



Growth and Characterization of SiGeSn Using Ultra-High-Vacuum Plasma-Enhanced Chemical Vapor Deposition Technique for Silicon Based Mid-infrared Laser and Detector Applications

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14. ABSTRACT The research activities during the project period was focused on the following directions: 1- Growth of (Si)GeSn materials grown via UHV-CVD and RP-CVD; 2- Characterization of (Si)GeSn materials using PL, Raman, Ellipsometry, XRD, TEM, SIMS, to investigate Si and Sn composition, lattice constants, strain, relaxation, crystallinity, and epitaxial film quality; 3- Systematic study of GeSn/GeSn/GeSn and SiGeSn/GeSn/SiGeSn QW structures with Ge and GeSn buffer layers to achieve direct bandgap type-I band alignment GeSn QW for photonics applications; 4- Design, fabrication, and characterization of GeSn lasers and photodetectors for mid-infrared photonics and optoelectronics.					
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Growth and Characterization of SiGeSn Using Ultra High-Vacuum Plasma-Enhanced Chemical Vapor Deposition Technique for Silicon Based Mid-Infrared Laser and Detector Applications

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Final Technical Report

“Growth and Characterization of SiGeSn Using Ultra High-Vacuum Plasma-Enhanced Chemical Vapor Deposition Technique for Silicon Based Mid-Infrared Laser and Detector Applications”

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The final technical report includes the summary of all achievements from the year 2014 to 2018 with emphasize on results obtained in the final year. After receiving the award in 2014, the University of Arkansas at Pine Bluff (UAPB) collaborated closely with the University of Arkansas Fayetteville (UAF) to establish a comprehensive study on the growth and characterization of germanium-tin (GeSn) and Silicon-germanium-tin (SiGeSn) materials and devices for photonic applications. Systematic growth of Ge, GeSn and SiGeSn epitaxial films on Si substrate was performed using the ultra high-vacuum chemical vapor deposition (UHV-CVD) reactor at UAF. Silane (SiH_4), germane (GeH_4), and stannic chloride (SnCl_4) were used as Si, Ge, and Sn precursors, respectively. Preliminary material and optical characterization using Raman spectroscopy, photoluminescence (PL) measurement, Ellipsometry, and X-ray diffraction (XRD) system were conducted on the grown samples to evaluate the growth quality and provide feedback about the Sn percentage and material quality for the next round of growths. More in-depth material characterization, including Rutherford backscattering spectrometry (RBS), XRD reciprocal space mapping (RSM), secondary ion mass spectrometry (SIMS), energy dispersive X-ray spectroscopy (EDX) and high resolution transmission electron microscopy (TEM) were utilized to inspect accurate Sn mole fraction, in-plane and out-of-plane lattice constants, strain, dislocation densities and growth uniformity. Different UHV-CVD growth technique such as plasma enhanced (PE) and non-plasma enhanced (NPE) growth, hot-wire assisted growth with and without buffer layer was done in one-step and two-step growth in different pressures and temperatures. All growth recipes, samples, and characterization results were well organized (in both hard and soft copies) based on a documentation protocol established in our research team. As a parallel effort, our research team collaborated with ASM company to receive high quality GeSn and SiGeSn samples grown via reduced-pressure CVD (RPCVD) commercial system. Various GeSn and SiGeSn thin/thick films, PN and P-i-N, and quantum well structures were grown in ASM based on the design provided by UAF and UAPB. After systematic characterizations on ASM samples, device fabrication was conducted at High-Density Electronics Center (HiDEC) at UAF via standard lithography and etching process. Devices such as photoconductors, photodetectors, edge-emitting and surface-emitting LEDs, and ridge waveguides edge-emitting lasers were fabricated and tested.

Following is a brief summary of studies and achievements in the last three years of the project:

- More than 300 successful material growth using the UHV-CVD system
 - Ge growth using one-step and two-step growth with PE and NPE technique and hot-wire assisted process.
 - GeSn growth using one-step growth with both PE and NPE mechanism with maximum Sn composition p to 5.8 %.
 - SiGeSn growth using one-step growth with NPE mechanism with maximum Si composition of 4.8 % and Sn composition of 4.9 %.
 - For one-step growth, the temperature-dependent growth characteristics were studied. The film thickness, growth rate versus temperature, pressure, and gas flow rate were investigated.
 - For two-step growth, low temperature (LT) growth ($< 450\text{ }^{\circ}\text{C}$) was followed by high temperature (HT) growth ($> 500\text{ }^{\circ}\text{C}$). Compared to one-step growth, the growth rate of two-step growth increased dramatically at the same temperature.
- Extensive Ge, GeSn and SiGeSn material and optical characterization
 - Precise calculation of Si, Ge, and Sn mole fraction, lattice constants, strain, relaxation, crystallinity, epitaxial layer thicknesses, and threading dislocation density (TDD) of UHV-CVD and RP-CVD grown samples. Above $1\text{ }\mu\text{m}$ thick high-quality GeSn epitaxial films were achieved using RP-CVD and GeSn with 22.3% was demonstrated.
 - The temperature-dependent bandgap energy of (Si)GeSn materials was studied based on Si and Sn percentages and strain in the lattice.
 - Absorption coefficient and the refractive index of indirect and direct bandgap GeSn films were achieved using spectroscopic ellipsometry at room temperature.
 - Self-organized misfit dislocations (MDs) network formed during the GeSn growth on Ge buffer under biaxial compressive strain was studied. The behavior of spontaneous gradient Sn incorporation was thoroughly explained using Gibbs free energy calculation.
- Design and growth of GeSn and SiGeSn QW structures grown via RP-CVD
 - Direct bandgap Type-I band alignment GeSn/GeSn/GeSn and SiGeSn/GeSn/SiGeSn QW were studied. Optical transition energies, carrier confinements and barrier heights, directness/indirectness of QWs were calculated based on the effective mass and 6-band K.P method for valence bands and conduction bands.
 - GeSn buffer layer was proposed instead of Ge to have a less compressive strain and more Sn composition in the well resulting in more directness of the QW and carrier confinement enhancement.
- Demonstration of optically pumped GeSn edge-emitting lasers.
 - Temperature-dependent characteristics of laser-output versus pumping-laser-input and lasing operation up to 110 K was reported in 2016. The 10K lasing threshold and wavelength were measured as 68 kW/cm^2 and 2476 nm , respectively. The article published in APL based on this result was highlighted as one of the **most**

cited papers contributed to raise *APL impact factor* for the second year in a row (2017-18).

- The systematic study of optically pumped GeSn edge-emitting laser at different temperatures resulted in the first demonstration of GeSn lasers that covers an unprecedented broad wavelength range from 2 to 3 μm with a higher operating temperature (180 K) than all previous reports.
- Preliminary investigation on GeSn mid-IR LEDs
 - Electroluminescence (EL) study was conducted on GeSn p-i-n double heterostructures (DHS) surface-emitting and edge-emitting LEDs. Temperature-dependent EL spectra (from 77 to 300 K) under an injection current density of 255 A/cm² was demonstrated.

Besides the above-mentioned technical achievements, it should be noted that nine UAPB undergraduate and graduate students participated in this research project:

In Summer 2015, Eleni-James Becton joined UAF research team through Research Experiences for Undergraduates (REU) program to get trained on optical characterization setups including PL and Raman spectroscopy. Eleni-James Becton presented her research work at The Arkansas IDeA Network of Biomedical Research Excellence (Arkansas INBRE) 2015 Conference (Nov. 6~7, University of Arkansas, Fayetteville, AR), Arkansas Academy of Science 100th Meeting (April 1~2, 2016, Fayetteville, AR), and Arkansas NASA EPSCoR Conference (April 16, 2016, Hot Springs, AR).

On December 2015, two students graduated and received their Master Degrees: Bamidele Olaleye, continued his study and research as a Ph.D student at University of Arkansas at Little Rock (UALR), Little Rock, Arkansas; Luis Delgado, was hired as a CST Engineer at Schleuniger, Inc., Manchester, New Hampshire.

In Summer 2016, Bria Collier joined UAF research team through REU program to get trained on optical characterization setups including PL and Raman spectroscopy and photodetector measurements. Two UAPB undergraduate students, Joidan Romes and Octie Ashley, were trained in Optoelectronic Lab at UAPB for material characterization techniques under the supervision of Drs. Mortazavi and Du

On May 2017, Eleni-James Becton received her Bachelor Degree. Obiora Onyilagha and Emmanuel Fajemike started working on their Master degrees with partial support from this project.

In Summer 2017, Lauren Corby joined UAF research team through REU program to get trained on optical characterization setups including PL and Raman spectroscopy and photodetector measurements. Lauren Corby presented her research in Arkansas Space Grant Consortium (April 28~29 2017, Petit Jeans, AR) and NASA EPSCoR annual meeting (June 2~3, 2017, Little Rock, AR).

Drs. Fisher Yu and Wei Du gave several invited talks for the SiGeSn research community; On July 11~14, 2016, Dr. Du along with ASM collaborator Dr. John Tolle presented the research work in this project as an invited talk at IEEE Summer Topicals Meeting 2016 (Newport Beach, CA). He will give another invited talk on behalf of Dr. Yu at The Electrochemical Society (ECS) Fall Meeting (Oct 2~7, 2016, Honolulu, HI). Dr. Du also presented the research work on May 14~19, 2017, at the Conference on Lasers and Electro-Optics (CLEO) at San Jose, CA.

The final year of the project started with two University of Arkansas (UA) Fayetteville PhD graduates Drs. Mosleh and Ghetmiri from Dr. Fisher Yu's group joined into UA Pine Bluff (UAPB) and were hired as Assistant Professors of Physics and Nanoscience. They continue research and collaboration with UA Fayetteville in different projects. In addition, two UAPB graduate students: Obiora Onyilagha and Emmanuel Fajemike and two undergrad students: Lauren Corby and Bria Collier were graduated in May 2018. Both Lauren and Bria were admitted in direct PhD programs in the University of Mississippi and Vanderbilt University, respectively. At UA Fayetteville (UAF), Perry Grant, Wei Dou, and Thach Pham defended their PhD programs. Perry Grant was hired by Air Force Research Lab and Wei Dou was hired by Applied Materials.

During the final year, the research work was mainly focused on the followings:

- 1) Regular UHV-CVD machine maintenance in order to run efficiently based on the experience achieved from the previous years of the project.
- 2) Growth of device quality Ge, SiGe, and GeSn films via UHV-CVD system at UA Fayetteville; The team has been able to successfully grow Ge buffer layers using plasma to lower the thermal budget and grow GeSn films up to 5.3% on top. Additionally, the GeSn films growth using plasma enhancement has resulted in the growth of crystalline films up to 6%. Moreover, high-quality growth pathways were studied to optimize the growth of GeSn for device quality.
- 3) Growth and characterization of the high-Sn/high quality GeSn films; High quality GeSn film with 22.3% Sn composition was achieved using commercially available RP-CVD system and low-cost precursors. A systematic study on band structure, bandgap energy and photoluminescence emission wavelengths using different lasers at different temperature was performed on high quality GeSn films with high Sn composition. Near room temperature optically-pumped $\text{Ge}_{0.8}\text{Sn}_{0.2}$ laser was presented with an operating temperature of 280 K and threshold of 67 KW/cm².
- 4) Study of direct bandgap type-I band alignment GeSn QW structures; GeSn QW structures grown via RP-CVD with SiGeSn barriers and high Sn composition GeSn buffer layer were studied for low threshold and high operating temperature GeSn lasers. In fact, GeSn QW laser with 25 kW/cm² threshold at 10 K and maximum operating temperature of 90 K was achieved.
- 5) High-performance GeSn photodetector for IR imaging applications; A $\text{Ge}_{0.89}\text{Sn}_{0.11}$ photodiode was systematically investigated. A cutoff wavelength of 2.65 μm at 300 K and the peak detectivity of 4.3×10^9 Jones at 77 K was obtained. Moreover, an infrared imaging of an object was demonstrated using the single $\text{Ge}_{0.89}\text{Sn}_{0.11}$ photodiode.

In addition to the above achievements, several proposals were submitted through the collaboration between UAPB and UAF which are listed here:

- 1) Middle-Infrared Si-photonics for Integrated Microwave Photonics integrated on Si, \$735,000 AFOSR, (PI: Mortazavi, Co-PIs: Yu, Mosleh, Ghetmiri), Cont. No. FA9550-18-1-0361.
- 2) Fundamental Material Study of GeSn for Si Photonics Applications, \$600,000 DoD, (PI: Mortazavi, Co-PIs: Yu, Du) Cont. No. W911NF1910004.
- 3) Group IV-Based Material Development for Optoelectronic Device Application, \$600,000 DoD instrumentation, (PI: Mosleh), *Submitted*.
- 4) Acquisition Measurement System and Components for Development of Middle-IR Integrated Microwave Photonics, \$597,000 DoD instrumentation, (PI: Ghetmiri), *Submitted*.

The major research during the final year had been focused on the following directions:

- I) Maintenance and upgrading the UHV-CVD system at UAF
- II) UHV-CVD Ge and GeSn growth and characterization
- III) Characterization of GeSn/GeSn QW structures
- IV) Si-based GeSn lasers and photodetectors for Si photonic applications

I) Maintenance and upgrading the UHV-CVD system at UAF

In the final year of the project, the UHV-CVD system gone through different maintenance schedules and there was no major upgrading on the system. During last year, the University of Arkansas safety policies had changed which resulted in outsourcing the cylinder changes for the toxic/combustible gases in the gas farm with Airgas company. A response team is also formed to provide required service for future needs. The UHV-CVD system was down during this time while the university worked through the new policies. There was a failure in the gas sniffing system in which a sniffer module went bad causing a false leak detection alarm for Germane. A short in the heater system caused multiple growth failures and reduced the maximum temperature for growth. There was a failure of an RF dark space grid due to etching of the material. Following are the details of the maintenance and upgrades on the UHV-CVD system:

i. Gas detection system maintenance

Different parts of the gas detection system have gone through maintenance procedure last year including sensing unit, alarm panel, and detector cartridges.

a. GeH₄ sensing unit failure

The faulty GeH₄ sensing unit caused triggering false leak detection for GeH₄ in the chase. The troubleshooting verified that the gas sniffer was reading 0 PPB. The false alarm was detected again with the reading of 100 PPB on the sensor and control module. In order to address this issue, a new sensing module was ordered and installed. After the second false alarm, a full review of the lab safety procedures was conducted by the research group and the university. The review found no errors in the procedures and the system was returned to service.

b. Gas alarm panel programming fault

The alarm panel is a component of the alarm system that provides alarm notifications to the main building alarms system. They are tied to the emergency shutoff valves in our gas farm and the main building alarm. During troubleshooting of the Gas detection and alarm system, mentioned above, the alarm panel channels were renamed to match the current gas detection configuration. The vendor did not reprogram the sensitivity levels for the individual channels. This led to a false indication of the leak of the SiH₄ module on the alarm panel. The channels were reprogrammed to the correct settings for each of the individual gas sensing modules provided by the manufacturer.

c. Replacement of GeH₄ gas cartridges

Three new GeH_4 Gas sniffer cartridges were ordered to replace the expired units in three of the nine Honeywell Midas gas sensor modules. These cartridges were used to check for gas leaks in the system. The sensor modules are required safety mechanisms for the system. They not only detect dangerous and toxic gasses in the PPB (parts per billion) range and alert us to possible leaks but also are tied to the emergency shutoff valves in our gas farm and the main building alarm.

ii. Deposition chamber maintenance

In the last year, the heater module has gone through several maintenances as it is described below. The team has decided to plan for the purchase of 2 brand new heater modules in order to be able to replace it as soon as a failure happens in the heater so that the growth schedule would not be delayed so often.

a. *Heater module short problem*

A heater short was noticed during growth causing the failure of the fuse in the heater power supply (Fig.1). The chamber was opened and an excess buildup of germanium was detected on insulators designed to isolate the heater circuit from the grounded components of the process chamber. These insulators were cleaned and reinstalled and the system was returned to service. Shorting issues started recurring shortly afterward and the chamber was reopened for inspection. During the inspection, one ceramic insulator was noticed to have cracked and failed leading to the short heater circuit to ground through the chamber casing. A complete spare parts kit for the heater module was ordered and all new parts will be installed. Protocols were instituted that include replacing insulators with new parts during every major maintenance period and weekly checks on the resistance to machine ground from the power conductor terminals. The chamber was returned to service following the installation of the new parts kit and through testing of the heater circuit.



Fig. 1. Germanium buildup on the ceramic insulators of the heater power supply and the replacements.

b. *The RF dark space grid failure due to etching for the process chamber failed*

The RF grid failed as the center portion of the grid was etched away due to the creation of HCl during the reaction of GeH_4 and SnCl_4 during the growth process. The rate of this etching was increased due to the addition of a high temperature outgassing of the heater which reduces the amount of germanium buildup on the grid and heater resulting in clean surface area to be exposed to hot HCl gas during the growth process. The new grid was installed during the installation of a new heater module parts kit and the system was returned to service.

c. *Replacement of hotwire filament*

The hotwire filament was replaced (Fig.2) during major maintenance due to breakage caused by

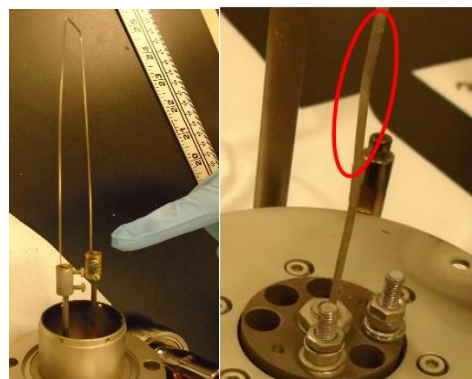


Fig.2 (left) Hot-wire filament replacement. (right) Ge and Sn deposition on the thermocouple.

excessive etching of the tungsten filament by HCl gas. The gas is produced as a byproduct of the chemical reaction between the GeH_4 and the SnCl_4 precursor gasses in the process chamber.

d. Thermocouple replacement due to failure

The thermocouple for the process chamber was damaged during maintenance and failed. The insulative exterior of the unit became brittle and flaked away due to excessive deposition of Ge and Sn on the outer surface. A new unit was ordered from the manufacturer and will be installed during the next maintenance cycle.

iii. Other UHV-CVD machine maintenance

a. Uninterrupted power supply (UPS) replacement

Three UPSs reached the end of service life and were replaced with new ones. The new UPSs were ordered to replace the units that had reached the end of their service life. These units are tied to the gas sensor module and process chamber turbo in the lab as well as the Fire panel. Their purpose is to provide backup power for the sensors and turbo pump in case of power failure in the building until a response team member can arrive and safely put the CVD system in standby while leaving the gas sensing system powered for protection of personnel and the building. This is the part of the safety protocol in case of power failure in the facility. After replacement, the systems were returned to operation.

b. Power supply transformer short problem

A new transformer unit was purchased from the original equipment manufacturer (OEM) to replace the failed transformer. This unit failed during high-temperature outgassing of the heater following maintenance on the growth process chamber of the CVD system. Checks were performed that included Ohm readings and continuity checks to the process chamber heater contacts. The system was returned to service.

c. Chiller water pump and motor failure

There was a failure of the chiller water pump and the associated drive motor that provides cooling water for the systems QDP40 corrosive resistant dry mechanical pump. The QDP 40 is responsible for roughly pumping the process chamber of the CVD machine and serves as a backing pump for the process chambers turbo pump. The water pump failed due to excessive wear of the internal vanes in the pump. The pump was replaced with a new unit. The system was returned to service after maintenance.

II) UHV-CVD Ge and GeSn growth and characterization

Overall, the growth plan in the last year of the project was on schedule and total 160 growths were done based on the growth recipes:

Daily feedback (PL, Raman, and ellipsometry measurements) for characterizing the grown wafers were provided and documented. Material characterization, such as XRD and TEM were conducted on some samples grown by UHV-CVD.

Plasma-enhanced Ge and GeSn growth on Si substrate in the UHV-CVD system

a) High quality Ge buffer layer grown by plasma enhancement in the UHV-CVD System

High quality Ge buffer layers were grown using plasma enhancement technique by a two-step method in a cold-wall ultra-high vacuum chemical vapor deposition system under low thermal budget. Low threading dislocation density on the order of 10^7 cm^{-2} with root mean square roughness values on the order of several nm were achieved. Photoluminescence and ellipsometry characterization revealed that the optical characteristics are comparable to the Ge buffer layer grown using conventional method, i.e., non-plasma enhancement at high temperatures. Moreover, growth comparison of an active group IV GeSn on (plasma enhancement) PE and non-plasma enhancement (NPE) Ge buffer layers was carried out to further examine the material and optical property for optoelectronic device applications, which indicated that the low temperature PE method exhibits the comparable quality with the high temperature NPE method. This work provides a promising growth process for industry to deposit Ge under conditions compatible with complementary metal–oxide–semiconductor technology.

In this study, a capacitively coupled plasma (CCP) setup in the UHV-CVD growth chamber with a base pressure of 3×10^{-9} Torr was utilized. The CCP was fed by a 13.56 MHz radio frequency (RF) power supply that is matched by an L-shaped automatic impedance matching network. Figure 3 shows the PE configuration. The substrate holder within the upper electrode setting was powered by the RF source while the lower electrode assembly was grounded. The electrode spacing was fixed at 20 mm. Four-inch Si (001) substrates were used after they were cleaned by the standard RCA wet-cleaning method with hydrofluoric acid dip. Prior to starting the growth process, the wafer was baked for 20 min at the desired growth temperature to remove the passivation layer and ensure film uniformity. Germane (GeH_4) as Ge precursor and argon (Ar) as a carrier gas and ion source were used. The flow rate and the chamber pressure were fixed at the optimal values of GeH_4/Ar (1:40) and 1 Torr, respectively. The growth of the (low temperature) LT seed layer was done at 375°C to promote the layer-by-layer growth mechanism. The flow of gases was then shut off, and the temperature was ramped up at a rate of $\sim 12^\circ\text{C}/\text{min}$ to the second step growth temperature.

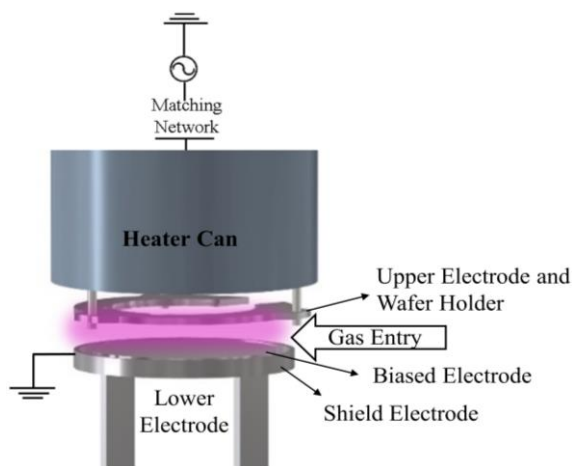


Fig. 3 Schematic of the PE configuration in the UHV-CVD chamber.

Growth optimization: A single step Ge layer was first grown in the range of temperatures from 400 to 525°C and the RF power range from 0 to 30 W to optimize the growth conditions. Figure 4 shows the variation of thickness with RF power at a fixed wafer temperature of 400°C . As compared to the NPE at $P = 0 \text{ W}$, the thickness increases monotonically until 5 W and starts to decline beyond 5 W . It must be noted that the substrate holder was powered; hence it is subjected to ion bombardment during deposition. The high growth rate at $P < 5 \text{ W}$ results from high

dissociation rate while at 5 W the decomposition rate is compensated by the etching rate. Above 5 W, the etching rate effect dominates, which causes a reduction in the film thickness. This could be due to excessive energetic ions that bombarded the film surface and displaced Ge adatoms.

To further improve the material quality a two-step approach was used for the Ge buffer layer. A set of five Ge samples were grown using this method with the second step grown by PE. For each sample, the seed layer growth was done using NPE at 375°C and 1 Torr. The thickness of the initially Ge seed layer was measured to be 230 ± 15 nm. The second step was grown at an RF power of 5 W, and at different temperatures in the range from 450 to 550° C. The results of the deposited thickness as a function of growth temperature are shown in Fig. 5(a).

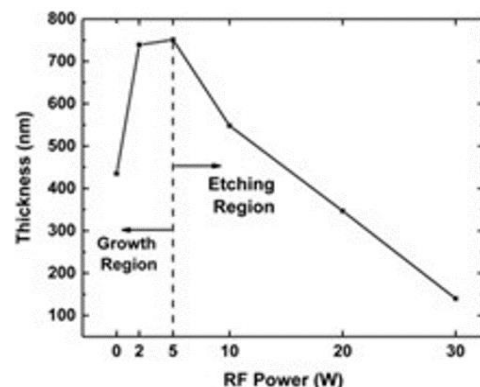


Fig. 4 Variation of thickness with the applied RF power for one-step Ge growth at 400 °C.

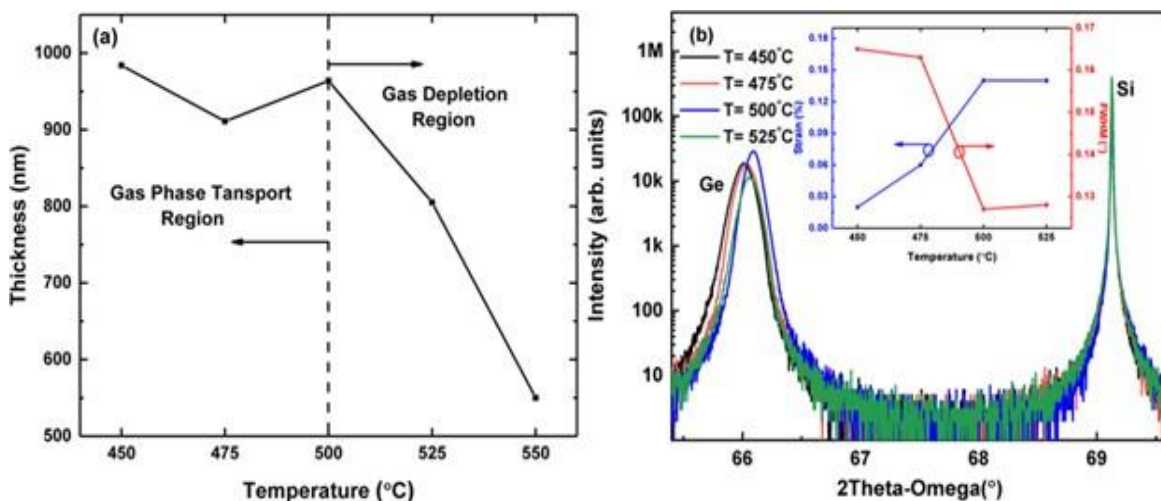


Fig. 5 Variation of thickness with the applied RF power for one-step Ge growth at 400°C. (b) The variation of the growth thickness with the temperature at an RF power of 5 W. (b) XRD of Ge grown at temperatures from 450 to 525°C around the Bragg angle of (004). The inset shows the calculated strain and FWHM of each Ge curve

It is observed that the Ge buffer thickness decreases with increasing the substrate temperature. The drop in the total thickness comes mainly from the second growth step. This could be a result of a low number of reactants in growth temperatures beyond 500°C. At this growth temperature range, the growth region moves from the gas-phase transport regime to the mass flow limited regime in which some reactants decompose faster and deposit on the heater components before reaching the growth zone. Further characterization was focused on the temperature range from 450 to 525°C. The XRD rocking curves from the (004) direction of this temperature range are plotted in Fig. 5(b). The plot shows two major peaks. The main sharp peak near 69° is attributed to the Si substrate while the peaks that appear near 66° are assigned to Ge films. Strain was calculated for each sample using Ge peak position from 2θ - ω scans; the computing hypothesis is described elsewhere. The inset of Fig. 5(b) shows a plot of the strain and the full-width at half-

maximum (FWHM) of each Ge peaks. In general, all samples possess tensile strain. However, as the temperature increases to 500 and 525°C, the amount of strain becomes one order of magnitude higher than 450 and 475°C. In addition, FWHM decreases with increasing the temperature. It shows a maximum at 450°C and a minimum at 500°C. The Ge peaks broadening are ranging from 0.127° to 0.165° at 500°C and 450°C; respectively, which indicates improved crystallographic quality with temperature.

Material characterization comparison between NPE and PE Ge buffers: In order to further explore the effect of PE on the material and optical quality, a comparison between PE and NPE is presented. Table I lists the growth conditions of one Ge buffer grown by NPE (buffer A) and two Ge buffer layers grown by PE method (buffers B and C). The growth temperature of the first step was fixed at 375°C for all buffers. The second step growth temperature was 600°C for buffer A, and it was dropped to 525°C for buffer B to compare how far the temperature reduction can affect the material and optical properties. For buffer C, the growth procedure was slightly different. The second step PE growth temperature was lowered further to 500°C while PE was used to grow the first step.

Table I Ge buffer IDs and growth conditions, RMS, and EPD of A, B, and C.

Buffer	Growth				Thickness (nm)	RMS (nm)	TDD (cm ⁻²)
	1 st Step		2 nd Step				
	P (W)	T (°C)	P (W)	T (°C)			
A	0	375	0	600	972	1.04	1.84×10 ⁷
B	0	375	30	525	627	2.80	2.7×10 ⁷
C	30	375	30	500	614	2.07	7.4×10 ⁷

The visual inspection of the surface after each growth was specular, however, further surface characterization was required. The surface roughness caused by the relaxation mechanism for the selected buffers was measured using an atomic force microscope (AFM). Figure 6 shows the results of a 10×10 μm² scans with the root mean square (RMS) values of the surface peak-to-valley height. The RMS value for sample A indicates atomically flat surfaces morphology with RMS value of 1.04 nm. However, as the PE was introduced in sample B, the RMS value increases to 2.80 nm, which is a sign of an increased

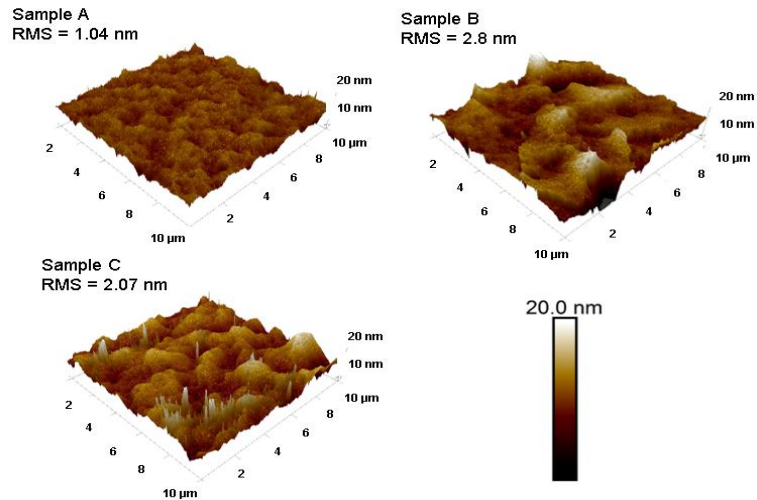


Fig. 6 Topographical three-dimensional AFM surface images and RMS values for buffer A, B, and C

adatoms surface mobility. By decreasing the growth temperature and using PE in the first step, the RMS surface roughness was reduced in sample C to 2.07 nm. Such an atomically flat surfaces is an ideal platform for subsequent epitaxy.

Figure 7(a) presents room temperature PL that was measured for each sample using a 1064 nm laser with 340 mW laser power. All samples exhibit similar peak shape with varied intensities. However, the PL spectra of buffers A and B are almost identical. These results are consistent with strain and threading dislocation density (TDD) calculations that were previously discussed. It is also clear that PL results were affected by strain. The low TDDs of samples A and B can contribute in higher PL intensity. On the other hand, higher TDD in buffer C deteriorates radiative recombination and reduces the PL intensity. It is also clear that PL results were affected by strain. The higher the tensile strain the smaller the energy difference between the direct and indirect valleys and thus the number of electrons occupying the direct valley becomes higher. This is noticed also as the peak positions (P.P.) are shifted to longer wavelengths as the strain values increase, which make the bandgap narrower.

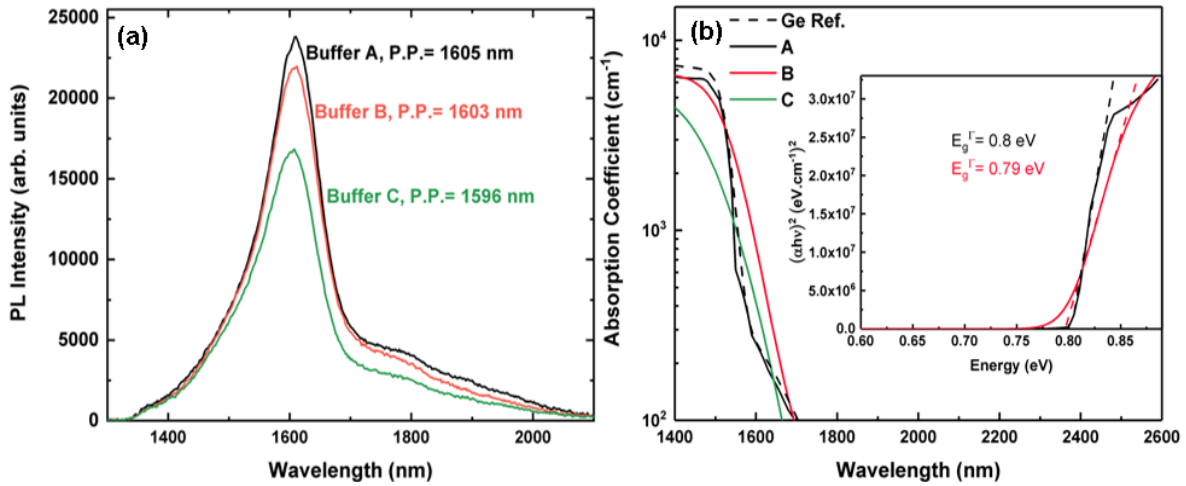


Fig. 7 (a) PL spectra of buffers A, B, and C. (b) Absorption coefficients of buffers A, B, and C. The dashed line is a Ge reference for comparison. Inset: absorption fitting and direct bandgap determination.

The absorption measurement of each buffer was taken using Ellipsometry in the wavelength range from 1400 to 2500 nm. The results are presented in Fig. 7(b). The dashed line represents bulk Ge reference for comparison. The absorption values of buffers A and B are slightly lower than the bulk Ge reference sample while buffer C exhibit the lowest absorption coefficient. All buffers possess an absorption edge close to the bulk Ge reference with a cutoff wavelength of nearly 1580 nm. Near the direct bandgap edge, the absorption coefficient can be fitted by using $(\alpha h\nu)^2 = A(h\nu - E_g^\Gamma)$ where α is the absorption coefficient of direct bandgap transition, $h\nu$ is the photon energy, A is the constant and E_g^Γ is the direct bandgap energy. The data fitting and the E_g^Γ extraction results are presented in the inset of Fig. 7(b), where E_g^Γ is evaluated from the intercept at $\alpha = 0$. Buffer A provides a E_g^Γ value similar to bulk Ge reference (0.8 eV) while the E_g^Γ value of buffer B is 0.79 eV. The lower E_g^Γ value is due to the tensile strain, which is consistent with the previous discussions. The E_g^Γ value of buffer C was not evaluated because the absence of the linearity near its direct bandgap edge.

NPE GeSn grown on NPE and PE Ge buffers in the UHV-CVD system

Two GeSn layers (samples D and E) were grown using the non-plasma method on Ge buffer layer (buffers A and B) for side-by-side comparison. This step was conducted to demonstrate the capability of the PE growth procedure for future photonic applications.

To validate the crystal quality, strain, and composition of each GeSn sample, XRD reciprocal space mapping (RSM) was employed. A summary of the extracted information is shown in table II. Both buffer layers of samples D and E have the same in-plane ($a_{||}$) and out-of-plane ($a_{\perp}$) lattice constants, i.e., the same values at 5.67 nm and 5.65 nm, respectively. For the active GeSn layers, sample E shows less pseudomorphicity compared to sample D. The strain was calculated as -0.51% and -0.33% for samples D and E, respectively. In addition, the FWHM of the diffraction patterns along the lateral correlation of the $a_{||}$ Ge buffer and the GeSn layer were extracted to highlight the material quality as well. The FWHM of Ge buffers and the GeSn films in both samples are close to each other indicating similar TDDs. Moreover, the calculations of Sn incorporation in both samples reveal similar Sn composition (see Table II). This is consistent with the PL measurements. Both samples were characterized using the 532 nm laser for PL study. From PL plot (not shown), not only PL intensities and FWHMs but also peaks positions of sample D (1930 nm) and sample E (1946 nm) are similar, which indicate similar Sn incorporation.

Table II RSM data of two GeSn films on NPE and PE buffers.

Sample	Ge Buffer		GeSn		FWHM of $a_{ }$ (Å)		Strain (%)	Sn (%)
	$a_{ }$ (Å)	$a_{\perp}$ (Å)	$a_{ }$ (Å)	$a_{\perp}$ (Å)	Ge	GeSn		
D	5.67	5.65	5.67	5.72	0.0043	0.01	-0.51	5.6
E	5.67	5.65	5.68	5.71	0.0046	0.03	-0.33	5.3

Figure 8 presents cross sectional TEM images of samples D and E viewed from the $[\bar{1}10]$ direction. A dark field TEM image of each sample is shown side by side in Fig. 8 (a) and (b) for comparison using 200 keV and 300 keV beam sources, respectively. The thicknesses of the Ge buffer and the GeSn layer of sample D (E) was measured to be 729 (740) and 319 (335) nm, respectively. The variation in the Ge buffer layer thickness was due to machine growth drift after regular maintenance. Both buffers are accommodated with TDDs that appear as dislocation cores propagating to GeSn films. High resolution TEM images were taken for the Ge/Si and GeSn/Ge interfaces of sample E that are presented in Fig. 8 (c) and (d), respectively.

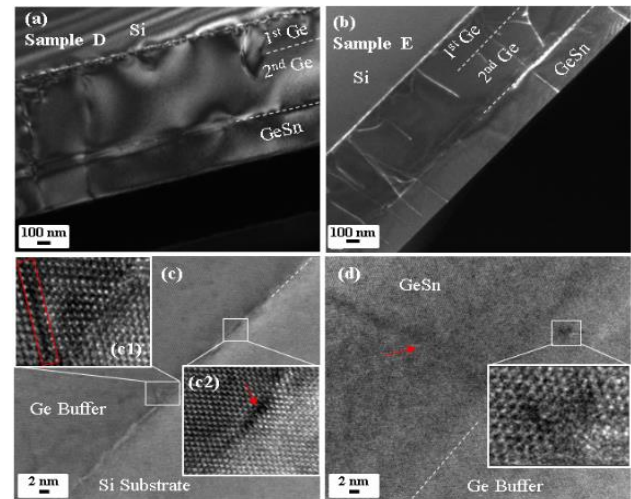


Fig. 8 Cross sectional TEM. Dark field TEM images of (a) sample D and (b) sample E. (c) High resolution TEM images of the first step Ge/Si interface of sample E. Insets: Dark field STEM images of two selected defects near the interface in (c1) highlighted by red frame and (c2) pointed by an arrow. (d) HRTEM of the second step GeSn/Ge interface of sample E. A TDD propagating the GeSn is pointed with an arrow. Insets: Dark field STEM image of an interfacial defect.

b) Buffer-free PE GeSn grown on Si substrate in the UHV-CVD System

Using plasma enhancement technique, low temperature growth at 350°C for GeSn epitaxy on Si substrate was achieved with the growth rate of 51.4 nm/min and Sn content up to 6%. The relaxed GeSn films with 1 μm thickness were able to be grown despite of the huge lattice mismatch between GeSn and Si. The PE-CVD technique has been demonstrated to enhance the Sn incorporation and the growth rate of GeSn epitaxy. The generation of energetic gas species with high reactivity in plasma discharge pushes the GeSn growth condition far beyond the normal equilibrium of conventional CVD. The surface reaction dynamics were strongly modified by plasma, which makes the growth rate less sensitive to the growth temperature compared to the traditional CVD. With plasma assistance, the precursors of GeH_4 and SnCl_4 are expected to be easily decomposed at low growth temperatures, which therefore ensures the high growth rate and high Sn incorporation of GeSn epitaxy on Si.

A general view of the growth mechanism of PE-CVD is illustrated in Fig. 9. The gases are dissociated into free radicals and ions in the plasma, and thus increase the growth rate at low temperature. The relative high growth rate could result in high Sn incorporation as more Sn atoms are buried inside the Ge lattice matrix before their segregation on the surface. Meanwhile, a high-voltage capacitive sheath is formed between the wafer and the bulk plasma. At the steady-state plasma discharge, the time-averaged electric potential V_p in bulk plasma is presented as a positive value and the potential drops sharply across the sheath. The ions of precursors in the bulk plasma could enter the sheath and be accelerated by the built-in electrical field in the sheath.

As a result, the ions gain sufficient energy when arriving at the GeSn surface and the collision probability among reactive ions increases at the surface. Therefore, the surface mobility of

adatoms enhances at low growth temperature and consequently increases the material crystallization. In order to explain the non-uniform plasma discharge across the wafer and its effects on the Sn incorporation, we divided plasma glowing region into area A and B (Please see Fig. 10). The area A (bright white glowing region) mainly corresponds to the discharge of Ar and GeH_4 while the area B (navy blue glowing region) corresponds to the discharge of GeH_4 and SnCl_4 . The non-uniform plasma discharge could be explained as follows: The gaseous SnCl_4 experiences a much higher decomposition rate than GeH_4 . As a result, the majority of SnCl_4 is immediately dissociated and depleted at the edge of bulk plasma at area B. High Sn-content GeSn film was deposited at the edge of Si wafer. In contrast, since most of the SnCl_4 was consumed at area B, the plasma discharge of SnCl_4 at area A is negligible. Therefore, comparing with area B, much less Sn was incorporated into Ge at area A.

In this study, three groups of GeSn/Si were grown as follows and the growth receipt is summarized in Table III:

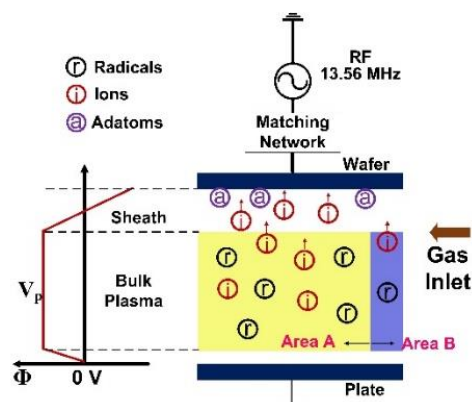


Fig. 9 Left: The buildup of electric potential in both bulk plasma and sheath. Right: The ion transportation process from bulk plasma to Si wafer.

- i) Samples A and B in group I are GeSn alloys that were grown with plasma enhancement at 350 and 400°C, respectively. To control the growth rate at low temperature, the Ar flow rate for sample A was 100 sccm in contrast with 200 sccm for sample B.
- ii) Samples C and D in group II are Ge that were grown with plasma enhancement aiming to be compared with samples A and B. During the Ge epitaxy, the wafers were rotating at 20 revolutions per minute (rpm).
- iii) Sample E in group III is GeSn that was grown via conventional CVD thermal method without plasma enhancement. During the GeSn epitaxy of sample E, the wafer was rotated at 20 rpm. The

growth temperature and pressure of sample E were 350°C and 0.5 Torr, respectively. The flow fraction of GeH₄ for sample E is 0.286, which is 5.7 times higher than 0.05 of sample A by PE-CVD. The high flow fraction of GeH₄ ensures the GeSn deposition at growth temperature of 350°C. The flow rate of SnCl₄ was 0.02 sccm in order to minimize the HCl etching effect that results from the byproduct reaction of gaseous during GeSn epitaxy. The growth time was fixed at 120 minutes to obtain the comparable thickness with other samples.

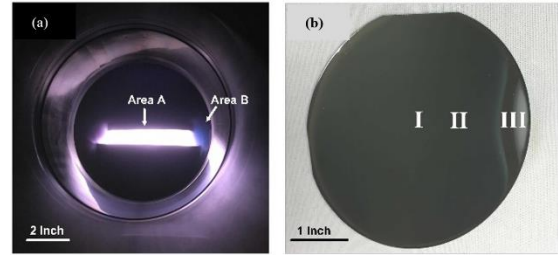


Fig. 10 (a) The generation of plasma between the cathode plate and Si wafer in the CVD reactor. (b) The grown GeSn on Si wafer after PE-CVD process. The probing spots I, II, and III were marked on the wafer.

Table III Summary of growth recipes of five GeSn samples by both PE-CVD and conventional CVD

Technique		Temperature (°C)	Pressure (Torr)	Flow rate (sccm) (SnCl ₄ : GeH ₄ : Ar)	Growth time (min)
Group I: GeSn PE-CVD	A	350	0.3	1:5:100	20
	B	400	0.3	1:5:200	20
Group II: Ge PE-CVD	C	350	0.3	0:5:200	20
	D	400	0.3	0:5:200	20
Group III: GeSn CVD	E	350	0.5	0.02:10:25	120

Optical characterization: The Raman spectra of samples A and B at spots I, II, and III were performed to investigate the crystallinity of GeSn, as shown in Fig. 11 (a) and (b), respectively. The intensity of Raman spectra for sample A is low due to the high surface roughness and low material quality caused by low growth temperature (350°C). In order to obtain similar Raman intensity of sample A as sample B, the slit width of the light entrance of spectrometer for sample A was twice as big as sample B. The Ge-Ge longitudinal optical (LO) peaks of GeSn films were clearly observed, suggesting crystalline growth using PE-CVD technique was achieved. The Ge-Ge LO phonon of reference bulk Ge is located at 300 cm⁻¹. Note that the full width at half maximum of Raman spectra for sample A is larger than that of sample B due to the wider slit width of the spectrometer entrance. The Ge-Ge LO peak of GeSn film shifts to the lower

wavenumbers compared to bulk Ge due to the change of binding energy induced by Sn incorporation. From spot I to III of sample A (B), the Raman peak shifts from 297.8 (297.6) to 295.8 (296.7) cm^{-1} , which is due to the supply change of Sn atoms across the wafer. At spots III of samples A and B, the minimum values of Raman peak shift correspond to the maximum Sn incorporation. A comparison of Raman shift for five samples (Spot III for samples A and B) is shown in Fig. 11(c). For samples C and D, the Ge-Ge LO peaks are at 302.9 and 301.5 cm^{-1} , respectively. The longer wavenumber values of samples C and D, relative to bulk Ge reference, were attributed to the residual compressive strain at the low growth temperature. The Raman peak of sample E is located at 299.2 cm^{-1} , corresponding to the Sn content of 0.75%. Compared with bulk Ge reference, samples A and B show peak shifts of -4.5 and -3.3 cm^{-1} , respectively. According to the relationship between Raman shift ($\Delta\omega$) and Sn content (x_{Sn}): $\Delta\omega = a \cdot x_{\text{Sn}}$ for the relaxed GeSn layer, Sn contents of samples A and B at spots III were estimated as 5.1 and 3.8%, respectively, where the coefficient of a was adopted as -88 cm^{-1} for the fully relaxed GeSn layer.

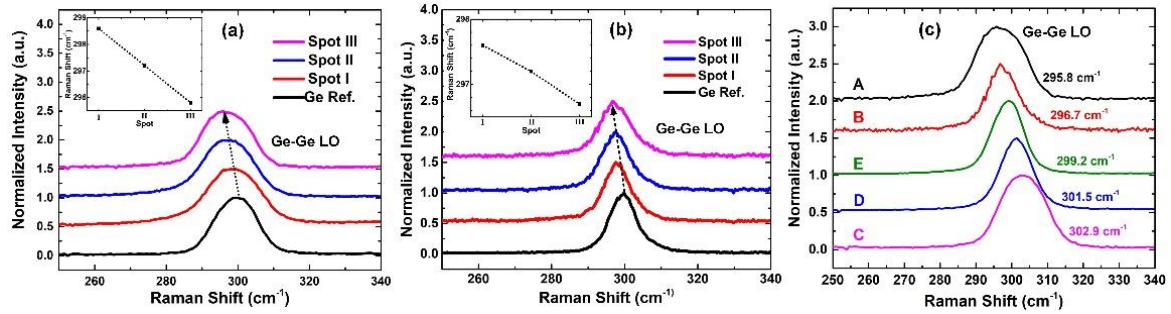


Fig. 11. Raman spectroscopies of (a) sample A and (b) sample B at the spots of I, II, and III. A comparison of the Raman spectra for all samples is shown in (c).

The room-temperature PL spectra at various spots of samples A and B were conducted, as shown in Fig. 12(a) and (b), respectively. A 1064 nm pulsed laser was used as a pumping source with a 500 mW average pumping power, 45 kHz frequency and 6 ns pulse width. A liquid nitrogen-cooled InGaAs detector was utilized with the cut-off wavelength of 2300 nm. The different shifts of PL spectra at the probing spots I, II, and III are due to the non-uniformity of GeSn epitaxy under the current PE-CVD configuration. The PL emissions of both samples come from the direct bandgap transition of GeSn. The indirect bandgap transition was not observed, which is suppressed by the fast nonradiative recombination induced by defects. For sample A, the PL peak at spot III was clearly shown to be at ~ 2000 nm, while the PL spectra at the spots I and II were too weak to be identified. For sample B, the PL spectra from spot I to III were observed with different red shifts of PL spectra. Starting from the spot I, the peak is at 1486 nm, corresponding to the direct bandgap emission of GeSn with negligible Sn incorporation, i.e., Ge direct bandgap. At spot II, the main PL peak shifts to 1556 nm and peak intensity increases in comparison with spot I, suggesting that Sn atoms start to be efficiently incorporated into Ge. The spot III has the PL emission with the broadening peak wavelength between 1800 and 1950 nm. For both samples A and B, the maximum PL peak intensity was obtained at the spot III. Meanwhile, the longest wavelengths of PL peaks at spot III of both samples suggest the highest Sn incorporation. We do notice that at spot III the broaden PL peaks for both samples A and B were observed, which is mainly due to the spatial variance of Sn incorporation confirmed by XRD analysis. The defects might contribute to the broadening of PL spectra as well, which,

however, could not be distinguished in PL spectra. The PL spectra for all samples were normalized and plotted side-by-side in Fig. 12(c). The PL spectrum of bulk Ge is also included as the reference. Compared with direct (0.8 eV) and indirect (0.66 eV) bandgap energies of bulk Ge, the PL spectra at spots III of samples A and B have a clear red-shift, suggesting that Sn atoms are efficiently incorporated into Ge lattice sites. Comparing with PL spectra of sample B, the PL peak of sample A exhibits the longer wavelength, indicating the higher Sn incorporation at lower temperature growth. No PL emission was observed for sample C. The non-radiative recombination introduced by defects dominates over both direct- and indirect-bandgap radiative recombination. Sample D shows the light emission of direct bandgap at the peak wavelength of 1500 nm, which has the blue shift compared with bulk Ge due to the residual compressive strain. The enhanced optical properties of sample D compared with sample C is due to the higher temperature growth. For sample E of GeSn by non-PE-CVD, the light emission from direct bandgap transition was observed at peak wavelength of 1650 nm, corresponding to the Sn content of 0.75%. According to the PL spectra of sample A, B, and E, the plasma enhancement dramatically increases the Sn incorporation at low temperature, which is evidenced by the clear red-shift of light emission.

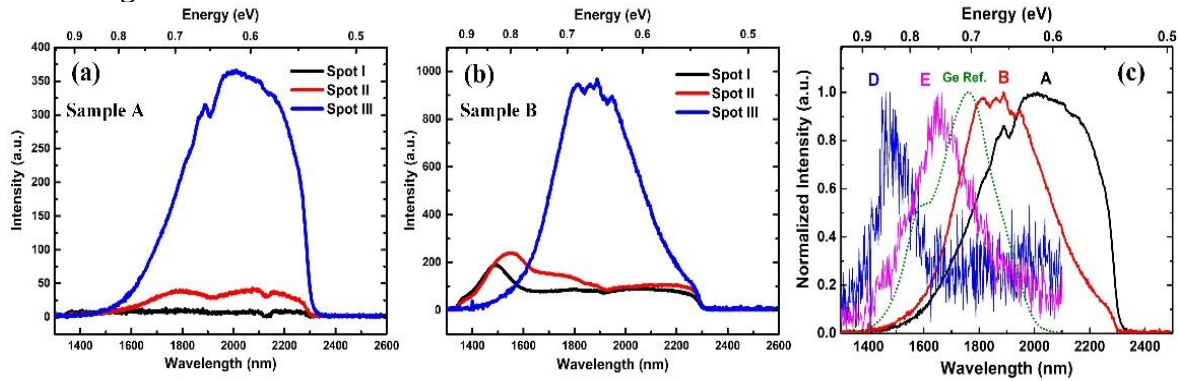


Fig. 12. Room-temperature PLs of (a) sample A and (b) sample B at different probing spots on the Si wafer. (c) The comparison of PL spectra for five samples.

The samples thicknesses were obtained by Ellipsometry measurements, as shown in Table IV. For GeSn on Si by PE-CVD, the growth rates at the spot III and I were measured as 57.7 and 35.2 nm/min for sample A, and 51.4 and 25.4 nm/min for sample B, respectively. For Ge on Si by PE-CVD, the growth rates are 21.1 and 21.9 nm/min for samples C and D, respectively. In comparison with Ge by PE-CVD, the growth rate of GeSn is significantly higher, suggesting that the introduction of Sn facilitates the film deposition on Si under the current PE-CVD configuration. For sample E using non-PE-CVD growth, the growth rate of GeSn is 5 nm/min, which is less than one-tenth of the growth rate of spot III of sample A by PE-CVD, indicating that the growth rate of GeSn increases dramatically with plasma enhancement.

Table IV Summary of film thicknesses and growth rates of five Ge(Sn) samples grown by PE-CVD and conventional CVD

Samples	Group I: Spot I/ III GeSn by PE-CVD	Group II: Ge by PE-CVD	Group III: GeSn by non-PE-CVD
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	A	B	C	D	E
Thickness (nm)	704 /1154	507 /1027	422	438	594
Growth rate (nm/min)	35.2/57.7	25.4/51.4	21.1	21.9	5.0

The absorption coefficients of the five samples were extracted by Ellipsometry as shown in Fig. 13. For samples A and B, the measurements were performed at spots III which shows the maximum Sn content. For all the samples both direct and indirect bandgap absorptions were observed. When photon energy $h\nu$ exceeds the direct bandgap energy E_g^Γ , the direct bandgap transition is dominant over the indirect bandgap transition. The absorption coefficients of samples C and D were mostly overlapped with that of bulk Ge. Compared to the bulk Ge, both direct and indirect absorption edges of samples A, B, and E show pronounced red shift, suggesting the reduced bandgap energies due to the incorporation of Sn. The absorption edges of samples A and B shift towards a lower energy numbers than the absorption edges of sample E while sample A exhibits the lowest energy values, which is consistent with the PL results.

Near the direct band edge, the interband absorption could be expressed as,

$$(\alpha h\nu)^2 = A(h\nu - E_g^\Gamma)$$

where α is the absorption coefficient of direct bandgap transition, $h\nu$ is the photon energy, A is the constant and E_g^Γ is the direct bandgap energy. By fitting the absorption coefficient of band edge, the direct bandgap energies E_g^Γ of samples A, B, and E were extracted. Fig. 13 (b) shows the data fitting process of E_g^Γ , where the direct bandgap energies E_g^Γ of samples A, B, and E were extracted as 0.690, 0.735 and 0.772 eV, respectively.

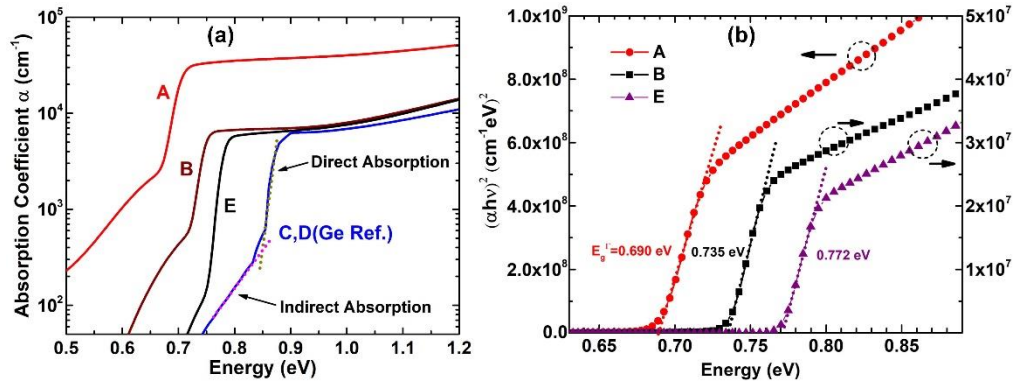


Fig. 13. (a) The absorption coefficients of five samples. (b) The data fitting of absorption edges for direct bandgap energy E_g^Γ for samples A, B, and E.

Growth of high quality GeSn on Ge buffers in the Non-PE UHV-CVD system

It has been acknowledged that the combination of Ge hydrides and SnCl₄ in the incorrect proportions can result in the severe etching effect, thus limiting the success of GeSn growth. The

etching effect originates from the generation of chlorinated species during the reaction between Ge hydrides and SnCl_4 . The overall growth of GeSn is the competition between deposition and etching, both of which heavily depends on the supply of SnCl_4 and growth temperature. In order to explore the optimal epitaxy window of GeSn, we designed the experiments by following three logic sequences. First of all, we grew the well-known Low/high temperature two-step Ge buffer layer to accommodate the lattice mismatch between GeSn and Si. Second, we demonstrated the success of GeSn growth directly on Si substrate based on the initial exploration of low temperature Ge growth, which has been reported in our previous work. The epitaxy of GeSn film on Si could be easily identified by visual inspection and subsequent material characterization. It also eases the efforts to determine the epitaxy window where the deposition dominates over the etching by visual contrast between GeSn and Si; Third, we grew the high quality GeSn on two-step Ge buffer layer. Based on the knowledge of GeSn growth on Si at the second step, we mainly focus on the optimization of two dominating factors for the effective Sn incorporation: ***SnCl₄ supply*** and ***growth temperature***.

All material growth work was done using p-type Si (001) 4-inch wafers as substrates. The wafers were processed using standard piranha etch and HF dip prior to growth as described in our previous work. Material growth was carried out in the cold wall UHV-CVD chamber with base pressures below 1×10^{-9} torr. The Growth was conducted using GeH_4 , SnCl_4 as precursors and Ar as the carrier gas. The Ge buffer layer with approximately 1 μm thickness was grown by low/high temperature two-step growth.

The 1st 100-nm Ge layer was grown as a seeding layer at 325°C temperature while the 2nd 900-nm Ge layer was grown at 600°C. After the growth of Ge buffer, the substrate temperature was cooled down to initiate the GeSn epitaxy. During the GeSn growth the process pressure was fixed at 2 torr. A wide range of growth temperature and SnCl_4 flow fraction were explored, as shown in Fig.14. The flow fractions of SnCl_4 was defined as $F_{\text{SnCl}_4} / (F_{\text{SnCl}_4} + F_{\text{GeH}_4} + F_{\text{Ar}})$, where the F_{SnCl_4} , F_{GeH_4} and F_{Ar} indicate the flow rate of SnCl_4 , GeH_4 and Ar, respectively. Three groups of GeSn was grown on Ge buffers. Please see Fig. 14.

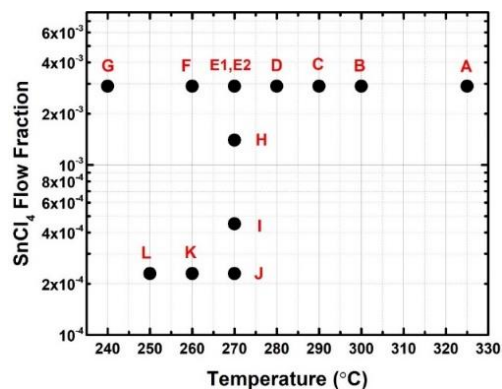


Fig. 14. The growth methodology and sample description of GeSn samples in this study.

Group 1: From sample A to G the growth temperature decreases from 325 to 240°C while the SnCl_4 flow fraction was fixed at 2.9×10^{-3} . The growth time of samples A, B, C, D, E1, F, G is 30 mins while sample E2 is 60 mins.

Group 2: From sample E2 to J, the SnCl_4 flow fraction decreases from 2.9×10^{-3} to 2.3×10^{-4} while the growth temperature was fixed at 270°C. The corresponding growth time for these samples is 60 mins.

Group 3: From sample J to L, the growth temperature decreases from 270 to 250°C while the SnCl_4 flow fraction was fixed at 2.3×10^{-4} . The corresponding growth time is 60 mins.

a) GeSn growth in the SnCl₄ overpressure regime

Visual inspection of the wafer after growth provides useful information about the film surface. Diffusion of light reflecting off the surface is quite noticeable by the human eye and can serve as an indicator of surface roughness. For this work, the film surfaces were divided into three categories: i) the sample surface was milky, in which visual reflections were not easily visible, ii) the sample surface was hazy, such that, visual reflections were easily visible but not clear, and iii) the sample surface was clear or mirror-like shining. Based on the subsequent SEM measurement, different surfaces correspond to the size of Sn droplets seen on the surface (milky: $\sim 3 \mu\text{m}$, hazy: $< 1 \mu\text{m}$, and mirror-like: no detectable droplets). The droplet density on the milky and hazy surfaces was less than 0.5 and more than 1 droplet per square micrometer, respectively. Visible and SEM images from these classifications are given in the next section. The Sn droplet formation could be best explained by the Ostwald ripening mechanism where inhomogeneous small particles dissolve over time and redeposit into larger particles. The formation of the Sn droplets thus leads to suppressing the effective Sn incorporation into Ge. These temperatures were varied from our starting point determined by the growth of previous materials. In this step of the optimization process, all the film surfaces were milky as Sn droplets dominated the surface of the film. The XRD RSM and TEM of a selected sample (sample E1) that was representative of all samples from A to G in this group is shown in Fig. 15.

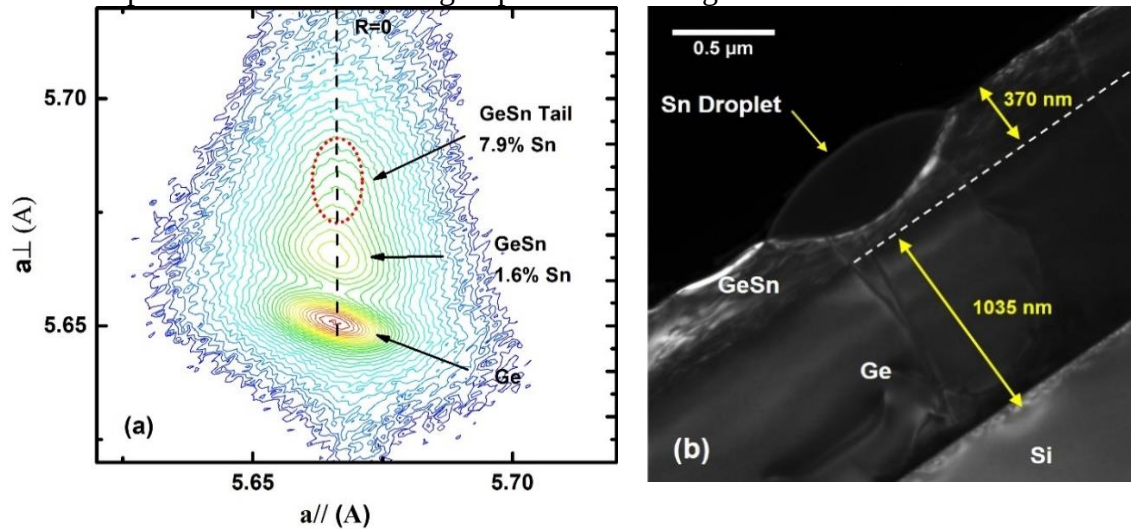


Fig. 15: a) XRD RSM of Sample E1 (grown at 270 °C for 30 min) showing the Ge buffer and GeSn peaks. The dashed line shows the relaxation for pseudomorphic growth ($R=0$), b) Corresponding dark field TEM image of an area with a Sn droplet.

The XRD RSM of sample E1 (grown at 270 °C for 30 min), in Fig. 15(a), shows three areas, 1) a Ge buffer peak displaying tensile strain, that was measured at 0.02%, 2) a pseudomorphic layer peak with low Sn composition, (1% Sn), 3) A broad high Sn composition peak (7.9% Sn). TEM imaging of this sample is shown in Fig. 15(b). A Ge buffer thickness was observed with a thickness of 1035 nm which was near the 1 μm targeted buffer thickness demonstrating good growth control. Also visible in Fig. 15(b) is the GeSn layer with a large Sn droplet on the surface which had a diameter of $> 1 \mu\text{m}$.

b) Role of SnCl_4 flow ratio in enhancing the material quality

To fully understand the effect of SnCl_4 in the growth of GeSn, the ratio of SnCl_4 gas flow ratios was calculated and showed that the first batch was grown under a SnCl_4 flow fraction of 2.9×10^{-3} . This value was two orders of magnitude above that which has been reported in the growth of high quality GeSn. Therefore, a series of growths were conducted with reduced SnCl_4 gas supply fraction. These growths were accomplished using the same temperature, pressure, and time (samples H, I, and J). The precursor and carrier gas flow rates were adjusted to reduce the SnCl_4 partial pressure. The SnCl_4 gas supply ratio was reduced by an order of magnitude from the starting condition to a condition that produced a clear mirror-like surface. The initial growth condition (Sample E2) showed Sn surface segregation and SnCl_4 reduction resulted in the elimination of surface Sn and clear films. Visual observation of the sample surface shown in Fig. 16 (a1)-(d1) gave evidence of successful Sn reduction. Pieces were taken of Samples E2, H, I, and J, for other measurements before imaging was accomplished. It can be seen in the initial state the sample surface (E2) was milky and sample H wafer surface is still hazy indicating Sn droplet formation on the surface which covers the entire wafer. As the SnCl_4 molar flow fraction reduces, the cloudiness of the sample surface clears up and sample optical quality improves. Visual observation of the samples shows that by sample I the wafer center is clear with only the outer edge being hazy. Sample J shows a mirror-like sample surface across the full wafer. This shows that there is a window for the growth with the upper limit on SnCl_4 molar flow fraction from the sample I is 4.5×10^{-4} . Sample J shows a clearer sample surface so the upper limit SnCl_4 molar flow fraction is just set to show where the surface Sn is removed, and the wafer surface begins to clear. This does not verify that all the Sn is removed from the surface. A more in-depth look at the sample surface was accomplished using the SEM as shown in the Fig. 16.

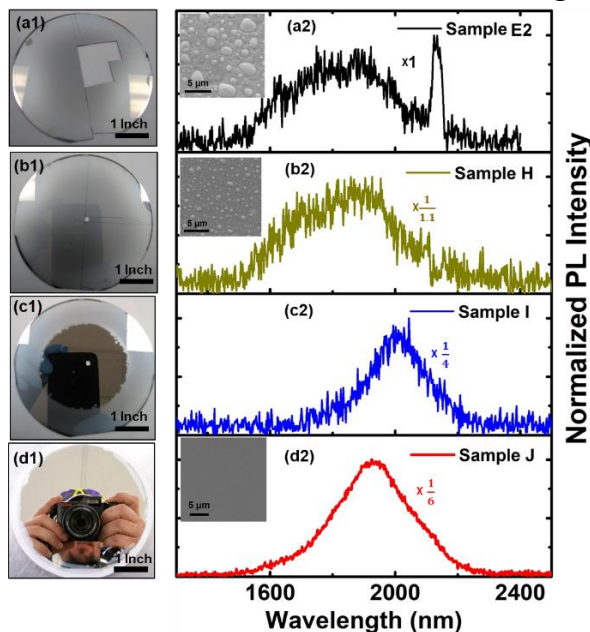


Fig. 16. Visual images of samples E2, H, I and J were shown in (a1), (b1), (c1) and (d1), respectively. From sample E2 to J the flow fraction of SnCl_4 decreases from 2.9×10^{-3} to 2.3×10^{-4} while the temperature was fixed at 270°C . Room-temperature PL of samples E2, H, I and J are shown in (a2), (b2), (c2) and (d2), respectively.

Visual observation of the samples shows that by sample I the wafer center is clear with only the outer edge being hazy. Sample J shows a mirror-like sample surface across the full wafer. This shows that there is a window for the growth with the upper limit on SnCl_4 molar flow fraction from the sample I is 4.5×10^{-4} . Sample J shows a clearer sample surface so the upper limit SnCl_4 molar flow fraction is just set to show where the surface Sn is removed, and the wafer surface begins to clear. This does not verify that all the Sn is removed from the surface. A more in-depth look at the sample surface was accomplished using the SEM as shown in the Fig. 16.

The XRD rocking curves contained in Fig. 17(a), show similar peak position for each sample regardless of the flow fraction of SnCl_4 or GeH_4 . The change of XRD peak position is <0.1 degrees suggesting the Sn composition between samples varies less than 1% and is most likely attributed to natural process variation in the growth chamber. More intense peaks from the sample I and J and the disappearance of the 1% peak show high material quality and suggest that the Sn has incorporated into the growing film instead of agglomerating on the surface. The composition of the film J was determined from XRD RSM shown in Fig. 17 (b), with the GeSn film comprising 5.6% Sn and 11% relaxation. The Ge buffer was found to be under 0.17%

tensile strain. The dark field TEM image of sample J was shown in Fig. 17 (c), in which no Sn segregation was observed on the surface. The GeSn film also exhibits no extended threading dislocation penetrating through the film. Improvement in the growth conditions allowing for high-quality growth sets the stage for continued GeSn growth to further increase the Sn incorporation.

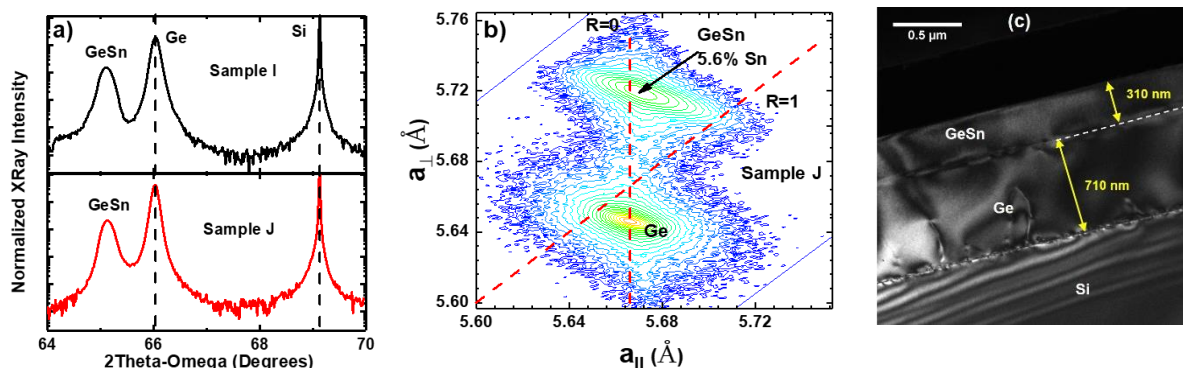


Fig. 17 (a) XRD rocking curves of Sn reduction Tests (samples I and J). The GeSn film thickness of 230 and 160 nm for sample I and J, respectively was derived using spectroscopic ellipsometry. (not shown); (b) XRD-RSM for sample J. Dashed lines show the relaxation when $R=0$ for pseudomorphic growth, while $R=1$ is for relaxed growth; (c) Dark field TEM image of sample J. No Sn droplets were observed on the GeSn surface.

c) Role of temperature in increasing Sn incorporation

The prior section showed improvements in the Sn incorporation and a reduction/elimination of Sn droplets on the surface by optimizing the SnCl_4 flow. In order to further increase the Sn incorporation, the growth temperature was designed to decrease while maintaining the Sn dilution ratio at 2.3×10^{-4} . By visual inspection after GeSn epitaxy, the surface morphology of GeSn film changes with decreasing growth temperature from 270 to 250°C. As shown in Fig. 18 inset, the majority of GeSn surface is mirror-like without the significant Sn droplet segregating on the surface at the temperature of 270°C. When the temperature drops to 260°C, the hazing area starts growing from the edge to center as the ring on the surface while the GeSn surface at the center is clear as shown in Fig. 18(c) inset. The hazing area is attributed to the aggregated Sn droplet on the GeSn surface. As the temperature continues decreases to 250 °C, the hazing area continues growing and covers the majority of the surface, leaving the clear surface only sparsely at the center of the surface. The segregation of Sn and droplet formation is attributed to both increased Sn incorporation and reduction in the reactivity of GeH_4 at lower temperatures. Lower GeH_4 reactivity results in less Ge crystal formation to host further incorporated Sn atoms and the excessive Sn would precipitate on the surface.

Room-temperature PL spectra was conducted in order to study the optical properties of GeSn films. As shown in Fig. 18, the PL spectrum of a commercial GeSn sample is shown as a reference for comparison with our CVD-grown GeSn samples from J to L. The GeSn reference sample was grown on Ge buffered Si substrate by using the ASM Epsilon[®] 2000 Plus reduced pressure CVD (RPCVD) system with commercially available precursors of GeH_4 and SnCl_4 . The film thickness of GeSn film is 83 nm. The corresponding Sn composition and compressive strain

of commercial sample was 5% and -0.52%, respectively. On the PL spectra of Fig. 18, the pumping power of 1064 nm laser for PL emission was 300mW and other PL setup conditions between GeSn reference and samples J to K were kept the same. From Fig. 18(a) to (d) only direct bandgap emission were observed for all the samples while the indirect bandgap emission was not detected. The inefficient indirect bandgap recombination is suppressed by the fast non-radiative recombination induced by defects. The PL comparison study further confirms the significant improvement of the optical performance of our grown GeSn samples as PL emission was not observed for other samples with 532 nm laser.

Based in the above three sections, in conclusion, a method to pursue growth of high quality GeSn on Ge buffered Si has been developed. The study started in a growth regime in which SnCl_4 overpressure dominated the overall growth of the GeSn material. The detrimental effects of SnCl_4 overpressure lead to a reduction of the SnCl_4 molar flow fraction. This reduction in SnCl_4 molar flow fraction provided better growth conditions to allow Sn to incorporate into the growing film and less agglomerating on the sample surface. Optimal growth conditions were achieved for the 270 °C growth temperature, producing high quality GeSn with a mirror-like surface.

III) Characterization of GeSn/GeSn QW structures

Prior reports on the analysis of Ge/GeSn/Ge QW structure indicated that it did not provide necessary carrier confinement, thus using the SiGeSn ternary material as a barrier was proposed. Recent reports on the growth and characterization of strained SiGeSn/GeSn/SiGeSn indicated that while the carrier confinement was improved the compressive strain resulted in indirect material and quantum confinement inducing indirect behavior in the QWs. Our study on a GeSn QW indicates that using a relaxed GeSn buffer with Sn composition of 8.5% reduces the strain in the QW and acts as a barrier relative to the higher composition GeSn QW. Band structure analysis and temperature dependence PL spectra of a $\text{Ge}_{0.92}\text{Sn}_{0.08}/\text{Ge}_{0.86}\text{Sn}_{0.14}/\text{Ge}_{0.92}\text{Sn}_{0.08}$ single QW sample showed that the direct bandgap type-I emission was achieved. However, the carrier confinement is still insufficient, which could reduce the QW light emission efficiency. Hence a QW structure featuring stronger carrier confinement is highly desirable. Band structure

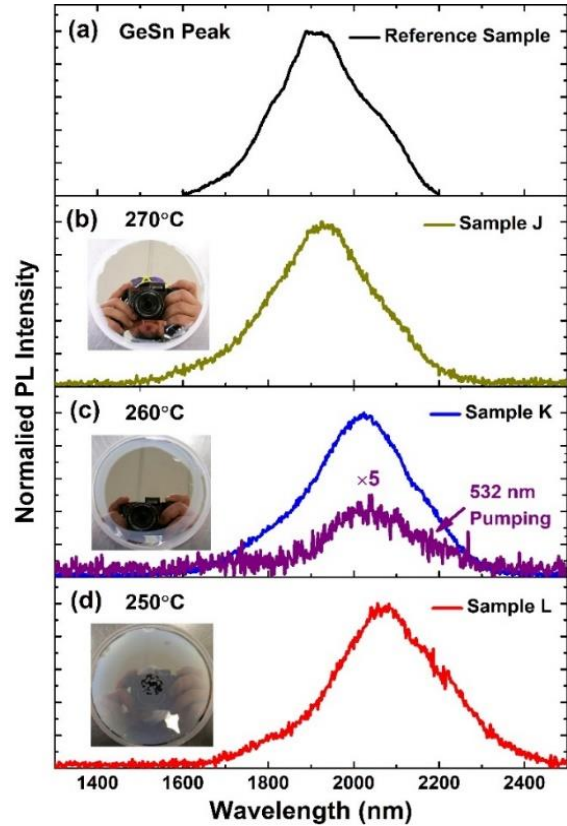


Fig. 18. Room-temperature PL spectra of (a) reference sample, (b) sample J, (c) sample K and (d) sample L, respectively. The 1064 pulsed laser was used as the pumping source for reference sample and samples J, K and L while the 532 nm continuous wave laser was used for sample K as a comparison.

calculations of two $\text{Ge}_{0.91}\text{Sn}_{0.09}/\text{Ge}_{0.85}\text{Sn}_{0.15}/\text{Ge}_{0.91}\text{Sn}_{0.09}$ double QW samples with the thicknesses of $\text{Ge}_{0.85}\text{Sn}_{0.15}$ well of 6 and 19 nm revealed that both samples feature type-I band alignment. Compared with the single QW sample, by increasing the Sn composition in the GeSn barrier and well, the QW layer featured increased energy separation between the indirect and direct bandgaps towards a better direct gap semiconductor. Moreover, the thicker double QW sample exhibited improved carrier confinement compared to the thinner double QW sample due to lowered first quantized energy level in the Γ valley. The PL spectra confirmed the direct bandgap well feature and the improved carrier confinement, as significantly enhanced QW emission from the thicker double QW sample was observed. In this section, first, the single QW sample is introduced briefly for comparison with two double QW samples. After that, the double QW samples were investigated in details. All QW samples were grown by an ASM Epsilon[®] reduced pressure chemical vapor deposition (RPCVD) reactor using commercially available and low-cost precursors (GeH_4 and SnCl_4).

Direct bandgap Type-I GeSn/GeSn single QW

Material growth and characterization and band structure: The actual structure of this sample was shown by TEM image with the SIMS measurement overlaid on the image in Fig. 19 (a). The band structure, shown in Fig. 19(b), was calculated using the measured QW data and applying the effective mass approximation and propagation matrix approach for the electronic band structure and quantized energy levels, respectively. Direct bandgap Type-I band alignment for the QW was achieved according to the band structure. Based on Vegard's law, the $\text{Ge}_{0.863}\text{Sn}_{0.137}$ well is a direct bandgap material with the Γ -L valley difference of 24 meV.

Optical characterization: Figure 20 (a) shows the normalized temperature dependent PL spectra stacked for clarity. Peak 1 located at 2200 nm at 300K is attributed to Γ -LH transition in the upper barrier. Most absorption from the 532 nm laser occurs in the first 20 nm of the sample and since the upper barrier is 46.6 nm thick, most absorption occurs in this layer. The GeSn barrier emission almost disappears below 70 K. Peak 2 located at 2500 nm at 300K is

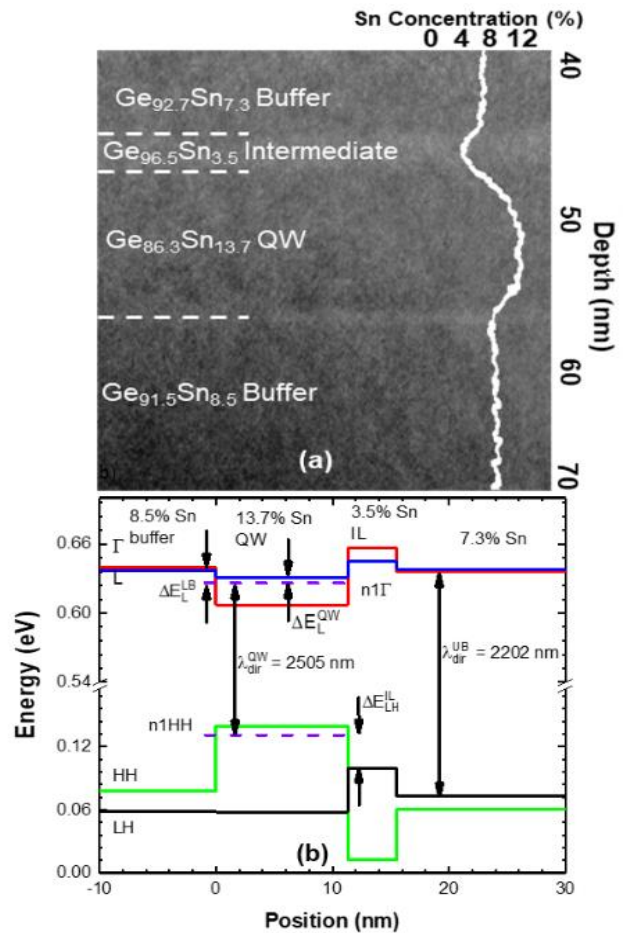


Fig. 19 (a) TEM image of the GeSn/GeSn/GeSn QW. The SIMS measurement is overlaid on the image to show the composition profile for each grown layer. (b) The calculated band structure of the QW sample. Direct bandgap and Type-I band alignment were achieved.

attributed to the Γ -HH transition in the $\text{Ge}_{86.7}\text{Sn}_{13.7}$ QW. Figure 20(b) shows the integrated PL intensity and full width half maximum (FWHM) derived from the Gaussian fitting of the two dominant peaks seen in the spectra. The large increase of the integrated PL at low temperature clearly indicates the direct bandgap behavior. The increased line width of peak 1 at every temperature indicates bulk emission with some overlapping transitions.

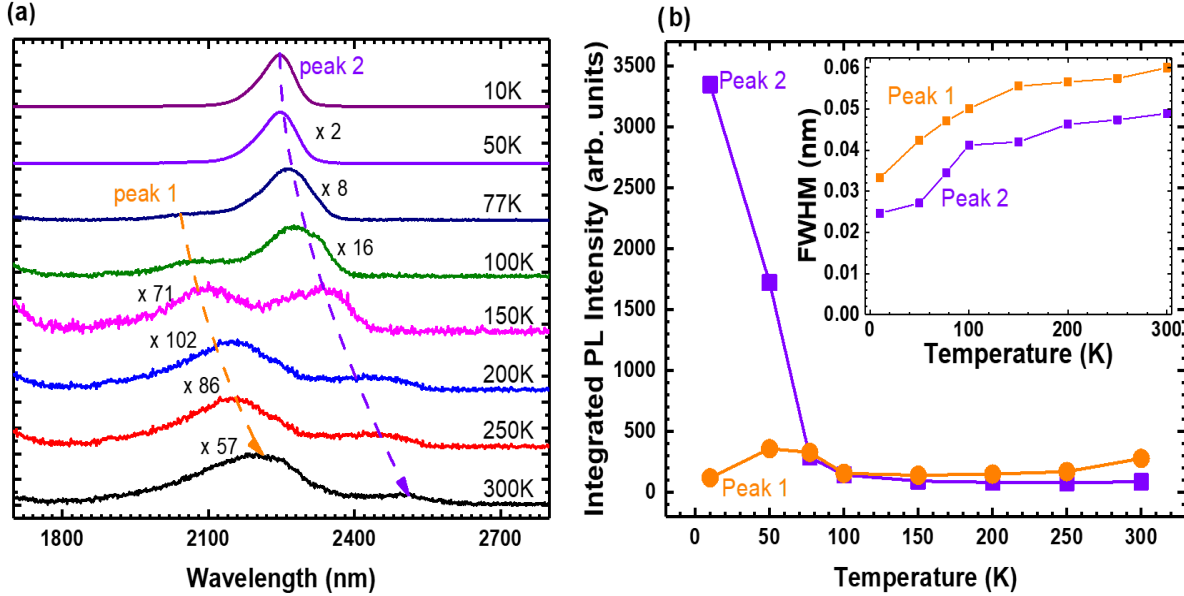


Fig. 20. (a) Temperature dependent spectra of the GeSn QW sample. Peak intensities of temperatures above 10K have a multiplication factor to normalize it to the 10K measurement. (b) Gaussian fitting of the PL spectra as used to derive the temperature dependent integrated PL intensities and FWHM (Inset) for peaks 1 and 2.

Direct bandgap Type-I GeSn/GeSn double QWs with improved carrier confinement

Material growth and characterization: For two double QW samples (annotated as A and B), the 700-nm-thick Ge buffer layer was grown prior to QW growth by a two-step growth method. The nominally designed QW structures consist of the followings from the bottom to top:

- i) the 600-nm-thick $\text{Ge}_{0.91}\text{Sn}_{0.09}$ buffer for both samples A and B;
- ii) two $\text{Ge}_{0.85}\text{Sn}_{0.15}$ wells (5- and 20-nm-thick for samples A and B, respectively) separated by a 2-nm-thick $\text{Ge}_{0.91}\text{Sn}_{0.09}$ barrier;
- iii) the Ge cap layer.

For sample A, the well thickness of 5 nm features pseudomorphic growth to ensure the high material quality. While for sample B, the 20-nm thick well is partially relaxed, aiming to offer the improved carrier confinement.

After the growth, the SIMS, high-resolution XRD 2θ - ω scan and RSM were employed to identify and cross check the Sn compositions and the degree of strain of each layer. The bowing parameter of -0.066 was used for the lattice constant. The TEM was used to examine the material quality and layer thickness, which were cross-checked by SIMS plots. Material characterization results are summarized in Table V.

Table V Information of GeSn double QW samples

Samples	Layer structure	Sn (%)		Thickness (nm)		Strain (%)
		Designed	Measured	Designed	Measured	
A	Ge cap (top barrier)	0	0	17.0	17.0	0.9
	GeSn well	15	14.7	5.0	6.5	-1.05
	GeSn barrier	10	8.8	2.0	1.5	-0.26
	GeSn well	15	14.7	5.0	6.0	-1.05
	GeSn buffer (bottom barrier)	10	8.8	600	600	-0.14
	Ge buffer	0	0	700	700	0.2
B	Ge cap (top barrier)	0	0	7.0	7.0	1.15
	GeSn well	15	15.3	20.0	19.0	-0.91
	GeSn barrier	10	9.4	2.0	2.0	-0.11
	GeSn well	15	15.3	20.0	19.0	-0.91
	GeSn buffer (bottom barrier)	10	9.4	600	600	-0.11
	Ge buffer	0	0	700	700	0.21

* Negative value indicates the compress strain.

Band structure calculation: The band diagrams as shown in Fig. 21 of the double QW samples at 300 K were calculated using the measured QW structure data in Table V. The bowing parameters $b_{\Gamma}=1.95$ and $b_L=0.68$ were selected to determine the direct and indirect bandgap energies based on the quadratic equation, which are valid for the high-Sn material. The effective mass approximation and the propagation matrix approach were used to calculate the electronic band structure and quantized energy levels.

Figure 21(a)-(d) illustrate the band structures at conduction band (CB) and valence band (VB) and possible optical transitions of sample A. Using selected bowing parameters $b_{\Gamma}=1.95$ and $b_L=0.68$, and considering the compressive strain of -1.05%, the direct bandgap $\text{Ge}_{0.853}\text{Sn}_{0.147}$ well was obtained with the energy difference between Γ -L valley of 26 meV. Figure 21(a)-(d) shows the barrier heights at each layer interface, which revealed that the type-I band alignment was achieved. Particularly, in Fig. 21(a), in the CB, the barrier height between GeSn barriers (including bottom barrier and inter-barrier) and GeSn well was calculated as 17 meV; while the barrier height at GeSn well/Ge top barrier interface is 93 meV. In the VB, the residual strain results in the split of HH and light hole (LH) bands. The barrier heights at GeSn barrier/GeSn well and GeSn well/Ge barrier interfaces are 54 and 160 meV, respectively.

Figure 21(e)-(h) illustrate the band structures and possible optical transitions of sample B. The energy separation between Γ -L valley of direct bandgap $\text{Ge}_{0.847}\text{Sn}_{0.153}$ well was calculated as 52 meV, which is higher than that of sample A due to the higher Sn composition. It is worth noting that the $\text{Ge}_{0.906}\text{Sn}_{0.094}$ barrier also features direct bandgap, as the Γ valley is 19 meV below the L

valley. Particularly, in Fig. 21(e), in the CB, the barrier heights at GeSn barrier/GeSn well and GeSn well/Ge barrier interfaces were calculated as 35 and 99 meV in Γ valley, respectively; while in the VB the barrier heights are 54 and 166 meV at HH band, respectively. The improved electron confinement in Γ valley and HH band compared to sample A is mainly due to the higher Sn composition and a thicker GeSn well layer of sample B.

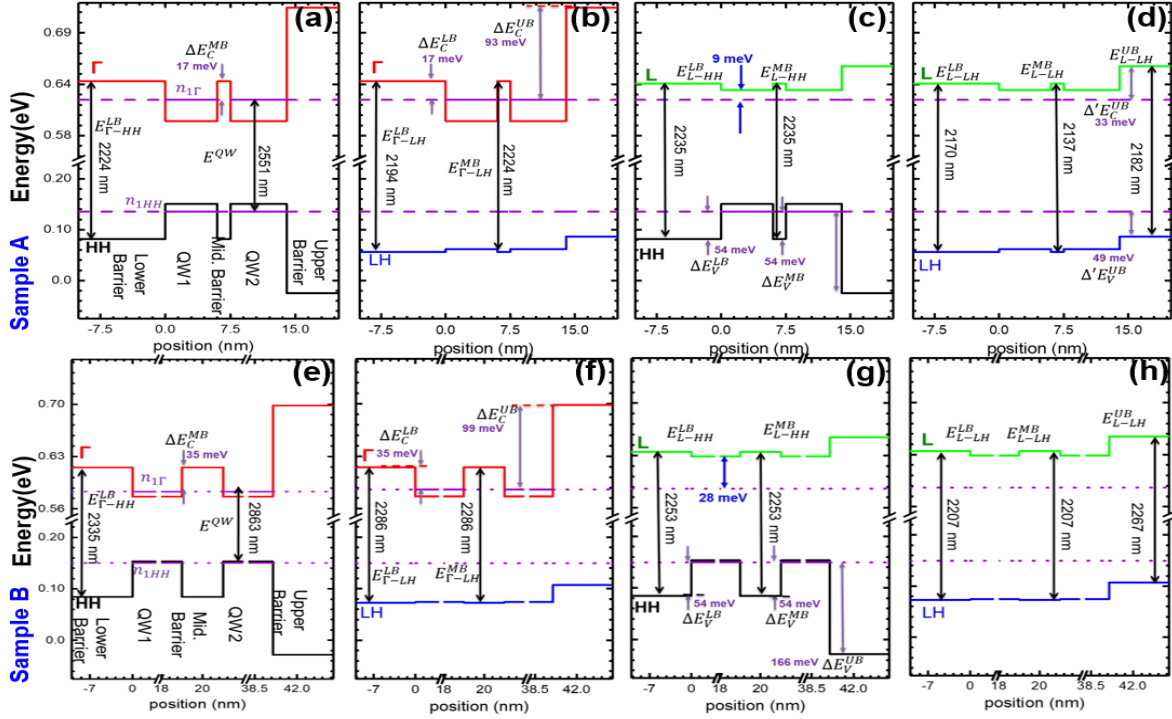


Fig. 21 Top: for sample A. Band diagram calculated based on measured material data, showing the carrier confinement and the possible band-to-band optical transitions between (a) Γ -HH; (b) Γ -LH; (c) L-HH; and (d) L-LH. Bottom: for sample B. (e)-(h) The similar band diagram and optical transition calculations.

Optical characterization: The temperature-dependent PL measurements were performed using a standard off-axis configuration with a lock-in technique (optically chopped at 377 Hz). The emissions were collected using a spectrometer equipped with a thermoelectrically cooled PbS detector with a cutoff at 3.0 μm . To pinpoint the optical transitions in QW, three lasers with various excitation conditions in terms of laser energy and beam penetration depth were utilized in this work: a 532-nm continuous wave (CW) laser, a 1550-nm CW laser, and a 1064-nm pulsed laser (pulse width of 5 ns and repetition rate of 45 kHz). The detailed parameters of pumping lasers are summarized in Table VI.

Table VI Parameters of pumping lasers

wavelength (nm)	Laser spot diameter (μm)	Averaged power density (kW/cm^2)	Photon injection density (Photon number/s/ cm^2)	Penetration depth in GeSn (nm)
532	65	15	4.1×10^{19}	21 ± 2
1064	52	6*	3.5×10^{22}	418 ± 21
1550	24	160	1.2×10^{21}	916 ± 46

* For 1064 nm pulsed laser, the peak power density is $2.7 \times 10^4 \text{ kW}/\text{cm}^2$.

The Gaussian fitting was used to investigate each peak in terms of peak position, full width at half maximum (FWHM), and integrated PL intensity. The integrated PL intensity vs. temperature for samples A and B are depicted in Fig. 22(a) and (b).

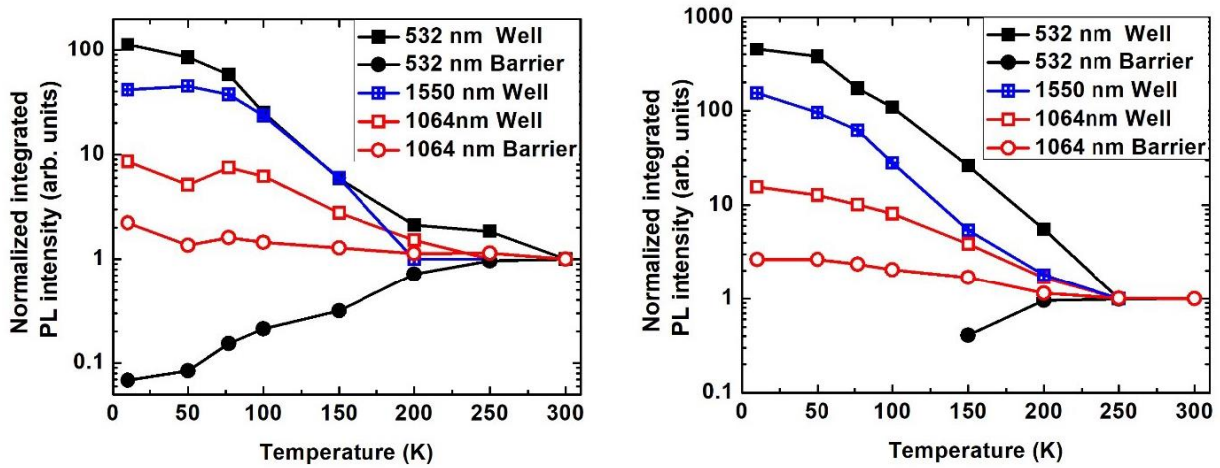


Fig. 22. Integrated PL intensity of (a) sample A; and (b) sample B using three different pumping lasers

Note that the temperature of barrier emission disappearing of sample B is 150 K, which is higher than that of sample A (100 K) and the single QW (70 K). This implies that: i) by using high Sn buffer, both samples A and B feature improved carrier confinement compared to the single QW; ii) compared to sample A, sample B exhibits further improved carrier confinement by using thicker GeSn well that further ease the compressive strain. The experimental evidence confirms the band structure calculation results shown in Fig. 21. The strong QW emission from Sample B can be explained as following: since the QW structure provides sufficient carrier confinement at a lower temperature, most photo-generated carriers eventually tend to populate the Γ valleys in GeSn well, resulting in that majority emissions are from band-to-band transitions in well. However, due to the high injection level, some electron-hole pairs could recombine before flowing into the well region, leading to emissions from Ge and GeSn barriers. In summary, the higher Sn composition in well and increased well layer thickness lead to the increased energy separation between the direct and indirect bandgap and significantly enhanced carrier confinement of sample B. Particularly at lower temperature, the sufficient carrier confinement results in hundreds of times integrated PL intensity increase under CW pump lasers, and the QW emissions dominating the PL under both CW and pulse pump lasers. Guided by the results provided in the work, more efforts would be made to optimize the QW structure such as well thickness to further improve the carrier confinement as well as discreteness of quantized state, towards the demonstration of room temperature operation devices such as lasers.

IV) Si-based GeSn lasers and photodetectors for Si photonic applications

Optically pumped GeSn bulk laser with wavelengths beyond 3 μm

In the past few years, the direct bandgap GeSn alloy has gained great attention as a group IV material which is fully compatible with the CMOS process. A series of Si-based GeSn lasers with broad wavelength coverage were recently realized, which is a major step towards high

performance Si-based mid infrared laser sources. In our study, an optically pumped 3 μm edge-emitting GeSn lasers with the world-record maximum Sn content of 22.3% was demonstrated.

Material growth and characterization: Thick GeSn films were grown using an ASM Epsilon[®] 2000-Plus reactor which is a RPCVD single wafer epitaxial deposition system. The commercially available precursors of GeH_4 and SnCl_4 were utilized and the growth temperature was kept below 450°C to be compatible with the CMOS process. Ge buffer was firstly grown with the thickness of 730 nm and then the GeSn virtual substrate (VS) was deposited on Ge buffer with the maximum Sn content of 16.5%. On GeSn VS, the GeSn film was grown using a multiple-step Sn-enhanced recipe. The Sn composition of the high quality GeSn top layer was 22.3% which was confirmed by SIMS and EDX measurements.

Band structure: The bandgap diagram along growth direction was calculated based on deformation potential theory. As shown in Fig. 23(b), four subbands were considered including indirect (E_{cL}) and direct (E_{cF}) valleys in the conduction band and heavy hole (E_{vHH}) and light hole (E_{vLH}) in the valence band, respectively. The uncertainty of E_{cL} and E_{cF} originates from different adoption of bandgap bowing parameters of indirect (b_{L}) and direct (b_{F}) band edge, which are crucial and have been predicted by the various research team. However, none of these reach an experimental agreement on the value of bowing parameters. For the best description of band diagram, the upper limits of $b_{\text{L}}=1.23$ eV, $b_{\text{F}}=2.49$ eV and lower limits of $b_{\text{L}}=0.68$ eV, $b_{\text{F}}=1.94$ eV were adopted, respectively. Ge buffer undergoes tensile strain as 0.19% after high temperature annealing due to the difference of thermal expansion coefficients between Si substrate and Ge. The tensile strain results in the decrease of the energy difference between E_{cL} and E_{cF} and the energy splitting between E_{vHH} and E_{vLH} . In contrast, GeSn grown on Ge buffer is under compressive strain, resulting in the E_{vHH} band lifting above E_{vLH} band. The whole GeSn layer exhibits the direct bandgap characteristics as the result of competition between Sn incorporation and compressive strain. From Fig. 23 (a), at region I of the 1st layer, the constant low Sn composition and high strain relaxation result in the small change of the bands. At region II, Sn content increases rapidly, leading to the sharp decrease of both direct and indirect bandgap. Meanwhile, the compressive strain accumulates during the epitaxy, resulting in the continuous increase of energy difference between E_{vHH} and E_{vLH} . The 2nd layer continues the change of band edge in region II. On the top of the 2nd layer of GeSn, the minimum bandgap was obtained between 0.275 and 0.360 eV.

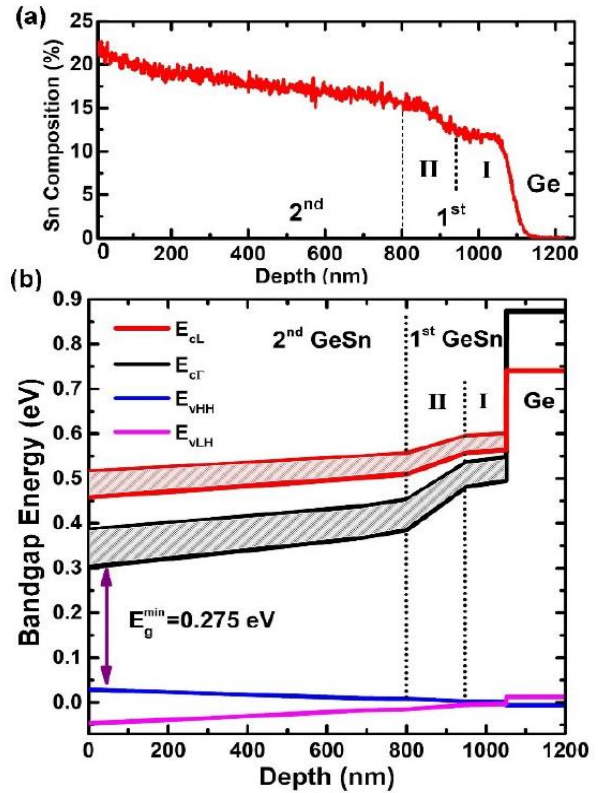


Fig. 23 (a) SIMS profile of sample A. (b) The band diagram calculation of sample A with Sn compositional graded GeSn structure.

Optical characterization: In order to assess the optical properties and the bandgap directness of GeSn, the temperature-dependent PL of the 22.3% GeSn sample was measured, as shown in Fig. 24(a1) and (a2). A continuous wave (CW) laser emitting at 532 nm wavelength was used as an optical pumping source. The beam size was 100 μm in diameter. PL emission was spectrally analyzed by the combination of iHR320 spectroscopy and liquid nitrogen cooled Indium Antimonide (InSb) detector with the wavelength detection cut-off at 5 μm . The blue shift of PL peak following Varshni model was clearly observed in PL spectra as the temperature decreases from 300 to 10 K. The PL intensity increases dramatically as the sample cools down. As Fig. 24(a2) shows, the peak PL intensity increases 65 times from 300 to 10 K.

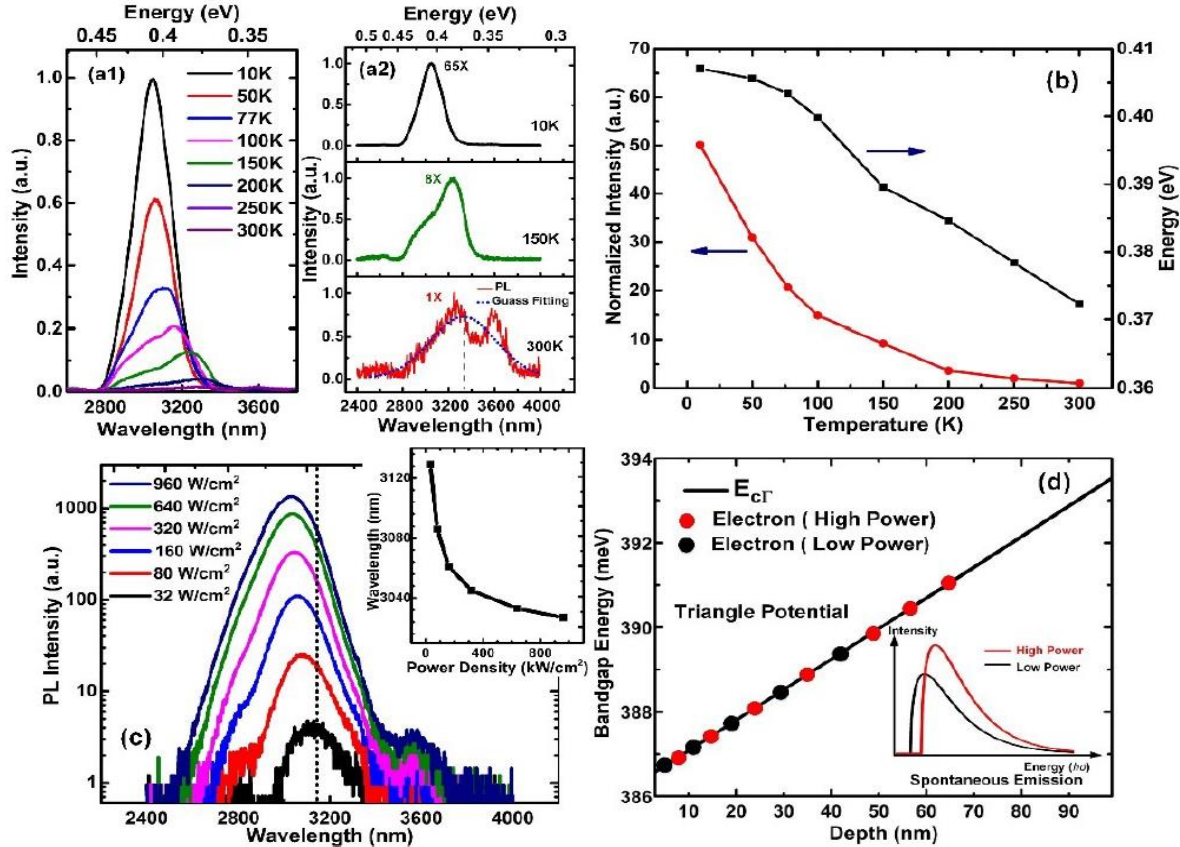


Fig. 24 (a1), (a2) Temperature-dependent PL spectra. (b) The integrated PL intensity and peak position as a function of temperature. (c) Power-dependent PL spectra at 10 K. Inset: the Blue shift of wavelength with increasing power density. (d) Band filling effect in the triangular potential model. Inset: calculation of spontaneous emission in triangular potential well

The integrated PL intensity and peak position at each temperature were extracted, as plotted in Fig. 24(b). The main peak in PL spectra shifts from 0.371 to 0.411 eV and the integrated PL intensity increases 50 times from 300 to 10 K. The power-dependent PL was also investigated, as shown in Fig. 24(c). The PL intensity increases significantly with the increase of excitation power density, as expected. The main peak of spectra exhibits a clear blue shift with high excitation power. The corresponding wavelength shifts from 3130 to 3032 nm when the pumping power density increases from 32 to 960 W/cm². Meanwhile, the FWHM of PL spectra increases dramatically as the pumping power increases. The clear blue shift of wavelength could be

explained by the typical band-filling effects, which is more pronounced in the tilted band diagram as a result of graded Sn composition. The E_{cF} band energy as the function of depth was drawn in Fig. 24(d). When the excitation rate of carriers exceeds the instantaneous recombination rate, the photogenerated carriers are spatially distributed within the penetration depth into GeSn for a laser source. Then the excess carriers redistribute and transport towards the top of GeSn layer where the narrowest energy band edge locates. At low excitation power, the majority of carriers accumulate at the surface region of GeSn and the interband optical transition mainly occurs at the narrowest energy band edge. As the excitation power increases, a large proportion of carriers populate at the wider energy band edge which spatially locates at the inner region of GeSn layer as a result of Pauli Exclusion Principle. Therefore, the light emissions occur at the wider band edge, leading to the blue shift of the main PL peak. The broad spatial population of carriers also results in the increase of FWHM. The theoretical spontaneous emission of the triangular potential model was calculated in the inset of Fig. 24(d), further confirming the blue shift of PL under high excitation power.

GeSn edge-emitting laser device: The GeSn sample was fabricated to the 5 μm -width and 1.25 mm-length strip waveguide as an optically pumped edge emitting device. The depth of waveguide was wet-etched as 800 nm. The optical pumped lasing performance was investigated using two pulsed lasers (1060 nm with 45 kHz repetition rate and 6 ns pulse width and 1950 nm pulsed laser with 10 kHz repetition rate and 10 ns pulse width). The laser beam was focused to a 20 μm -width and 3 cm-length pumping strip on to GeSn waveguide by a cylindrical lens. The schematic drawing of the edge-emitting ridge waveguide laser is shown in Fig. 25(a). The fundamental TE_{00} mode simulation is depicted in Fig. 25 (b).

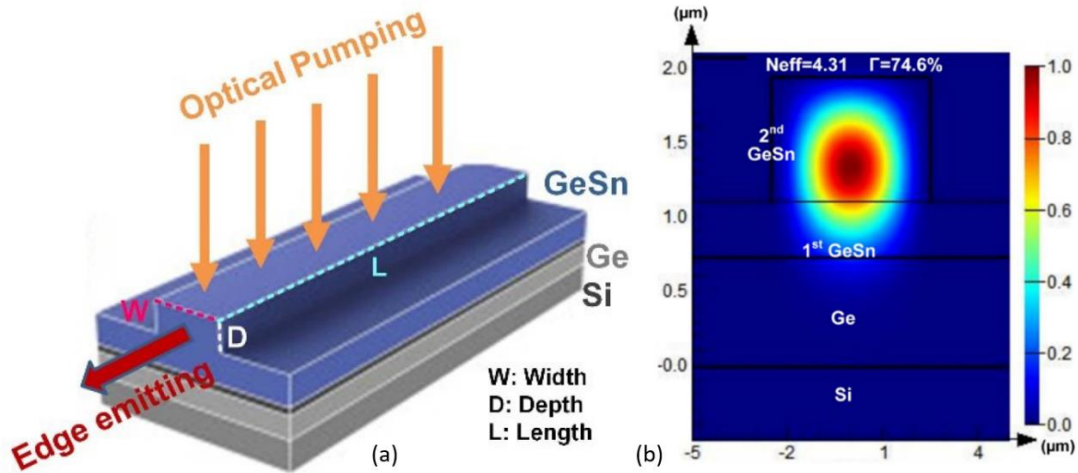


Fig. 25. (a) The schematic diagram of GeSn laser devices and optically pumped lasing setup. (b) The color contour of fundamental TE_{00} mode at 3 μm wavelength.

The samples were first mounted on a Si chip carrier and put into a liquid nitrogen cold-finger cryostat. The lasing emission was collected from one side of Fabry–Perot facet and sent to the spectrometer and InSb detector (cut-off wavelength: 5 μm) for further lasing measurements.

Optical characterization of the laser device: The temperature dependent laser-input versus laser-output (L-L) curves for the edge-emitting GeSn device were plotted in Fig. 26 (a). A clear “knee” characteristic on the L-L curves were shown as the temperature changes from 77 to 150 K. The sharp increase above the “knee” region indicates that the stimulated emission dominates over spontaneous emission. Through linear data fitting of the L-L curves, the lasing threshold was extracted. At the temperature of 77 K, the lasing threshold was obtained as 139 kW/cm². The lasing temperature was up to 150 K. The characteristic temperature of lasing T_0 was obtained as 83 K by data fitting of temperature dependent lasing threshold, which is comparable with previously published GeSn laser results. At 1.5 times lasing threshold the lasing spectra at the temperature of 77, 110 and 150 K were plotted in Fig. 26(b). Due to longitudinal Fabry-Perot resonances within 1.25 mm-long waveguide, the multimode characteristics was clearly observed on the lasing spectra. With increasing temperature, the lasing peaks have a red-shift as expected. At the maximum operating temperature of 150 K, the lasing peak was 3 μ m (0.413 eV). The 1950 nm pumping laser could reduce the heating effects significantly. Since the photon energy of 1064 nm pumping (1.17 eV) is higher than the bandgap energies of Ge buffer (0.8 and 0.66 eV for direct and indirect bandgap, respectively), large numbers of photons could be absorbed by Ge buffer, which results in the severe local heating. In contrast, the photon energy of 1950 nm pumping (0.64 eV) is smaller than bandgap energies of Ge and therefore the photons could only be absorbed by GeSn layer, resulting in no heating factor from Ge buffer. Additionally, the carriers at the Ge buffer excited by 1064 nm pumping have a transport process towards GeSn layer, which generates the heating during the interaction between carriers and phonons via the lattice scattering mechanism. While under the 1950 pumping, no carrier transport process from Ge buffer to GeSn is expected. Therefore, using the 1950 nm laser, the maximum lasing operating temperature was achieved as shown in Fig. 26(c).

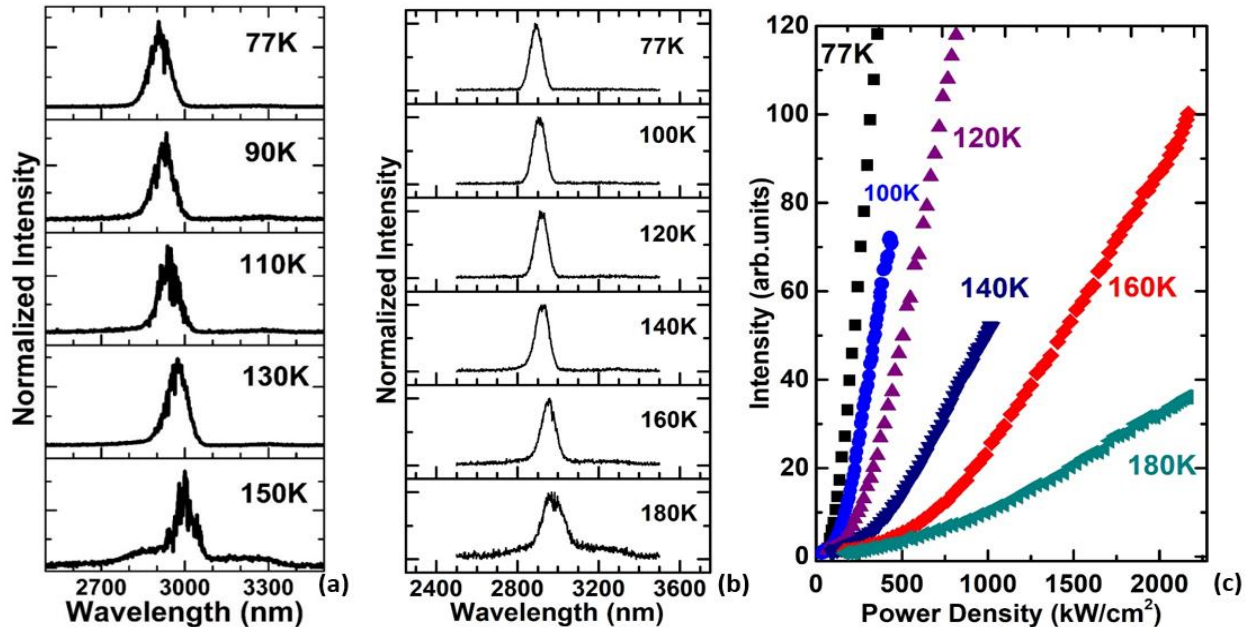


Fig.26 (a) and (b) Comparison between the lasing spectra using 1060 nm laser (left side) and 1950 nm laser (right side). (c) Temperature dependent L-L curves for GeSn edge-emitting device using 1950 nm laser indicating the laser operating temperature up to 180 K.

Optically pumped GeSn QW laser on Si operating up to 90 K

It is generally acknowledged that the quantum well (QW) structures could be applied to the laser structures to improve their device performance which eventually may lead to room temperature operation. Our previous study indicated that by appropriately selecting the Si and Sn compositions, using GeSn as a buffer (with Sn composition lower than that in GeSn well) on Ge virtual substrate and SiGeSn as barrier could achieve direct bandgap well with type-I band alignment, as well as sufficient carrier confinement. In this work, an MQW sample with 4-well structures was investigated. The distinct results could provide effective guidance for future QW laser design especially for the selection of active region structure.

Material growth and characterization: The MQW sample was grown using an industry standard ASM Epsilon[®] 2000-Plus RPCVD system. SiH₄, GeH₄, and SnCl₄ were used as Si, Ge, and Sn precursors, respectively. The Ge buffer layer with 1000 nm-thickness was grown on Si substrate by a two-step growth method. A relaxed GeSn buffer was grown prior to QW growth to reduce the strain of the MQW layer-stack. The barrier/well layer-stacks was then grown pseudomorphically to the relaxed GeSn buffer. After the growth, high-resolution X-ray 2 θ - ω scan and RSM were employed to identify Si and Sn compositions and the degree of strain of each layer. TEM images were utilized to determine the layer thickness and examine the material quality. Atom probe tomography (APT) and secondary ion mass spectrometry (SIMS) were performed to cross-check the Si and Sn compositions and the layer thickness. The Sn compositions in well layers were measured as 14.4%.

Atomic probe tomography (APT) measurement was performed to cross-check the Si and Sn composition in the well and barrier. Figure 27 shows the APT measurement result on the GeSn MQW sample. From the sample surface, the Sn composition in 1st, 2nd, and 3rd well was obtained as 14.4%, showing the identical Sn incorporation. There is almost no Si being incorporated in the well. The Si and Sn compositions in SiGeSn barrier were measured as 3.3% and 8.0%, respectively. The abrupt transitions between the barrier and well compositions indicate the high-quality material structure. The asymmetric increase in the Ge compositional profile at the well/barrier interface in Fig. 27 is a reconstruction artifact from the differences in the field evaporation strengths between the two materials. Although the 4th well was not measured because of the limited ability to sample through the entire tip, it is reasonable to believe that the Sn composition in the 4th well should be identical to other three wells since the growth condition was kept the same.

Optical characterization of the MQW sample: The temperature-dependent PL spectra are shown in Fig. 28(a). For each sample, as the temperature decreases from 300 K to 10 K, the PL

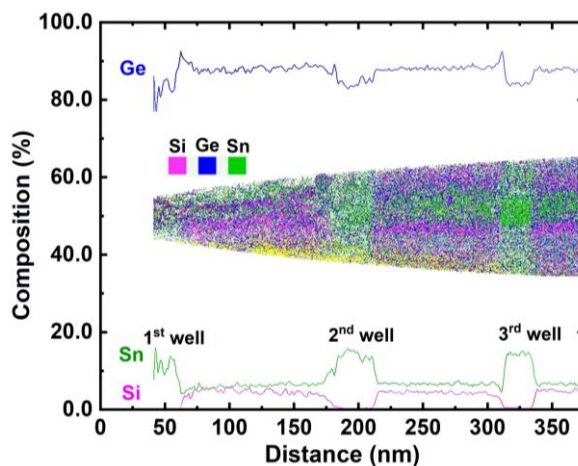


Fig 27. 1D APT composition scan of Si, Ge, Sn compositions. Inset: An atom map of Sample B reconstructed from the 3D APT.

intensity dramatically increases, showing the clear signature of the direct bandgap material. The observed PL peak features clear blue-shift at a lower temperature, which is expected due to the increase of the bandgap. Since the penetration depth of the 532-nm excitation laser beam is less than 100 nm in GeSn/SiGeSn, the major light absorption can occur only in the top layers including the top SiGeSn barrier and 1st GeSn well, and therefore the major emissions are from the 1st GeSn wells. The band structure of the GeSn MQW is shown in Fig. 28(b).

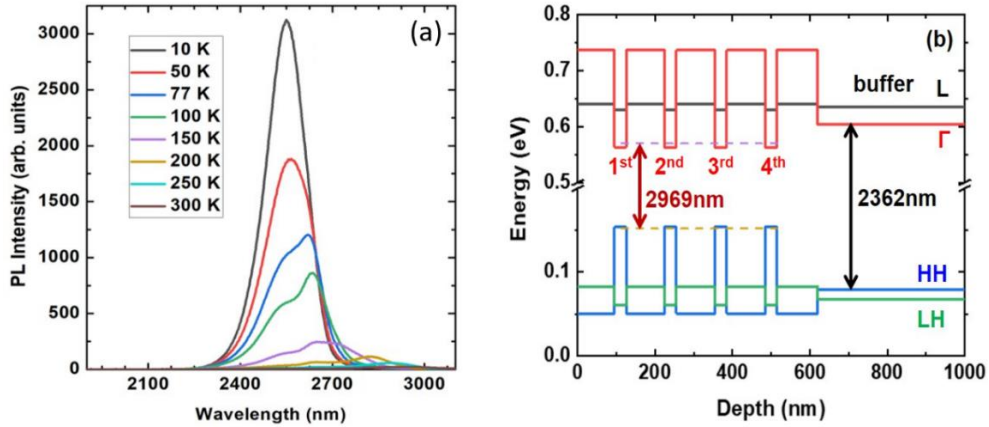


Fig. 28 (a) Temperature-dependent PL of the GeSn MQW sample. (b) Band structure calculation of the GeSn MQW. The direct bandgap wells show the energy difference between L and Γ of 67 meV. The optical transition in the well is 0.418 eV (2969 nm). The barrier heights in the conduction band (CB) and valence band (VB) are 174 and 102 meV, respectively.

Optical characterization of the laser devices: Ridge-waveguide-based edge-emitting lasers were fabricated by standard lithography and wet etching processes. The etching depth was selected as 800 nm to provide a sufficient mode confinement. After etching, the samples were lapped down to ~ 70 μm thickness and then cleaved to form the cavity. The optical pumping characterization was performed using a pulsed laser operating at 1950 nm with 10 kHz repetition

rate and 20 ns pulse width. The laser beam was collimated to a narrow stripe (~ 20 μm width and 0.3 cm length) via a cylindrical lens to pump the GeSn waveguide structure. The device was first mounted on a Si chip carrier and then placed into a continuous flow cryostat for low temperature measurement. The emission from the facet was collected by a spectrometer and then sent to an InSb detector. Note that the penetration depth of 1950-nm laser beam is deeper than 1000 nm so that all QWs are involved in the light absorption. The temperature-dependent lasing behavior as shown in Fig. 29 can be explained as following: as temperature increases, the ratio of radiative over non-

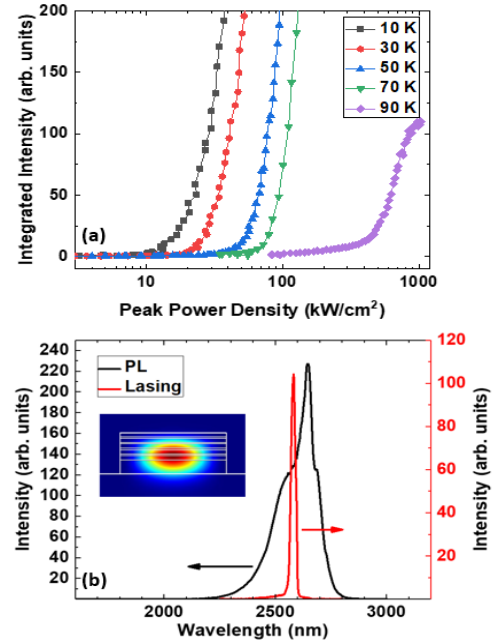


Fig 29. Temperature dependent L-L curves for GeSn edge-emitting device using 1950 nm laser indicating the laser operating temperature up to 90 K. (b) Comparison of Lasing and PL spectra for GeSn MQW sample temperature of 10 K. Inset: The pattern of TE₀ mode.

radiative recombination might decrease, which requires increased injection level for a compensation to maintain lasing operation. The 30nm-thick GeSn active layer leads to a high gain volume, which might offer sufficient compensation via increasing injection until 90 K. The results reported in this work provide the guidance for the design and optimization of the future higher-performance GeSn QW lasers.

Near room temperature (280 K) optically pumped GeSn laser

As previously stated, GeSn device performance has been dramatically improved in terms of lasing threshold and operation temperature; however, the room temperature or near room temperature lasing operation is highly desired and is being considered is one of our major milestones. The GeSn sample with 20% Sn composition was grown using ASM RP-CVD system with 970 nm of high-quality top GeSn layer as a gain medium. The temperature-dependent PL behavior (as indicated in Fig.30(a)) showed an explicit signature of the direct bandgap material. After evaluating the high material and optical quality of the GeSn sample, it was fabricated into a ridge waveguide with 100 μm with and 800 nm depth to provide a sufficient mode confinement. The sample was lapped down to ~ 70 μm thickness and then cleaved to form the cavity with the length of 2.75 mm. Earlier in the report, it was specified that pumping photon energy of 1064 nm laser (1.165 eV) is much higher than the emission photon energy (less than 0.469 eV); therefore, the quantum defect, i.e., the energy difference between absorbed and emitted photons could deteriorate lasing performance by a local heating. To further investigate the lasing characteristics, a 1950-nm laser with 10 kHz repetition rate and 20 ns pulse duration was used as excitation source.

The maximum operating temperature is increased to 280 K as shown in Fig.30(b) and (c), which is near room temperature. At 77 K, the lasing thresholds were extracted as 67 kW/cm^2 much smaller than those under 1064-nm laser excitation even with a lower absorption coefficient of 1950 nm. We attribute the increased operating temperature and dramatically reduced thresholds to the following aspects: i) the duty cycle of the 1950-nm laser is only 0.02%, which is smaller compared to the 1064-nm laser of 0.027%. Smaller duty cycle reduces the thermal generation time and the heat accumulation; ii) the quantum

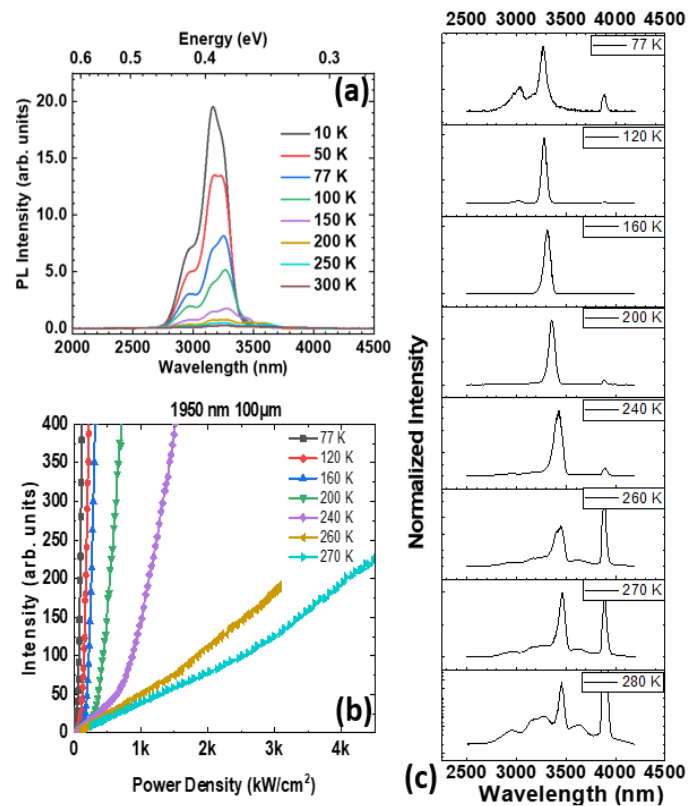


Fig. 30 (a) Temperature dependent photoluminescence using 532 nm CW laser, (b) L-L curve under 1950 nm laser for the 100 μm ridge waveguide device, (c) Lasing spectra at $2 \times$ threshold under 1950 nm laser at temperatures from 77 K to 280 K.

defect of ~ 170 meV is 45% smaller for the 1950-nm laser compared to the 1064-nm laser of ~ 700 meV, and therefore less excess phonon energy converts into thermal energy under the 1950-nm pumping. Figure 30(c) shows the lasing spectra measured at 2-times lasing threshold pumping power density. The multimode lasing characteristic was observed at each temperature.

High performance GeSn photodiodes for low-cost shortwave infrared imaging

The $\text{Ge}_{0.89}\text{Sn}_{0.11}$ photodiode structure was grown using an industry standard ASM Epsilon[®] 2000-Plus RPCVD system. A 1160-nm-thick p-type ($1 \times 10^{19} \text{ cm}^{-3}$) Ge buffer was first grown on the Si substrate. Then a 550-nm-thick p-type ($1 \times 10^{17} \text{ cm}^{-3}$) $\text{Ge}_{0.89}\text{Sn}_{0.11}$ layer was grown followed by a 150-nm thick n-type ($2 \times 10^{18} \text{ cm}^{-3}$) $\text{Ge}_{0.89}\text{Sn}_{0.11}$ layer. The growth was completed by capping with a 60-nm-thick heavily doped n-type (2×10^{19}) Ge layer. The samples were then fabricated into circular mesas with 250 and 500 μm diameters by using standard photolithography and wet etching processes. A 10/200 nm Cr/Au was deposited to form metal contacts of the photodiode. Temperature-dependent measurements were conducted by using a Janis cryostat with the liquid nitrogen cooling system. The current-voltage measurement was conducted using a DC current source. The spectral response measurement was performed by using Fourier transform infrared (FTIR) spectrometer system. For the responsivity measurement, a 2 μm laser diode optically chopped at 380 Hz and a lock-in amplifier were used. Moreover, the obtained responsivity and dark current were used to calculate the D^* . To demonstrate the infrared imaging, the halogen lamp with a wavelength ranging from 360 nm to 2.4 μm was used to illuminate the object with a long-pass filter above the wavelength of 1.6 μm . The 500 μm device was mounted to a two-dimensional stage and automatically scanned the reflected image of the object (golden star).

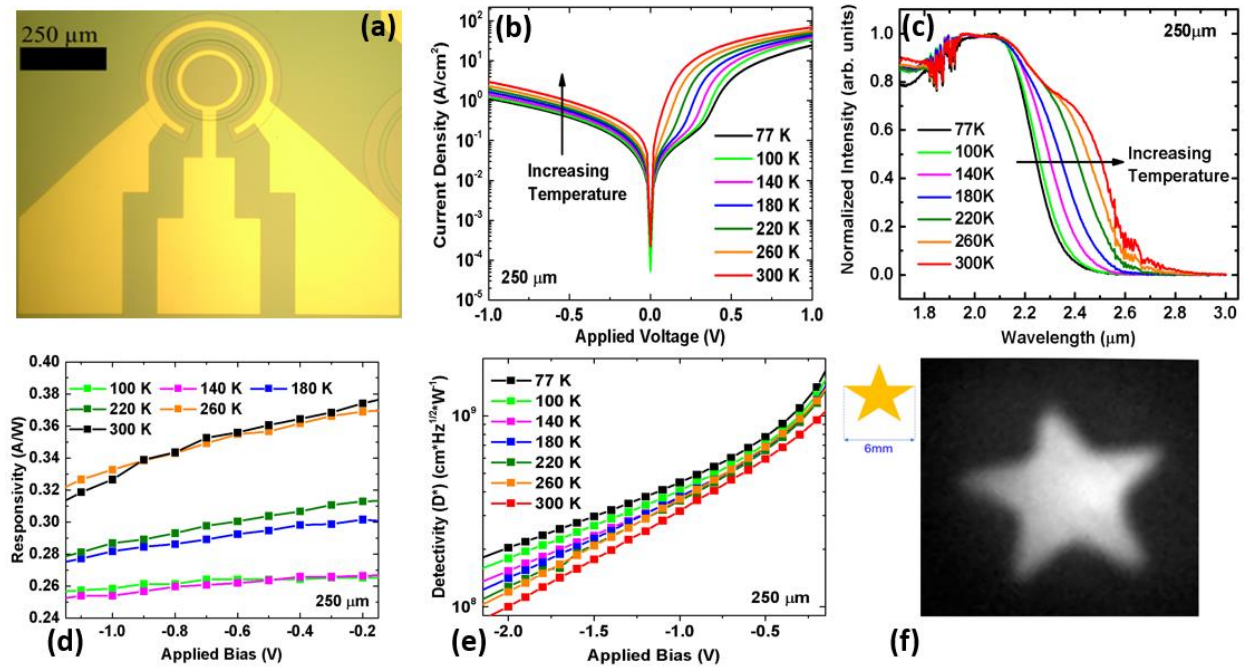


Fig. 31 (a) The optical image top view of the photodiode. (b) Current-voltage characteristics of 250 μm mesa device at temperatures from 300 to 77 K. (c) Spectral response at temperatures from 300 to 77 K. (d) Responsivity of the 250 μm mesa device at temperatures from 300 to 77 K. (e) D^* of the 250 μm mesa device at temperatures from 300 to 77 K. (f) The infrared reflected image of the star object achieved using GeSn photodiode.

The top view optical image of the 250 μm device is shown in Fig. 31(a). The rectifying behavior of the current-voltage characteristics of the $\text{Ge}_{0.89}\text{Sn}_{0.11}$ photodiodes with 250 μm diameter at different temperatures from 300 to 77 K was observed, as shown in Fig 31(b). The current density increases by increasing the temperature due to more thermal activated carriers. To further understand the origin of the dark current, the dynamic resistances were extracted from I-V characteristics. In fact, the dynamic resistance is a combination of series, shunt, trap-assisted tunneling (TAT), and forward bias resistances. From TAT resistance measurement, the trap density and trap energy at different temperatures were extracted. The trap density changed from 7×10^{12} to $1 \times 10^{14} \text{ cm}^{-3}$ as temperature increases. The traps were populated at a deep level of 208 meV at low temperature and then, at a shallow level of 38 meV at room temperature. Further analysis suggested that the surface and sidewall leakage currents dominated the dark current. Figure 31(c) depicts the temperature-dependent spectral response from 77 to 300 K. A blue shift behavior was observed as temperature decreases. The cutoff wavelength was extended up to 2.4 and 2.65 μm at 77 and 300 K, respectively, which is far beyond the band to the band absorption edge of Ge (1.55 μm). This wavelength extension is mainly due to GeSn absorption. The temperature-dependent responsivity of 250 μm mesa sample at 2.0 μm is shown in Fig. 31(d) with a peak responsivity of 0.37 A/W at -0.1 V at 300 K. The responsivity was reduced to 0.32 A/W as the reverse voltage increased to -1 V. This behavior may be due to the Franz-Keldysh effect where the absorption coefficient changes as the applied voltage varies [4]. In addition, the responsivity drops when the temperature decreases. It could be explained as the non-radiative recombination due to the trap states. Figure 31(e) shows temperature-dependent D^* . The peak D^* of 5.7×10^9 and $4.3 \times 10^9 \text{ cmHz}^{0.5}\text{W}^{-1}$ was found at 77 K for 250 μm and 500 μm mesa sizes, respectively. Although responsivity at 77 K is smaller than those at higher temperatures, the reduced dark current results in the overall enhanced detectivity. Figure 31(f) shows the infrared image of the star-shaped object obtained from the single photodiode, which scanned an area with the dimensions of 7 mm $\times$ 7 mm in 16 minutes.

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