-art analogs. Direct gap Sn concentrations as high as $y = 0.14$ are readily obtained as required for fabrication of high efficiency LEDs in the mid IR and beyond. We were the first to introduce digermene for $\text{Ge}_{1-y}\text{Sn}_y$ growth and the compound has since become the industry standard. We expect that commercially available trigermene developed under this program will become the source of choice for production of next generation Si-Ge-Sn technologies. Particular interest has already been shown in this technology by groups in Asia.

At the initial stage of the project a systematic study was conducted to measure $\text{Ge}_{1-y}\text{Sn}_y$ direct gap and indirect gap photoluminescence from over 50 optimized samples with Sn compositions spanning the range of 0.3 to 11 % Sn. The indirect to direct gap cross over was unambiguously determined to be at 8.7 % Sn ($E_0 \sim 2300\text{ nm}$) by measuring the separation of their energies as a function of Sn content for the first time. The 8.7 % Sn is significantly lower than

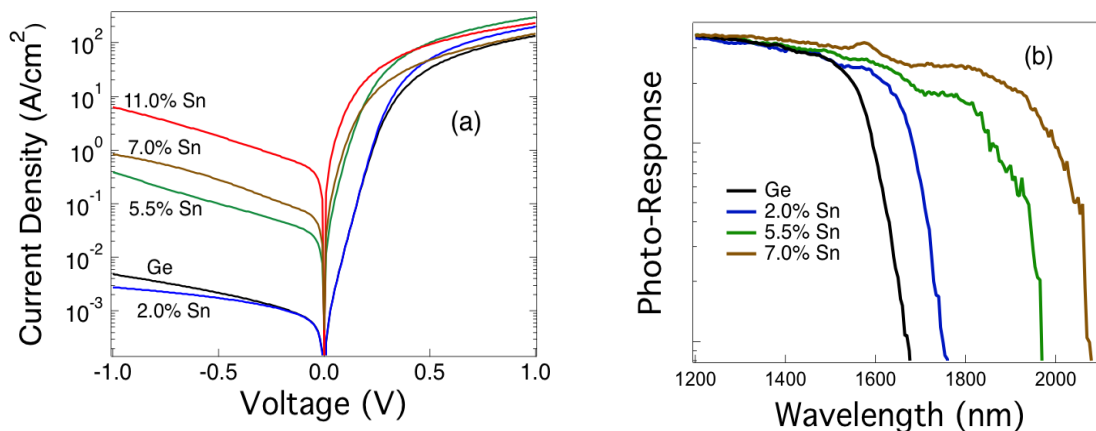


Figure 3: (a) Dark current characteristics of $p\text{-Ge}_{1-y}\text{Sn}_y/i\text{-Ge}_{1-y}\text{Sn}_y/n\text{-Ge}$ diodes. (b) Optoelectronic response at 0V bias for samples with up to 7% Sn demonstrating an extension of the absorption edge beyond $2\ \mu\text{m}$.

predicted using virtual crystal approximation theory (20% Sn) but much closer to recent calculations using supercells to simulate the alloy (6% Sn). We note that we were the first to report that the bowing parameters of $\text{Ge}_{1-y}\text{Sn}_y$ are not constant, but a function of composition. This discovery has led to an accurate determination of the direct gap crossover. Figure 2 shows direct and indirect gaps of $\text{Ge}_{1-y}\text{Sn}_y$ alloys as a function of composition. The plots also compare a quadratic fit (constant bowing parameter, red trace) and a cubic fit (composition-dependent bowing parameter, green trace) of the direct gap dependence on composition. The cubic fit gives a superior fit, and the compositional dependence of the bowing parameter obtained from the fit was justified via perturbation-theory calculations.

Under prior AFOSR support (MURI 2006-2011) we demonstrated the first $\text{Ge}_{1-y}\text{Sn}_y/\text{Si}(100)$ LED and prototype photodetector covering all communication bands. Under this AFOSR grant we initiated the fabrication of extended range detectors and next-generation $\text{Ge}_{1-y}\text{Sn}_y$ LEDs ($y = 0-11\%$) with Sn contents spanning the indirect to direct band gap crossover. These devices featured superior designs relative to the state-of-the-art leading to significant performance gains. Up to now, the main problem with hetero-structure LEDs ($n\text{-Ge}/i\text{-Ge}_{1-y}\text{Sn}_y/p\text{-Ge}$) reported in the literature is that in most cases they contain two defected interfaces due to strain relaxations of the mismatched $p\text{-}i\text{-}n$ layers, adversely affecting the optical/electrical properties, particularly at the high Sn concentrations that are required for fabrication of direct-gap lasers. To circumvent this problem we introduced new and improved device architectures that eliminate the need for pure Ge layers. The first such design involved stacks of $p\text{-Ge}_{1-y}\text{Sn}_y/i\text{-Ge}_{1-y}\text{Sn}_y/n\text{-Ge}$ containing a single defected interface rather than two. These devices exhibited adjustable band gaps from 1600 nm to 2400 nm and superior light emission relative to defected hetero-structure analogs. The devices also exhibited longer recombination lifetimes paving the way for the development of group IV lasers fully integrated on Si. Figure 3 plots the current voltage curves and absorption edges of representative $p\text{-Ge}_{1-y}\text{Sn}_y/i\text{-Ge}_{1-y}\text{Sn}_y/n\text{-Ge}$ diodes with active layer Sn compositions up to 11%. The plots indicate that the dark currents increase with decreasing band gap. The plots also show that the $\text{Ge}_{0.98}\text{Sn}_{0.02}$ device exhibits comparable electrical performance to a pure Ge reference, a testament to the high crystal quality of our materials.

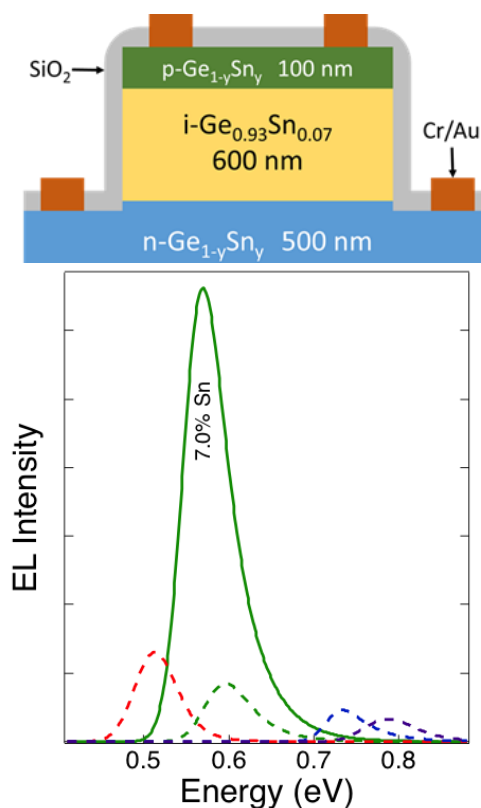


Figure 4 (Top) Schematic of pseudomorphic pin diode ($n\text{-Ge}_{1-x}\text{Sn}_x/i\text{-Ge}_{1-y}\text{Sn}_y/i\text{-Ge}_{1-z}\text{Sn}_z$) with lattice matched interfaces. (Bottom) EL spectra of 7% Sn device (solid green line) showing a 5-fold increase in emission intensity relative to hetero-structure analogs containing 0.0-10.5% Sn (color lines). The plots represent EMG fits of the direct gap peaks.

A new and improved diode design was then pursued featuring homo-structure stacks based on a layer sequence of $p\text{-Ge}_{1-y}\text{Sn}_y/i\text{-Ge}_{1-y}\text{Sn}_y/n\text{-Ge}_{1-y}\text{Sn}_y$ containing all pseudomorphic, non-defected interfaces. This architecture was initially adopted to demonstrate proof-of-concept prototypes containing 7% Sn, as shown in Figure 4 (top) which illustrates a basic schematic of the diode stack. This design avoids the reduction of EL intensity by preventing the creation of non-radiative recombination pathways. The active layer is an intrinsic $\text{Ge}_{0.93}\text{Sn}_{0.07}$ alloy, while the top/bottom electrodes contain slightly lower Sn content in the 6-7% range. This is intended to maximize the quantum efficiency while keeping the lattice mismatch minimal so that the interfaces grow fully coherent and defect free. The Ge buffer platform (1-1.5 μm) is produced via depositions of Ge_4H_{10} using procedures developed under the AFOSR grant. Figure 4 (bottom) compares EL spectra vs. Sn content of a largely-relaxed 7% homo-structure device (green line) devoid of interface defects with a series of 0.0-10.5% Sn hetero-structure analogs (dashed lines) containing a single defected interface. All devices are built using similar film parameters and processing conditions. The plots show a 5-fold increase in emission intensity for the homo-structure indicating that strain relaxation plays a major role in quenching the emission intensity. Another important consideration is that the active regions of these improved designs exhibit only minor residual compressive strains that do not alter the electronic properties in any significant manner. This represents a major design advantage over fully compressed devices produced by MBE. The strains in the latter case reduce the directness of the materials.

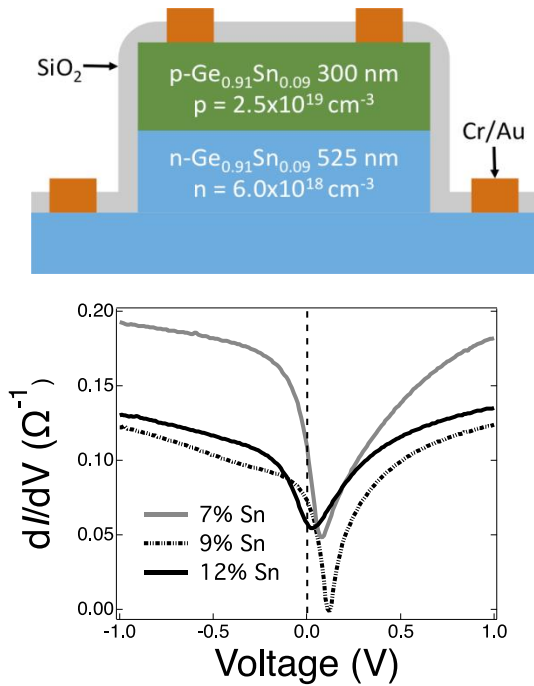


Figure 5: (top) Schematic of $\text{Ge}_{0.91}\text{Sn}_{0.09}$ pn junction showing p - and n -type active carrier concentrations and total layer thickness. The devices are grown on Ge-buffered Si(100). (bottom) dI/dV plots for $\text{Ge}_{1-y}\text{Sn}_y$ tunnel diodes ($y=0.07, 0.09, 0.12$) with $45 \mu\text{m}$ mesa radii illustrating a conductance minimum less than $0.2 \Omega^{-1}$ in each sample.

(e) $\text{Ge}_{1-y}\text{Sn}_y$ tunneling diodes with degenerate p - n junctions

To further explore the device potential of the $\text{Ge}_{1-y}\text{Sn}_y$ systems for quasi-direct emission, we fabricated p - n diodes without the intrinsic layer. These new devices represent a basic building block for the creation of quasi-direct diode lasers. The device samples comprise thick, heavily doped p - and n -layers with direct gap compositions as shown in Figure 5 (top) for a representative $\text{Ge}_{0.91}\text{Sn}_{0.09}$ alloy. The structures contain a single interface that is lattice-matched and defect free. This was the first demonstration of a working prototype featuring $\text{Ge}_{1-y}\text{Sn}_y$ alloys. The key to the successful fabrication is the ability of our deposition methods to readily yield p and n type layers and integrate them into a single junction using a single-step process. The I-V measurements demonstrate the tunneling behavior that corroborates the formation of p^+/n^+ junctions between the $\text{Ge}_{1-y}\text{Sn}_y$ layers in these samples. This is illustrated in Figure 5 (bottom), which shows plots of

differential conductance (dI/dV) vs. applied bias for 7%, 9%, and 12% Sn p^+/n^+ diodes. Room temperature electroluminescence spectra have been measured and representative plots are shown in Figure 6 for the $\text{Ge}_{0.91}\text{Sn}_{0.09}$ device using two complementary InGaAs and PbS detectors. The InGaAs detector allows collection of the EL signal vs pumping current from 0.2-0.5 A out to 2300 nm, but its detection cutoff prevents inclusion of the entire peak. The PbS detector spectrum of the same device contains the entire peak extending down to 2700 nm as shown in inset panel of Figure 6 inset. The solid line is a fit to the raw data by an exponentially modified Gaussian (EMG) representing the direct-gap emission profile for $\text{Ge}_{0.91}\text{Sn}_{0.09}$. The demonstration of working p - n junctions has stimulated further studies to produce entire families of devices with varying film parameters whose optical and electrical properties are currently being analyzed. The observation of significant light emission represents a key milestone for the development of electrically pumped quasi-direct $\text{Ge}_{1-y}\text{Sn}_y$ lasers. The EL intensity vs pumping current dependence can provide information about the effects of the long minority carrier diffusion lengths on the optoelectronic properties of the alloys.

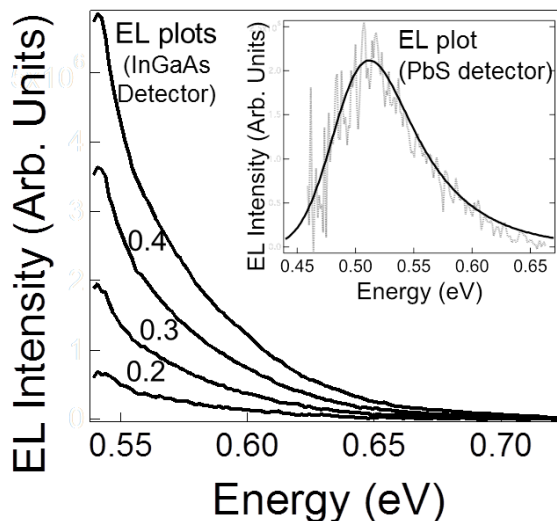


Figure 6: Room-temperature EL spectra measured as a function of injection current using an InGaAs detector. (inset) EL spectrum acquired with a PbS detector showing the entire peak profile corresponding to direct gap emission.

(f) n -type Si-Ge-Sn technologies

(i) **Doping capabilities:** Practical approaches were developed to dope and super-dope Si-Ge-Sn alloys

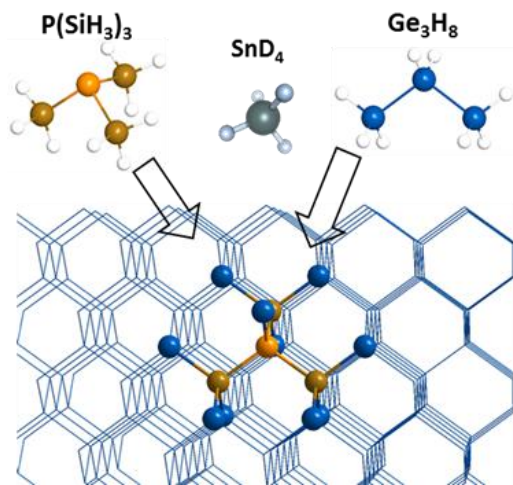


Figure 7: Schematic illustrating the n -type doping strategy of GeSn alloys via in situ deposition of $\text{P}(\text{SiH}_3)_3$. Blue lines show the diamond like alloy lattice.

using specially designed chemical sources $\text{P}(\text{GeH}_3)_3$, $\text{P}(\text{SiH}_3)_3$, and $\text{As}(\text{SiH}_3)_3$. The new technologies enable fabrication of devices based entirely on group IV components. This is in contrast to recent device fabrication studies presented in the literature by other groups, where apparent constraints in doping Si-Ge-Sn materials have limited device architectures to hybrid heterostructure designs utilizing Ge electrodes. Figure 7 shows a schematic of GeSn lattice co-doped with P and Si via reactions of $\text{P}(\text{SiH}_3)_3$, Ge_3H_8 and SnD_4 . The PSi_3 unit is shown embedded within the bulk GeSn host lattice (blue lines) as expected by the intact incorporation of the molecular core of $\text{P}(\text{SiH}_3)_3$. The bonds of the Ge/Sn atoms are shown as lines and only Ge atoms bonded to the PSi_3 are drawn as blue spheres to emphasize the tetrahedral bonding environment about the P site.

(ii) Light enhancement via *n*-type doping: The emission intensities in the PL spectra of GeSn materials were found to significantly enhance by at least an order of magnitude via heavy *n*-type doping with P/As atoms at levels up to $7 \times 10^{19} \text{ cm}^{-3}$ using the above $\text{P}(\text{GeH}_3)_3$, $\text{P}(\text{SiH}_3)_3$, and $\text{As}(\text{SiH}_3)_3$ precursors, indicating that desirable direct gap conditions can be approached even at relatively modest 6-8 % Sn contents in this alloy system. This is highly desirable for some applications relating to optically pumped lasers. Moreover these studies elucidated band gap renormalization effects attributed to donor atoms in the lattice and the results are expected to have important implications in device design using this class of materials as active components.

(iii) Optically pumped waveguides: The fact that the recent observation of lasing in direct gap $\text{Ge}_{1-y}\text{Sn}_y$ laser structures was limited to cryogenic temperatures, whereas lasing in quasi-direct Ge was observed at room temperature, suggested that the quasi-direct route is worthy of further research in the case of $\text{Ge}_{1-y}\text{Sn}_y$ alloys. The advances in $\text{Ge}_{1-y}\text{Sn}_y$ materials growth under this grant and the ability to heavily dope the material has led to the fabrication of *n*-type waveguide structures on Ge-buffered Si platforms comprising highly activated $\text{Ge}_{1-y}\text{Sn}_y$ layers with carrier densities approaching $1 \times 10^{20} \text{ cm}^{-3}$. The devices possess large thickness up to 700 nm, thereby allowing the formation of large volume active regions away from the defected Ge/ $\text{Ge}_{1-y}\text{Sn}_y$ interface, thus minimizing the deleterious effects of dislocations on the emission properties. The top panel in Figure 8 shows a schematic representation of the waveguide patterns. The latter comprises high aspect ratio mesas with dimensions of $\sim 4 \text{ mm} \times 1.6\text{-}100 \text{ }\mu\text{m}$ as seen in the bottom panel of the figure, which illustrates several patterns of the fabricated devices. These are passivated with a thin SiO_2 coating intended to minimize the reflectance of the incident light on the sample. The samples are currently being tested by measuring their stimulated emission over a broad spectral range in collaboration with University of Dayton. Although the current samples contain amounts of Sn between 4% - 7% Sn which should be adequate to study lasing feasibility from devices operating on the basis of quasi-direct materials, higher concentration analogs in the direct gap regime should be straightforward to make. This should be the immediate goal of further research in this area.

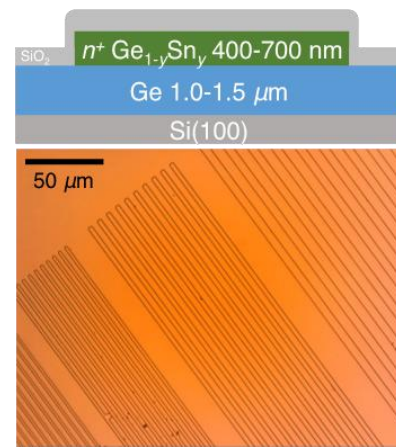


Figure 8: (top) Schematic of *n*-type $\text{Ge}_{1-y}\text{Sn}_y$ waveguides. (bottom) Optical image of waveguide patterns with SiO_2 passivation layers. Samples with same design architecture are currently being tested for lasing capability in collaboration with University of Dayton.

6.0 Summary and conclusions

The work initially focused on growth of next generation $\text{Ge}_{1-y}\text{Sn}_y$ alloys on Ge buffered Si wafers via UHV CVD depositions of Ge_3H_8 , SnD_4 . The compositional dependence of the direct and indirect band gas were measured using room temperature PL and the crossover transition to direct gap material was determined to occur near 8-9 % Sn. The work also produced new designs of direct gap $\text{Ge}_{1-y}\text{Sn}_y$ LEDs and photodetectors with wavelengths spanning from 1700-2500 nm which includes the indirect to direct

gap regime. These devices were made to contain lattice-matched interfaces devoid of defects that adversely affect the device performance, yielding superior optical and electrical response relative to state-of-the-art heterostructure analogs with inherently defected junctions. The first generation prototype devices in this class of $\text{Ge}_{1-y}\text{Sn}_y$ semiconductors were made possible by the ability to dope the materials p - and n -type at levels up to $10^{20}/\text{cm}^3$ using in situ CMOS compatible methods. The ability to dope has finally led to the development of GeSn LEDs with degenerate p - n junction designs representing the basic building blocks for electrically injected lasers.

The project also performed extensive growth studies aimed to create entire new families of $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ materials on industrially compatible group IV platforms (Si, Ge and Ge buffered Si) via ultra-low temperature routes using reactions of highly reactive Ge_3H_8 , Si_4H_{10} and SnD_4 hydrides. Materials with compositions $x/y \sim 4$ (Si rich) were initially produced on Ge wafers and then used as active components to fabricate near IR photodiodes that possessed tunable absorption edges up to 1.2 eV and superior electrical response relative to conventional group IV systems due to the exact lattice matching of the films with the underlying platform. Materials with compositions $y > x$ (Sn rich) were then grown mostly relaxed either directly on Si(100) or on Ge buffered Si(100) wafers. The latter samples were found to exhibit improved crystallinity compared to the former yielding significantly stronger photoluminescence signals that allowed the determination of the direct and indirect edges over a broad compositional range. The PL results indicated that the ternary can be made to mimic the optoelectronic properties of the binary including highly sought transitions to direct gap semiconductor. Most importantly, the enhanced thermal stability of the ternary makes the material an attractive and technologically viable alternative route to next-generation devices rivaling current IR systems. In this connection prototype LEDs with high emission efficiencies and tunable wavelengths were fabricated under this program for the first time corroborating the potential of the material to be a bona fide semiconductor in its own right. The main conclusion of the Si-Ge-Sn growth studies is that the alloys can also be made to exhibit direct gap conditions over a broad wavelength range (by adjusting composition/strain) for applications in photodetectors and LEDs fully compatible with Si-based technologies.

7.0 List of archival publications for AFOSR FA9550-12-1-0208 (2012-2115)

- [1] "Next generation of $\text{Ge}_{1-y}\text{Sn}_y$ ($y = 0.01$ - 0.09) alloys grown on Si(100) via Ge_3H_8 and SnD_4 : Reaction kinetics and tunable emission", G. Grzybowski, L. Jiang, R.T. Beeler, D.J. Smith, J. Menéndez and J. Kouvetakis, *Applied Physics Letters* **101(7)**, 072105/1-072105/5 (2012). <http://scitation.aip.org/content/aip/journal/apl/101/7/10.1063/1.4745770>.
- [2] Compositional dependence of the absorption edge and dark currents in $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y/\text{Ge}(100)$ photodetectors grown via ultra-low-temperature epitaxy of Ge_4H_{10} , Si_4H_{10} , and SnD_4 , R.T. Beeler, D.J. Smith, J. Menéndez and J. Kouvetakis, *Applied Physics Letters* **101(22)**, 221111(2012). <http://scitation.aip.org/content/aip/journal/apl/101/22/10.1063/1.4768217>.

- [3] “High performance Group IV photodiodes with tunable absorption edges based on ternary SiGeSn alloys” R.T. Beeler, J. Menéndez, D.J. Smith, and J. Kouvetakis, *Electrochemical Transactions* **50 (9)**, 591-599 (2012). <http://ecst.ecsdl.org/content/50/9/591>
- [4] “GeSn alloys on Si using deuterated stannane and trigermane: synthesis and properties”, G. Grzybowski, R.T. Beeler, L. Jiang, D.J. Smith, J. Kouvetakis, and J. Menéndez, *Electrochemical Transactions* **50 (9)** 865-875 (2012). <http://ecst.ecsdl.org/content/50/9/865>
- [5] “Nano-synthesis approach to the fabrication of monocrystalline silicon-like (III-V)_yIV_{5-2y} semiconductors”, A.V.G. Chizmeshya, J. Kouvetakis, G. Grzybowski, R. Beeler, and J. Menendez, *Electrochemical Transactions* **50 (9)**, 623-634 (2012). <http://ecst.ecsdl.org/content/50/9/623.full.pdf>
- [6] “Fundamental experimental and theoretical aspects of high-order Ge-hydride chemistry for versatile low temperature Ge-based materials fabrication” G. Grzybowski, A. V. G. Chizmeshya, C. Senaratne, J. Menendez and J. Kouvetakis, *Journal of Materials Chemistry C, Materials for Optical and Electronic Devices* **1(34)**, 5223-5234(2013). <http://pubs.rsc.org/en/content/articlepdf/2013/tc/c3tc30865k>
- [7] “Molecular synthesis of high-performance near-IR photodetectors with independently tunable structural and optical properties based on Si-Ge-Sn” Chi Xu, R.T. Beeler G. Grzybowski, A.V.G Chizmeshya J. Menendez and J. Kouvetakis *Journal of the American Chemical Society* **134(51)**, 20756-20767 (2012). <http://pubs.acs.org/doi/ipdf/10.1021/ja309894c>
- [8] “Bandgap-engineered Group-IV optoelectronic semiconductors, photodiodes and prototype photovoltaic devices” Richard T. Beeler, James Gallagher, Chi Xu, Liying Jiang, Charutha Senaratne, David J. Smith, José Menéndez, A.V.G. Chizmeshya and John Kouvetakis, *ECS Journal of Solid State Science and Technology* **2 (9)** Q172-Q177 (2013). <http://jss.ecsdl.org/content/2/9/Q172.full.pdf>
- [9] “Fundamental band gap and direct-indirect crossover in Ge_{1-x-y}Si_xSn_y alloys” J.D. Gallagher, Chi Xu, Liying Jiang, John Kouvetakis, and José Menéndez, *Applied Physics Letters* **103**, 202104 (2013). <http://scitation.aip.org/content/aip/journal/apl/103/20/10.1063/1.4829621>.
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- [32] "Enhanced performance designs of group-IV light emitting diodes for mid IR photonic applications" J. D. Gallagher, C. L. Senaratne, C. Xu^a, P. M. Wallace, J. Menéndez, and J. Kouvetakis *Electrochemical Society Transactions to be published Oct. 2 2015*.
- [33] "Doping of direct gap Ge_{1-y}Sn_y alloys to attain electroluminescence and enhanced photoluminescence" C. Senaratne, J. Gallagher, Chi Xu, P. Sims, J. Menendez, J. Kouvetakis, *Electrochemical Society Transactions to be published Oct. 2 2015*.
- [34] "CMOS compatible in-situ n-type doping of Ge using new generation doping agents P(MH₃)₃ and As(MH₃)₃ (M=Si, Ge)", C. Xu, J. D. Gallagher, C. Senaratne, P. Sims, J. Kouvetakis, and J. Menendez, *Electrochemical Society Transactions to be published Oct. 2 2015*.
- [35] "Temperature-dependence of tensile-strain for Ge_{0.985}Sn_{0.015}/n-Si using photorefectance spectroscopy" Hyun-Jun Jo, Geun Hyeong Kim, Jong Su Kim, Mee-Yi Ryu, Yung Kee Yeo, and J. Kouvetakis, *Current Applied Physics*, under revision.

1.

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Next generation, Si-compatible materials and devices in the Si-Ge-Sn system

Grant/Contract Number**AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".**

FA9550-12-1-0208

Principal Investigator Name**The full name of the principal investigator on the grant or contract.**

John Kouvetakis

Program Manager**The AFOSR Program Manager currently assigned to the award**

Dr. Gernot S. Pomrenke

Reporting Period Start Date

07/01/2012

Reporting Period End Date

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Abstract

The work initially focused on growth of next generation Ge_{1-y}Sn_y alloys on Ge buffered Si wafers via UHV CVD depositions of Ge₃H₈, SnD₄. The compositional dependence of the direct and indirect band gap were measured using room temperature PL and the crossover transition to direct gap material was determined to occur near 8-9 % Sn. The work also produced new designs of direct gap Ge_{1-y}Sn_y LEDs and photodetectors with wavelengths spanning from 1700-2500 nm which includes the indirect to direct gap regime. These devices were made to contain lattice-matched interfaces devoid of defects that adversely affect the device performance, yielding superior optical and electrical response relative to state-of-the-art heterostructure analogs with inherently defected junctions. The first generation prototype devices in this class of Ge_{1-y}Sn_y semiconductors were made possible by the ability to dope the materials p- and n-type at levels up to 10²⁰/cm³ using in situ CMOS compatible methods. The ability to dope has finally led to the development of GeSn LEDs with degenerate p-n junction designs representing the basic building blocks for electrically injected lasers.

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[1] "Next generation of $\text{Ge}_{1-y}\text{Sn}_y$ ($y = 0.01-0.09$) alloys grown on Si(100) via Ge_3H_8 and SnD_4 : Reaction kinetics and tunable emission", G. Grzybowski, L. Jiang, R.T. Beeler, D.J. Smith, J. Menéndez and J. Kouvetakis, Applied Physics Letters 101(7), 072105/1-072105/5 (2012).

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Changes in research objectives (if any):

None

Change in AFOSR Program Manager, if any:

None

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
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

Report Document - Text Analysis

Appendix Documents

2. Thank You

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