GeSn alloys fabricated by modified sputtering deposition

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**NANYANG
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SINGAPORE

**GESN ALLOYS FABRICATED BY MODIFIED
SPUTTERING DEPOSITION**

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SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

2019

GESN ALLOYS FABRICATED BY MODIFIED SPUTTERING DEPOSITION

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Prof. Zhang Dao Hua

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals where I was the first and/or corresponding author.

Chapter 4 is published as Li Qian, W. J. Fan, C. S. Tan, and Dao Hua Zhang, Temperature enhanced spontaneous emission rate spectra in GeSn/Ge quantum wells. *Optical Materials Express* 7(3): 800, 2017. DOI: 10.1364/OME.7.000800

The contributions of the co-authors are as follows:

A/Prof. Fan provided the initial project direction and edited the manuscript drafts.

Prof. Zhang and A/Prof. Tan supervised the project and revised the manuscript.

I prepared the manuscript drafts.

I co-designed the study with A/Prof. Fan and performed all the experimental work including simulation and calculation at the school of Electrical and Electronic Engineering.

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I prepared the manuscript drafts and co-designed the study with Prof. Zhang. I performed all the experimental work including simulation and calculation at the school of Electrical and Electronic Engineering.

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I prepared the manuscript drafts and co-designed the study with Prof. Zhang. I performed all the experimental work including thin film deposition and characterization at the school of Electrical and Electronic Engineering.

Dr. Ni assisted in collecting atomic force microscope data. Dr. Xu and Dr. Tong helped with magnetron sputtering deposition.

A/Prof. Fan revised the manuscript.

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QIAN LI

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List of Abbreviations

2DSHA	2-dimensional subwavelength hole array
AFM	atomic force microscope
APCVD	atmospheric pressure chemical vapor deposition
CBM	conduction band minimum
CVD	chemical vapor deposition
DC	direct-current
DOS	density of states
DTGS	deuterated triglycine sulfate
EBL	electron beam lithography
FDTD	finite-difference time-domain
FTIR	Fourier transform infrared spectroscopy
FWHM	full width half maximum
HH	heavy hole
HR-XRD	high-resolution X-ray diffraction
IR	infrared
I-V	current-voltage
LH	light hole
MBE	molecular beam epitaxy
MCT	mercury cadmium telluride
MSM	metal-semiconductor-metal

PL	photoluminescence
PVD.....	physical vapor deposition
QD	quantum dot
QW.....	quantum well
RF	radio-frequency
RHEED.....	reflection high-energy electron diffraction
RSM	reciprocal space mapping
RTA	rapid thermal annealing
RTP	rapid thermal process
SEM.....	scanning electron microscope
SERS.....	spontaneous emission rate spectrum
SO.....	spin-orbit
SPP.....	surface plasmon polariton
SPR	surface plasmon resonance
TE	transverse electric
TEM	transmission electron microscope
TM	transverse magnetic
VBM.....	valence band maximum
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Abstract

Direct band-gap semiconductors have always been an interest to the research community in the area of photonics and optoelectronics. Most commonly used group IV semiconductors such as silicon and germanium have shown their capabilities in the application of microelectronics, however, lack in breakthroughs of the photon-electron related application because of the natural indirect energy band structure. Limitations in the photon-electron conversion lead to low effectiveness of their optoelectronic devices, which forces researchers to find substitutes of much higher cost and complexity. Most commercial and military optoelectronic devices are fabricated by direct band-gap group III-V compounds like GaAs, InSb, InAsSb, etc. Recently, group IV $\text{Ge}_{1-x}\text{Sn}_x$ alloy has been attracting great attention. By introducing a negative band-gap element Sn into Ge lattice, the band gaps decrease accordingly, especially the direct bandgap known as Γ valley. Sufficient incorporation can transform the alloy from an indirect band-gap semiconductor to a direct band-gap semiconductor. 8% of Sn is a widely accepted value for this transformation.

In this thesis, theoretical studies of bulk $\text{Ge}_{1-x}\text{Sn}_x$ and $\text{Ge}_{1-x}\text{Sn}_x/\text{Ge}$ quantum well were carried out by using the 8-band k.p method. The influences of growth condition and characterization environment were investigated, and the calculated parameters, such as spontaneous emission rate of the quantum well provide a good guide for the following experimental work on realizing direct band-gap $\text{Ge}_x\text{Sn}_{1-x}$ thin films.

Instead of the widely reported epitaxial growth methods, a modified magnetron co-sputtering method was used to fabricate $\text{Ge}_x\text{Sn}_{1-x}$ thin films. To figure out the proper deposition

parameters and environment, high-quality Ge and Sn thin films were separately fabricated at first. Various combinations of growth power, chamber pressure and growth time were performed to get high-quality films. The $\text{Ge}_x\text{Sn}_{1-x}$ thin films were fabricated on Si, Ge and GaAs substrates. Characterization techniques such as atomic force microscope, X-ray diffraction and Fourier transformation infrared microscopy were used to characterize the crystalline quality and optoelectronic properties. The peaks observed in the ω - 2θ spectra confirm the successful synthesis of $\text{Ge}_x\text{Sn}_{1-x}$ thin films, and the shifted transmittance spectra demonstrate that the bandgap of the material can be tuned by varying the growth parameters.

Optoelectronic applications based on the $\text{Ge}_x\text{Sn}_{1-x}$ thin films were explored. Metal-semiconductor-metal photoconductor, and $\text{Ge}_x\text{Sn}_{1-x}/\text{n-GaAs}$ hetero-structure photodetector were fabricated by standard optical photolithography technique associated with various deposition and etching methods. Current-voltage properties, photocurrent, photoluminescence, responsivity, and specified detectivity of the devices were characterized. The performance parameters of such devices show the high potential of the $\text{Ge}_x\text{Sn}_{1-x}$ alloys prepared by the modified co-sputtering for photodetection.

Enhancement techniques have been applied to the GeSn/GaAs hetero-structure photodetectors. Instead of GeSn thin film, GeSn quantum dot sheet was fabricated on GaAs substrate by taking advantage of sputtering deposition and rapid thermal annealing. The enhancement factor of the specific detectivity for this configuration is around 3 to 6 times. Performances of such device were further optimized by fabricating a metallic 2-dimensional subwavelength hole array structure in the absorption window on the top of the GeSn quantum dot sheet. Surface plasmon resonance occurred when the light of specified wavelength

interacted with the metallic structure, resulting in an enhancement of 2 to 4 times on the basis of GeSn quantum dot/GaAs hetero-structure photodetector. The final detectivity of the 2DSHA GeSn quantum dot/GaAs hetero-structure infrared photodetector reaches a considerable high value of 2.3×10^{10} jones at 1450 nm.

Chapter 1. Introduction

1.1 Motivation

Semiconductors can be basically divided based on their band structure into two categories: direct band-gap materials and indirect band-gap materials. Whether or not the bandgap is direct has a profound influence on their suitability for the use in optoelectronic devices. As shown in Figure 1.1, GaAs is one of the typical direct band-gap semiconductor materials where its conduction band minimum aligns with its valence band maximum at the same k point in the reciprocal space. In contrast, misalignment occurs in the band structure of Ge. For any electron transition, the conservation of total energy and momentum must be fulfilled. These requirements could be easily met for direct band-gap materials, while for indirect band-gap materials, phonon included interaction is necessary which highly suppresses the effectiveness of light absorption/emitting.

Fig. 1.1 Energy band structures of direct band-gap material GaAs and indirect band-gap material Ge. The bandgap of GaAs is 1.42 eV located at the direct Γ valley, while the bandgap of Ge is 0.66 eV located at indirect L valley[1, 2].

Group IV semiconductors such as silicon and germanium have been in the dominant place in the area of electronic applications for over two decades. Their advantages, for example, their abundance in earth's crust, very mature fabrication technology, and very stable oxide structure have made them the most widely used semiconductors. Unfortunately, both materials are indirect band-gap that immensely restricts the development in optoelectronic applications [3-8]. Many research groups have to find alternative direct band-gap materials.

Group IV $\text{Ge}_{1-x}\text{Sn}_x$ alloy is one of the most prospective candidates. By incorporating Sn into the Ge lattice, the band structure can be tuned, and at some point, sufficient substitution of Sn will transform this material from indirect band-gap material to direct band-gap material. Its bandgap lies in the near-infrared and mid-infrared range that is rare for existing optoelectronic materials. Most importantly, this material is a germanium based alloy which means its related fabrication and integration process is fully compatible with the silicon technology.

$\text{Ge}_{1-x}\text{Sn}_x$ alloy was first predicted in 1987 [9] being turned into direct band-gap material when the Sn composition rises up to 20%. Considering the beneficial effect of in-plane lattice strain, two hetero-epitaxial systems were proposed to have direct bandgap in the 2.2 – 2.4 μm range which were biaxially strained $\text{Ge}_{0.98}\text{Sn}_{0.02}$ on unstrained Ge upon Si (001) or (110), and biaxially strained Ge on unstrained $\text{Ge}_{0.87}\text{Sn}_{0.13}$ upon Si (001) or (110) [10]. Many different calculation methods and simulation models have been tried by research groups. Empirical pseudopotential method has been tried to analyze the energy band structure of GeSn in zinc-blende structure with the prediction of the direct bandgap in the infrared range [11]. Studies using this method in recent years focused on more specific parameters like effective masses of electron/hole on various crystal planes [12] and biaxial external strain [13], or structures like

strained GeSn/GeSiSn hetero-structure [14]. Another method that is widely used for the calculation of energy band structure for especially novel materials known as the first-principle method, was also used by many groups to analyze the band structure of GeSn alloy. By using a state-of-art linear combination of atomic orbitals method in the framework of density function theory, researchers presented the equilibrium structural properties, band structure, dielectric constant and reflectance spectrum of GeSn alloy in zinc-blende phase [15]. Structural stability, elastic, dynamical and thermos-dynamical properties are also predicted by first-principle method [16, 17]. Other methods such as scalar-relativistic linear-muffin-tin-orbital method [18] and full potential linearized augmented plane [19, 20] wave method have demonstrated their contribution to the calculation of the structural and electronic properties of GeSn alloy. The most favorable calculation method for engineering, meanwhile the method that was used in this thesis, is k.p method. It is simple but accurate especially in a short range near the Γ point in the reciprocal space, which is of most interest to optoelectronic applications. Structures with quantum confinement effect such as GeSn/SiSn quantum dots [21] and GeSn/Ge quantum wells [22] were simulated by k.p method, as prior work for probable applications. This method is also widely applied to provide simulation reference to experimental performances of structures like GeSn bulk laser [23] and GeSn n-field effect transistor [24].

These theoretical works have attracted great interest and pushed plenty of experimental efforts to grow such compounds. Since researchers successfully grew diamond-structured semimetal α -Sn by molecular beam epitaxy on lattice-matched InSb and CdTe substrates, epitaxial growth of $\text{Ge}_{1-x}\text{Sn}_x$ is achievable. Two challenges faced are the non-ignorable mismatch between the lattice constants of Ge and Si and the instability of the cubic α -Sn at

room temperature. From the 1980s to 1990s, metastable $\text{Ge}_{1-x}\text{Sn}_x$ alloy at different alloy compositions was fabricated by MBE [25]. Major problems encountered included the propensity for Sn segregation, inferior crystallinity, and poor thermal stability. Recently, advance in chemical vapor deposition has made it possible to grow binary $\text{Ge}_{1-x}\text{Sn}_x$ semiconductor alloys. This approach directly deposited the material on silicon substrates. In this case, the lattice mismatch between $\text{Ge}_{1-x}\text{Sn}_x$ alloy and Si substrate was relieved by the periodic misfit dislocations located at the interface that ensured no dislocations propagating into the thin films. This feature highly enhanced the crystal quality of the thin film and improved the optoelectronic performances based on the material. In year 2015, a research group has firstly reported the observation of direct transition in bulk $\text{Ge}_{1-x}\text{Sn}_x$ alloy in terms of photoluminescence[23]. The key point of their achievement is growing a high-quality Ge virtual substrate between $\text{Ge}_{1-x}\text{Sn}_x$ layer and the Si substrate. The high density of misfit dislocations appeared in the interface of $\text{Ge}_{1-x}\text{Sn}_x$ layer and the virtual substrate that is the most efficient type of dislocation to induce strain relaxation. No threading dislocations reached to the surface of $\text{Ge}_{1-x}\text{Sn}_x$ layer due to the existence of the virtual substrate. Very strong enhancement of PL signal in low temperature confirmed that it originated from direct band-gap transition within the high-quality strain-relaxed $\text{Ge}_{1-x}\text{Sn}_x$ layer. Lasing under optical pumping was observed by fabricating Perot resonators based on the material.

Since optoelectronic performances was demonstrated experimentally, much interest is paid to the application of $\text{Ge}_{1-x}\text{Sn}_x$. The p-i-n photodiode is one of the optoelectronic devices that draws attention. Direct-gap dominated optical transitions were observed in the electroluminescence spectrum in a Si/ $\text{Ge}_{1-x}\text{Sn}_x$ heterostructure p-i-n photodiode [26]. In a

comparison between GeSn p-i-n photodiode and unstrained pure Ge photodiode, a 20 meV shift of peak location from GeSn to Ge was observed, indicating the change in energy bandgap [27]. Great effort has been made to introduce larger Sn composition into Ge lattice. Up to 8% of Sn was achieved by a double heterojunction Ge/GeSn/Ge photodiode [13] and GeSn/Ge p-n heterojunction [28]. Both groups reported the observation of the peak near 2.15 μm . As the Sn composition goes higher (more than 10%), the lattice mismatch becomes a big issue to the quality of the material. Growing a virtual substrate of high-quality Ge thin film proved to be one of the probable solutions [23]. In this case, the location of the signal peak in the electroluminescence spectrum red-shifted further.

Photodetection is another important application of $\text{Ge}_{1-x}\text{Sn}_x$ alloy. Its theoretical detective range starts from 1.8 μm to 3 μm depending on the Sn concentration in the material which happens to be the wavelength range commonly used in the telecommunication area. Therefore, a reasonable responsivity or detectivity of $\text{Ge}_{1-x}\text{Sn}_x$ photodetector is highly expected. It is found that even at very low Sn concentration (2%), the quantum efficiency of GeSn photodetector is higher than that in comparable pure Ge device at low temperature [29]. The spectral range of the GeSn device responsivity is obviously increased to around 1.7 μm , beyond the direct bandgap of Ge. This makes it possible to cover the whole telecommunication band just using group IV semiconductor materials. Increasing the Sn concentration to 4% in a GeSn p-i-n photodetector on Si substrate, the responsivity observed at 1.6 μm is increased more than a factor of 10 in the comparison of Ge reference diode [30]. High responsivity is achieved by upgrading the fabrication technique and increasing the quality of GeSn active layer [28, 31-33]. Different types of photodetectors are explored by the researchers, for example, GeSn p-i-

n waveguide photodetector, GeSn/Ge quantum-well photodetector, GeSn/Ge multi-quantum well photodetector[34]. The dark current of the GeSn/Ge quantum well photodetector is highly reduced due to the relaxed suppressive strain in the multi-quantum well structure, hence increasing the signal-to-noise ratio of the responsivity. And due to the quantum confinement in the quantum well, the detective range of the device is further increased to larger wave with the help of higher Sn concentration.

Popular fabrication techniques to grow GeSn alloy are chemical vapor deposition and molecular beam epitaxy which are time-consuming and expensive. Researchers once tried using magnetron sputtering to deposit GeSn alloy in 1990 [35]. GeSn p-i-n photodetector has also been manufactured by sputtering [36]. In this thesis, the author explores the possibility of the fabricating high-quality GeSn thin film and its related application using a modified magnetron sputtering method. Reasonable quality of the material and responsivity of the GeSn based optoelectronic device are obtained. It provides a competitive alternative for the mass fabrication of GeSn based devices.

1.2 Objectives

1. To theoretically calculate and simulate the band structure of bulk $\text{Ge}_{1-x}\text{Sn}_x$ material and $\text{Ge}_{1-x}\text{Sn}_x$ quantum well and estimate the spontaneous emission rate of the specified $\text{Ge}_{1-x}\text{Sn}_x$ material with various Sn concentration. The author wants to have a clear understanding of the factors that have influences on the band structure and their associated effect reflected on the photonic performances. It serves as theoretical guidance of the following experimental work. The model used in this simulation is based on an 8-band k.p method.

2. To realize synthesizing $\text{Ge}_{1-x}\text{Sn}_x$ thin film using our modified magnetron sputtering deposition system. Despite the widely used epitaxial growth methods such as CVD and MBE for $\text{Ge}_{1-x}\text{Sn}_x$, the author wants to explore the possibility of acquiring high-quality $\text{Ge}_{1-x}\text{Sn}_x$ thin films using a modified magnetron sputtering system. The upgraded deposition system significantly reduces the deposition rate and increase the fineness of the material particle which highly improves the quality of the thin film deposited.

3. To characterize the crystalline and optoelectronic properties of $\text{Ge}_{1-x}\text{Sn}_x$ thin films. X-ray diffraction method is the major tool to analyze the crystalline quality of $\text{Ge}_{1-x}\text{Sn}_x$ thin film. By figuring out the relative displacement of the peaks in the XRD spectrum, the elementary composition can be calculated with the help of Vegard's Law and Bragg's equation. The optoelectronic properties of the $\text{Ge}_{1-x}\text{Sn}_x$ are mainly analyzed by FTIR measurement. The transmittance spectrum of the thin film revealed the change in the bandgap of different samples fabricated in various environment.

4. To fabricate and characterize GeSn based photodetectors. The performance of photoelectron conversion will be measured by characterizing various GeSn devices. Standard optical photolithography associated with various fabrication methods such as wet/dry etching, E-beam evaporation, and lift-off process are used to define the structure of the photodetectors. The author designed an optoelectronic performance measuring platform which is flexible for particular devices in different cases.

5. To apply advanced enhancement methods on the basis of GeSn quantum-dot infrared photodetectors. The GeSn quantum-dot sheet is fabricated by sputtering deposition with rapid thermal annealing process. The 2-dimensional subwavelength hole arrays are defined by

electron beam lithography designed for specific resonance wavelength in the infrared range for the enhancement of surface plasmon polaritons. The responsivity and detectivity of the photodetectors can be increased by confining the light at the interface between metallic hole array and active GeSn layer.

1.3 Major achievements

The major achievements are listed below:

1. The author calculated and simulated the band structure, E-k dispersion relation, density of states, electron-hole state distribution, and spontaneous emission rate spectrum of GeSn/Ge quantum well using an 8-band k.p method. The parameters, conditions, and environments are well studied. The shrinking of the energy bandgap, the change in the electronic band structure and the shift in the spontaneous emission rate spectrum with respect to the elementary composition are well understood. An abnormal room temperature enhancement in the Spontaneous Emission Rate Spectrum (SERS) in the indirect band-gap GeSn/Ge quantum well is observed.

2. Ge and Sn thin films were deposited using single-target magnetron sputtering. Before co-sputter $\text{Ge}_{1-x}\text{Sn}_x$ alloy, unitary deposition was applied for finding out the proper deposition environment and growth parameter for high-quality thin film. The morphology of the thin film was characterized mainly by the atomic force microscope and scanning electron microscope. The surface roughness was the major index to estimate the uniformity and crystallinity. A series of parameters including chamber pressure, deposition power, deposition time, pre-deposition time and pre-deposition pressure was figured out for the compromise of two-target co-

sputtering.

3. $\text{Ge}_{1-x}\text{Sn}_x$ thin film was synthesized by co-sputtering on different substrates including Si, Ge and GaAs substrates that have a similar lattice constant. The elementary composition of the thin film was controllable through changing the ratio between Ge and Sn sputtering power. The morphology properties of the thin film were mainly characterized by atomic force microscope and the surface roughness is the major index for estimating the quality of the thin film. The crystallinity was characterized by XRD. The peaks that refer to $\text{Ge}_{1-x}\text{Sn}_x$ layer were observed in the 2θ - ω spectrum indicating the successful synthesizing of GeSn alloy. The actual Sn/Ge ratio was confirmed by analyzing the relative peaks' location in the 2θ - ω spectrum. The relation between the energy band and its elementary composition was revealed by the transmittance spectrum measured by FTIR. A red shift with increased the Sn/Ge ratio in the absorption edge was clearly observed which corresponds to the simulation result. Photoluminescence measurements carried out by a 1064 nm solid-state laser indicated the allowed transition wavelength of the $\text{Ge}_{1-x}\text{Sn}_x$ alloy is near 2 μm .

4. GeSn metal-semiconductor-metal photoconductor was fabricated on a GaAs substrate using a hard mask. The photoelectric conversion efficiency was evaluated by a 1064 nm solid-state laser as it has much smaller photon energy than the bandgap of GaAs, which eliminated the contribution of the substrate. This GeSn photoconductor has a reasonable responsivity that is comparable to the reported GeSn photoconductor fabricated by CVD.

5. GeSn/GaAs hetero-structure photodetectors were fabricated by a standard optical photolithography method. The devices are based on two types of GeSn material with different Sn/Ge ratios. The author characterized the responsivity and specific detectivity of the devices

and observed different behaviors to the same tunable-wavelength laser source. This originated to the different electronic band structures induced by adjustable Sn composition. Current-voltage characteristic of the devices showed a junction resistance that is 4 orders larger than that of the photoconductor, highly reducing the magnitude of the dark current and improving the signal-to-noise ratio. The author also solved the metal contact potential barrier issue by using a multilayer-structure contact with a thermal treatment. It ensures the contribution of possible potential barriers coming from the contact is excluded from the hetero-junction.

6. Enhancement techniques were explored for the GeSn quantum dot/GaAs hetero-structure infrared photodetector. By replacing the GeSn thin film with GeSn quantum dot sheet, the corresponding responsivity and detectivity were enlarged 3-6 times. 2D subwavelength hole array was fabricated in the absorption window on the top of quantum dot sheet to confine the light at the interface between hole array and GeSn layer. Surface plasmon resonance at a specified wavelength increased the enhancement factor of responsivity and detectivity to 11 times.

1.4 Organization of the thesis

This thesis consists of 9 chapters in total, starting with the motivations, objectives, major contributions and organization that have already been discussed in chapter 1.

Chapter 2 covers background information on theories and calculation methods. It includes the introduction of direct and indirect band-gap semiconductors, the fundamental of k.p method that is used in simulation and calculation and the development in GeSn alloy and its optoelectronic applications.

Chapter 3 introduces the methods and tools that are used in this thesis including the fundamental of magnetron sputtering deposition, X-ray diffraction characterization, photoluminescence measurements platform, FTIR, and X-ray photoelectron spectroscopy.

Chapter 4 discusses the theoretical study of $\text{Ge}_{1-x}\text{Sn}_x$ material using 8-band k.p method. Band structure, energy band lineup, electronic band structure and density of states of a $\text{Ge}_{1-x}\text{Sn}_x/\text{Ge}$ quantum well are calculated. The spontaneous emission rate and optical gain are then calculated based on the band structure and density of states. The author focused on the influences of Sn composition, in-plane strain, temperature and the width of well on the performances of the GeSn quantum well. A room temperature enhanced spontaneous emission rate in a naturally strained $\text{Ge}_{1-x}\text{Sn}_x/\text{Ge}$ quantum well is studied. The compressive strain in the GeSn layer is proved to be the major obstacle for the photoelectric performances.

Chapter 5 discusses the growth and characterization of high-quality Ge/Sn thin films. Unitary-target sputtering is used for the growth of Ge and Sn thin films. The morphology is analyzed by AFM and SEM. The surface roughness of samples is the key factor to estimate the quality. This chapter serves as the preparation for the fabrication of GeSn thin films by magnetron co-sputtering.

Chapter 6 discusses the fabrication of $\text{Ge}_{1-x}\text{Sn}_x$ thin films and the metal-semiconductor-metal photoconductor based on GeSn thin film. After figuring out the proper deposition parameters and environment for the compromise of depositing both materials in good quality, the co-sputtering is used to fabricate GeSn films. The $\text{Ge}_{1-x}\text{Sn}_x$ thin films with various Sn/Ge ratio are characterized. AFM is used for analyzing morphology. XRD and XPS methods measure the crystallinity and chemical bond distribution. FTIR measures the transmittance

spectrum of the thin films that reflect the band structure of the samples. Photo-electron conversion effectiveness is examined through the MSM structure. This device is defined by a hard mask using optical lithography. The photocurrent of the device is stimulated by a continuous solid-state 1064 nm laser. Performances including dark current, bias-dependent photocurrent and responsivity are measured.

Chapter 7 discusses the fabrication and characterization of GeSn/GaAs hetero-structure infrared photodetector. The mesa of the device is defined by standard optical photolithography combined with the wet-etching method. The metal contact is deposited by E-beam evaporation. Challenges including the elimination of Schottky barrier for both active layer and substrate, and selecting etching solvent for both layers are studied and solved. The device is packaged by wire bonding technique. Optoelectronic performance of the device is carried out by a tuneable-wavelength laser. Responsivity and detectivity as the function of the incident light wavelength are measured. The resistance in the heterostructure is 4-order increased and responsivity is 2-order increased in comparison to the photoconductor in the previous chapter.

Chapter 8 explores the advanced enhancement techniques on the GeSn/GaAs hetero-structure photodetector. By taking advantage of the modified magnetron sputtering deposition, GeSn quantum dot sheet instead of GeSn thin film is fabricated on the GaAs substrate. 2D SHA metallic structures defined by electron-beam lithography is fabricated on the top of the device. Obvious enhancement in responsivity and detectivity is observed. Surface plasmon resonance wavelength determined by the period of hole array is reflected in the selective enhancement at a different wavelength in the responsivity and detectivity spectra. Electric field confinement and surface plasmon resonance are simulated by software and are in consist of experimental

performances.

Chapter 9 discusses the conclusions of this project and the recommendations for future work.

Chapter 2. Background

Almost all the optoelectronic and electronic performance of a semiconductor material relies on the energy band structure. Researchers could estimate the properties of a material by studying its band structure. This chapter firstly introduces how the energy bands are formed from discrete energy states in a single atom, the equation to describe an electron in periodic potential and the Brillouin zone, followed by the calculation method of the electronic band structure. Then the development in the theoretical analysis is discussed, which provides the prospective properties of the GeSn alloy. The last session of this chapter introduces the experimental realization methods of GeSn related works.

2.1 Electronic band theory

In solid-state physics, band structure, also known as electronic structure, E-k dispersion curves or E-k relations, describes the allowed states and the disallowed states that an electron stays in solid. The allowed states are called energy bands, and the disallowed states are called energy gaps.

In free space, the electrons of a single isolated atom occupy discrete energy levels. When multiple atoms join together to form a molecule, their atomic orbitals which stand for different states will overlap. The Pauli Exclusion Principle describes that no two electrons can have the same quantum numbers (energy states) in a molecule. In this case, a diatomic molecule that has two identical atoms binding with each other, splits each of the atomic orbitals into two molecular orbitals of different energy, allowing both electrons in the molecule to occupy one orbital without having the same energy. If we consider expanding diatomic molecule to a

crystal lattice that a number N of identical atoms join together to form a solid, similarly the overlapped orbital of number N will split into N discrete orbitals with different energy of number N . For a piece of solid, the number N normally is on the scale of 10^{22} , making the energy difference between each discrete energy level in the scale of 10^{-22} eV. Each adjacent energy levels are so closely distributed, that can be considered as a continuum like an energy band, as shown in Figure 2.1. Band gaps are formed in the energy range that two adjacent energy bands are not able to cover. Energy states that lie in the gap are prohibited for the electrons to occupy.

Fig. 2.1 The splitting of the energy states and the formation of Energy bands. The energy bands are formed when atoms are densely packed in a crystal lattice, and there will be gaps between the bands where no electrons are allowed to occupy[37].

The probability of an electron to occupy an energy state (E) at thermodynamic equilibrium can be described by Fermi-Dirac distribution written as:

$$f(E) = \frac{1}{1 + e^{(E-\mu)/k_B T}} \dots\dots\dots (1)$$

where $k_B T$ is the product of Boltzmann's constant and temperature and μ is the total chemical potential of electrons (Fermi level). There could be infinite energy states for a single atom that

extends to extremely high energy, hence there could be infinite numbers of energy bands. Those bands corresponding to very high energy can be ignored because there is not much chance for an electron to occupy. Bands corresponding to very low energy associated with core orbitals can be ignored too because they are always fully occupied by electrons. The most interesting bands for us are the bands near the Fermi level, which meanwhile significantly determines the electronic and optoelectronic properties of a material. For non-conductive materials such as semiconductors and insulators, Fermi level lies within a bandgap. The closest band above Fermi level is named conduction band, and the closest band below Fermi level is named valence band. For conductive materials such as metals and semi-metals, Fermi level lies inside a band which can be a valence band or a conduction band depending on what type of charge transport it is.

2.2 Description of an electron in a lattice

Bloch wave function is a type of function to describe a particle in a periodically-repeating environment, most commonly an electron in a crystal lattice. The solution for the single-electron Schrodinger equation in a periodic potential is in a form of Bloch waves:

$$\Phi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \dots\dots\dots (2)$$

where $\mathbf{k}$ is the wavevector, $\mathbf{r}$ is the position, u is the periodic function that has the same periodicity as the crystal. For each value of $\mathbf{k}$, there are multiple solutions to the Schrodinger equation labeled by n , also known as the band index. As the wavevector smoothly changes, we can define a function $E_n(\mathbf{k})$, which is the dispersion relation for electrons in the energy band.

In solid-state physics, the Brillouin zone is a uniquely defined cell in reciprocal space.

The boundaries of the cell given by planes are related to points in the reciprocal lattice. It is found that the solutions of the Bloch wave can be completely characterized by their behavior in a single Brillouin zone. The wavevectors can take any value inside the Brillouin zone. Wavevectors outside the Brillouin zone are physically identical to the states within the Brillouin zone. Special high symmetry points/lines in the Brillouin zone are assigned labels like Γ (000), Δ (100), Λ (111), and Σ (110). With the help of the Brillouin zone, we are able to define the direct band-gap material and indirect band-gap material. When the lowest energy state of the conduction band (conduction band minimum) and the highest energy state of the valence band (valence band maximum) take the same wave vector value, we call it a direct bandgap. When they are misaligned in the k space, we call it an indirect bandgap.

Fig. 2.2 The schematic of the first Brillouin zone. High symmetrical points are denoted in the first Brillouin zone[38].

For the optoelectronic application of semiconductors, transition in direct band gap gains much

more interest than indirect bandgap because interactions among electrons, holes, photons, and phonons must obey the conservation of total momentum, which in another word direct transition is much more effective than indirect transition. Taking the process of recombination as an example, an electron near the conduction band minima annihilates a hole in the valence band with photon released. It is possible in a direct band structure because the momentum of electron remains unchanged during the process, but not for an indirect band structure since the conservation of the momentum is violated. A photon cannot carry the crystal momentum. As a result, the interaction with phonon must be included whose momentum equals the momentum difference between the electron in the conduction band and the hole in the valence band (Figure 2.3). The involvement of phonon makes the process much less likely to happen in comparison to direct transition. This is the reason that most light-emitting devices and laser diodes are made of direct band-gap semiconductors.

Fig. 2.3 The schematic of direct and indirect transition. The direct transition process only contains the release or absorption of energy, while the indirect transition process includes both the change of momentum and energy[39].

2.3 Calculation method – k.p model

Studying a single isolated band can help to reveal the physics of $k.p$ method, which can be substituted by conduction band of many semiconductors and even by valence band under certain circumstances. Starting from one-electron Schrodinger equation as following:

$$\left(\frac{p^2}{2m} + V\right)\psi = E\psi \dots\dots\dots (3)$$

wave function ψ is substituted by periodical Bloch wave function as discussed in the last section. p is the quantum-mechanical momentum operator, V is the periodical potential with the same periodicity as the crystal lattice. The Schrodinger equation is rewritten in terms of $u_{nk}(r)$ as:

$$\left[\frac{p^2}{2m} + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + \frac{\hbar^2 k^2}{2m} + V(r)\right]u_{nk}(\mathbf{r}) = E_n(k)u_{nk}(\mathbf{r}) \dots\dots\dots (4)$$

$\mathbf{k}$ is the wave vector consisting of three real numbers with dimensions of inverse length in reciprocal lattice. $\mathbf{p}$ is the 3-dimensional momentum operator. The term $\mathbf{k} \cdot \mathbf{p}$ has a form as below:

$$\mathbf{k} \cdot \mathbf{p} = k_x(-i\hbar \frac{\partial}{\partial x}) + k_y(-i\hbar \frac{\partial}{\partial y}) + k_z(-i\hbar \frac{\partial}{\partial z}) \dots\dots\dots (5)$$

The Hamiltonian is expressed by the sum of two terms:

$$H = H_0 + H_k', \quad H_0 = \frac{p^2}{2m} + V \dots\dots\dots (6)$$

This expression is the basis of $k.p$ perturbation theory. The first term H_0 with no interference of the wave vector where $\mathbf{k}=0$ (i.e., Γ point) is “unperturbed Hamiltonian”. Term H_k' is the perturbation. The solution of this analysis is an expression for $E_{n,k}$ and $u_{n,k}$ in terms of eigenvalue energies and wavefunctions at $\mathbf{k}=0$.

Using the second-order perturbation theory, we find the result $E_{n,k}$ and $u_{n,k}$ are in forms as

below:

$$E_{n,\mathbf{k}} = E_{n,0} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\langle u_{n,0} | \mathbf{k} \cdot \mathbf{p} | u_{n',0} \rangle|^2}{E_{n,0} - E_{n',0}} \dots\dots\dots (7)$$

$$u_{n,\mathbf{k}} = u_{n,0} + \frac{\hbar}{m} \sum_{n' \neq n} \frac{\langle u_{n,0} | \mathbf{k} \cdot \mathbf{p} | u_{n',0} \rangle}{E_{n,0} - E_{n',0}} u_{n',0} \dots\dots\dots (8)$$

In this way, the energy $E_{n,k}$ as a function of wavevector k can be calculated.

More precise E - k relations can be calculated by including the spin-orbit interaction. The spin-orbit interaction term is added to the Hamiltonian written as:

$$H = \frac{p^2}{2m} + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + \frac{\hbar^2 k^2}{2m} + V(r) + \frac{\hbar}{4m^2 c^2} [\nabla V \times (\mathbf{p} + \hbar \mathbf{k})] \cdot \vec{\sigma} \dots\dots\dots (9)$$

where $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ is a vector consisting of three Pauli matrices. Similar perturbation analysis can be applied to get the new E - k relations. In chapter 3, a strained GeSn/Ge quantum well structure is studied. The influences of the indirect L valley is included in the calculation. The 8-band k .p Hamiltonian for the strained quantum well is written as below (details can be found in Ref [40]):

$$H^i = \begin{bmatrix} E^c & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. \\ 0 & E^c & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. \\ \frac{1}{\sqrt{2}}P_- & 0 & HH & c.c. & c.c. & c.c. & c.c. & c.c. \\ -\frac{\sqrt{2}}{\sqrt{3}}P_z & \frac{1}{\sqrt{6}}P_- & S^* & LH & c.c. & c.c. & c.c. & c.c. \\ -\frac{1}{\sqrt{6}}P_+ & -\frac{\sqrt{2}}{\sqrt{3}}P_z & -R^* & 0 & LH & c.c. & c.c. & c.c. \\ 0 & -\frac{1}{\sqrt{2}}P_+ & 0 & -R^* & -S^* & HH & c.c. & c.c. \\ -\frac{1}{\sqrt{3}}P_z & -\frac{1}{\sqrt{3}}P_- & \frac{S^*}{\sqrt{2}} & -D & -\sqrt{\frac{3}{2}}S & \sqrt{2}R & SO & c.c. \\ -\frac{1}{\sqrt{3}}P_+ & \frac{1}{\sqrt{3}}P_z & -\sqrt{2}R^* & -\sqrt{\frac{3}{2}}S^* & D & \frac{S}{\sqrt{2}} & 0 & SO \end{bmatrix} + VBO \quad \dots(10)$$

VBO is abbreviation of valance band offset. *LH*, *HH* and *SO* are the abbreviations of light hole term, heavy hole term and spin-orbit hole term. *R*, *S* and *D* the interaction term among light hole heavy hole and SO hole. In the case of GeSn, the contribution of indirect L valley should be included for its really small difference in the band edge of the conduction band. The Hamiltonian of L conduction subbands can be written as:

$$H_L = -\frac{\hbar^2}{2} \frac{\partial}{\partial z} \left(\frac{1}{3m_{l,L}} + \frac{2}{3m_{t,L}} \right) \frac{\partial}{\partial z} - i \frac{\sqrt{2}\hbar^2 k_1}{6} \times \left[\frac{\partial}{\partial z} \left(\frac{1}{m_{l,L}} - \frac{1}{m_{t,L}} \right) + \left(\frac{1}{m_{l,L}} - \frac{1}{m_{t,L}} \right) \frac{\partial}{\partial z} \right] \dots\dots\dots(11)$$

$$+ \left(\frac{2}{3m_{l,L}} + \frac{1}{3m_{t,L}} \right) \frac{\hbar^2 k_1^2}{2} + \frac{\hbar^2 k_2^2}{2m_{t,L}} + V^{[111]}(z) + V_\varepsilon^{[111]}(z)$$

where,

$$V_\varepsilon^{[111]}(z) = a_L \left(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \right) \dots\dots\dots(12)$$

$$k_1 = \frac{1}{\sqrt{2}} \left(k_x + k_y - \frac{2\pi}{a} \right) \dots\dots\dots(13)$$

$$k_2 = \frac{1}{\sqrt{2}} \left(-k_x + k_y \right) \dots\dots\dots(14)$$

$m_{l,L}$ and $m_{t,L}$ are the longitudinal and transverse effective masses along the [111] direction, k_l and k_2 are wave vectors along [110] and [-110] direction, a is the lattice constant of $\text{Ge}_x\text{Sn}_{1-x}$ which is assumed linearly proportional to the material composition given by [22]:

$$a_{\text{Ge}_{1-x}\text{Sn}_x} = 5.657 \cdot (1-x) + 6.489 \cdot x \dots\dots\dots (15)$$

$V^{llll}(z)$ is the energy band offset without inducing any strain, and $V_\epsilon^{llll}(z)$ is the strain-involved energy shift for L valley, ϵ_{xx} and ϵ_{yy} are the in-plane strain, ϵ_{zz} is the strain in the Z direction.

The expression of direct band spontaneous emission rate (SER) can be written as:

$$R_{sp}(E) = \frac{ne^2 E}{\pi m_0^2 \epsilon_0 \hbar^2 c^3} \sum_c \sum_{n_v} \iint \frac{Q_c^{n_c n_v}}{4\pi^2 l} f_c f_v \times \frac{1}{\pi} \frac{\hbar/\tau}{(E_{eh} - E)^2 + (\hbar/\tau)^2} dk_x dk_y \dots\dots\dots (16)$$

E is the photon energy, ϵ_0 is the free-space dielectric constant, n is the refractive index, c is the light speed, $Q_c^{n_c n_v}$ is the squared optical transition matrix element, E_{eh} is the transition energy, and τ is the intraband relaxation time.

2.4 Properties of GeSn alloy

$\text{Ge}_{1-x}\text{Sn}_x$ has gained plenty of interest in the research community because of two reasons. First, it is a semiconductor material composed entirely of group IV material. Second, its bandgap can be adjustable from the near-infrared region to mid-infrared region [41-51]. These two features make this alloy a strong candidate in the competition of next-generation photoelectric material of mass-production manufacturing.

2.4.1 Crystallographic characterization of GeSn thin films

Early researches in the area of $\text{Ge}_{1-x}\text{Sn}_x$ fabrication started in the early 1990s [52]. Molecular beam epitaxy was first tried to synthesizing GeSn on InSb and GaAs (001) substrates. An InSb buffer layer was pre-deposited on the substrates. The $\text{Ge}_{1-x}\text{Sn}_x$ film was deposited on the buffer layer using an electron beam gun for germanium and pyrolytic boron nitride crucibles for Sn. The temperature of the substrates was kept between -25 to -10 °C. Reflection high-energy electron diffraction was used for the classification of the thickness-dependent phases during the growth of the thin film. X-ray diffraction was used to examine the origin and quality of the thin film. As shown in Figure 2.4(a), 2θ - ω scan on 1500Å-thick $\text{Ge}_{0.92}\text{Sn}_{0.08}$ film on (001) InSb substrate with InSb buffer layer showed the peaks corresponding to the periodicity along the growth direction (001). Two peaks at $2\theta=56.8$ and $2\theta=57.8$ observed in Figure 2.4(a) belonged to the buffer InSb layer and GeSn layer respectively. Because pure α -Sn has a larger lattice constant than InSb, if α -Sn were present in the layer, a shoulder should appear at the left side of InSb peak.

Fig. 2.4 (a) XRD 2θ - ω scan of 1500Å-thick $\text{Ge}_{0.92}\text{Sn}_{0.08}$ film on (001) InSb substrate with InSb buffer layer. (b) The rocking curve of InSb buffer layer. (c) The rocking curve of GeSn thin film. The FWHM is larger than of InSb buffer layer, suggesting the lattice quality is poorer.

Rocking curves as shown in Figure 2.4(b), revealed the spread in orientations of the lattice constants in the film. A sharp rocking curve indicated that all the lattice constants are the same,

i.e., good crystal quality. If the orientation of the lattice constant varied in orientation in the film, the curve will broaden (Figure 2.4(c)). This work demonstrated the first synthesis of GeSn alloy with its structural and electrical characterization.

Atmospheric pressure chemical vapor deposition (AP-CVD) was tried on the growth of metastable GeSn alloy on Ge substrate with Sn component up to 8% [53]. Ge_2H_6 was chosen as the Ge precursor and SnCl_4 as Sn precursor to meet the requirement of growing in low temperature. Before the deposition of GeSn, Ge substrate was baked at 650 °C, kept at 320 °C during growth. Figure 2.5(a) shows the cross-section picture taken by a transmittance electron microscope with X-ray diffraction reciprocal space mapping of a 40 nm thick GeSn layer deposited on a Ge substrate. A defect-free GeSn/Ge interface was observed in the TEM photo, demonstrating a high quality that the thin film had. RHEED analysis in Figure 2.5(b) showed a strong surface reconstruction along the [110] direction. In the next figure, RMS clearly showed the appearance of fully strained GeSn peak on (224) Bragg reflections. Post-deposition thermal treatments by rapid thermal annealing method at different temperatures were tried to investigate the thermal stability of GeSn. Similar XRD analysis was used to figure out the influences on the quality of the thin film after annealing. In the ω - ω_0 scan, the FWHM value of GeSn peaks remained almost unchanged for different annealing temperatures, confirmed that they stayed in monocrystalline after thermal treatment. Meanwhile, the relaxation effect was clearly observed in the shift of GeSn peaks in 2θ locations (Figure 2.5(d)).

Fig. 2.5 (a) Cross-sectional image of the sample taken by TEM. (b) The RHEED spectrum of GeSn thin film grown on Ge substrate. Constructive interference of the electron diffraction is observed on GeSn [110] phase. (c) Reciprocal lattice mapping on (224) Bragg reflections showing the full relaxation of compressive strain. (d) $\omega-\omega_0$ scan for a different growth environment.

2.4.2 Optical characterization of GeSn thin films

The electronic band structure of Ge has determined its property as a pseudo-direct semiconductor material that the energy difference between Γ and L valley are very small. By incorporating α -Sn into the Ge lattice, the energy difference between the two gaps increases continuously as increasing the composition of Sn. Previous theoretical works [54] predicted that around 17% Sn in the strain-relaxed GeSn material can realize the transition from indirect bandgap to direct bandgap. Recently, the amount of Sn has been largely decreased to 4% to realize an indirect-to-direct transition [55]. A widely-accepted value of this transition is around 8% that has been experimentally verified [56, 57].

Photoluminescence measurement is one of the important characterization methods to determine the electronic band structure of a material [58, 59]. The characteristic wavelength measured in PL measurement directly reflects the bandgap of the material. the strength and

sharpness of the signal reflect the quality of the material and the nature of the band structure (direct and indirect). PL spectrum of the samples fabricated with various Sn component is shown in Figure 2.6 [60]. Ge thin film as a reference showed a peak located at around 0.8 eV which corresponds to the direct gap of Ge (0.79 eV). Colored curves representing the GeSn thin films slightly shifted to smaller photon energy (longer wavelength), indicated the direct energy gap kept decreasing as the Sn component in the GeSn alloy going higher. However, they are still indirect band-gap semiconductors because their Sn component is not sufficient to convert the band structure. The strength of the GeSn peaks showing in the graph is comparable to Ge peak which is a typical indirect band-gap material.

Fig. 2.6. PL spectrum of the samples fabricated by GeSn with various Sn component. The blue shift of the peaks reflects the decrease in the bandgap of GeSn alloy with higher Sn fraction.

A research group studied the competition between the two gaps [61]. GeSn alloys with Sn component of 0.9%, 3.2%, and 6% were fabricated by a reduced pressure-CVD method. The

PL measurements conducted on each of the samples under different temperatures showed the competition between the direct (Γ) valley and indirect (L) valley. Firstly, a similar red shift of the peak locations was observed when the Sn component increases from 0.9% up to 6% in Figure 2.7. Secondly, as Sn component grew, the indirect peak and direct peak were red-shifting meanwhile moving towards each other and got almost overlapped in the case Sn component equals to 6%. This phenomenon originated to the Vegard's Law which determined the energy band gap of a binary alloy, written as:

$$E_{g,\Gamma}^{GeSn} = E_{g,\Gamma}^{Ge}x + E_{g,\Gamma}^{Sn}(1-x) - b_{\Gamma}^{GeSn}x(1-x) \dots\dots\dots (17)$$

$$E_{g,L}^{GeSn} = E_{g,L}^{Ge}x + E_{g,L}^{Sn}(1-x) - b_L^{GeSn}x(1-x) \dots\dots\dots (18)$$

$E_{g,\Gamma}^{Ge}$, $E_{g,L}^{Ge}$, $E_{g,\Gamma}^{Sn}$ and $E_{g,L}^{Sn}$ represent the direct and indirect bandgap of Ge/Sn respectively. By substituting with the experimental value, we find that the indirect bandgap of GeSn alloy changes faster than the direct bandgap and moves closer to the direct gap as Sn component increases, the same as the graphs illustrated. More importantly, the total strength of the PL signal kept rising from the first sample to the third. Because as two valleys get closer, the GeSn alloy became more direct-like, that there were more chances for the electron-hole pair in the direct valley to perform recombination. Hence, the population of photons generated in a unit time (PL strength) was enhanced when the Sn component increased. We could imagine that if the Sn component of the samples keep increasing when the positions of two valleys exchanges, the PL signal would be much stronger since the material transforms from indirect-like band-gap to direct band-gap. Similar GeSn alloy fabricated by MBE with Sn component up to 10% was also reported [57]

Fig. 2.7 Temperature-dependent PL spectrum of (a) 330 nm $\text{Ge}_{0.991}\text{Sn}_{0.009}$, (b) 130 nm $\text{Ge}_{0.968}\text{Sn}_{0.032}$, (c) 80 nm $\text{Ge}_{0.94}\text{Sn}_{0.06}$. Both direct and indirect bandgaps are decreasing with higher Sn fraction, but the direct bandgap decreases faster than the indirect bandgap. They are overlapped when Sn fraction is 6%. (d) PL spectrum fitted by Gaussian distribution.

A challenge in front is the large compressive strain between the GeSn alloy and commonly used substrate such as Si and Ge. The influences that compressive strain brings in are totally opposite to the influence of introducing Sn. In other word, the compressive strain prohibits the tuning of the electronic band structure in GeSn. A research group has worked out an effective way of fabricating partial-relaxed GeSn alloy on Si substrate [62, 63]. A high-quality Ge buffer layer was deposited on Si substrate as a virtual substrate ahead of depositing GeSn alloy. This layer was grown at 400/750 °C containing a biaxial tensile strain of 0.16% at room temperature as a result of the difference between the thermal expansion coefficients of Si and Ge. Cross-

sectional transmission electron microscopy photos showed a high density of misfit dislocations at the interface between the GeSn layer and the Ge virtual substrate. These dislocations acted as the key point for the relaxation of strain.

Photoluminescence spectra of samples grown on a virtual substrate with different Sn component are shown in Figure 2.8. For Sample A ($X_{\text{Sn}}=8\%$), the strongest PL signal was measured at 300 K with a positive correlation between temperature and PL strength. For Sample B, C, and D, a negative correlation between PL strength and temperature was observed that maximum PL signal was measured at 20 K. Photoluminescence was tremendously enhanced at low temperature. This is a typical characteristic phenomenon for a direct band-gap material such as GaAs. Thermally stimulated electron-hole pairs are more likely to take part in the recombination process at low temperature because their thermal motion is reduced to the lowest level and stay in the conduction band minimum in Γ valley. As for an indirect band-gap material, thermally stimulated electrons stay at the conduction band minimum at L valley. A high temperature boosts the chance for the electrons to jump in Γ valley for recombination. Hence, direct and indirect band-gap materials act totally differently in photoluminescence performance as a function of temperature. A negative correlation between temperature and PL strength is strong evidence of achieving direct band-gap.

Fig. 2.8 Temperature-dependent PL spectrum of Sample A ($\text{Ge}_{0.92}\text{Sn}_{0.08}$) showing a positive correlation between temperature and PL strength, and sample B ($\text{Ge}_{0.904}\text{Sn}_{0.096}$), C ($\text{Ge}_{0.889}\text{Sn}_{0.111}$), D ($\text{Ge}_{0.874}\text{Sn}_{0.126}$) showing a negative correlation. This is regarded as the evidence of observing the transition from indirect GeSn to direct GeSn.

2.5 GeSn optoelectronic applications

It has always been a challenge to integrate optoelectronic devices on Si substrate in the past two decades. Conventional group IV semiconductors such as Si and Ge, have proven their great advantages in the applications of microelectronics but progressed very slowly in optoelectronic applications. One huge obstacle in front is their indirect band-gap nature that limited the quantum efficiency and spontaneous emission rate. Hence high effective optoelectronic applications on Si/Ge basis is extremely hard to achieve [64]. Most of the widely used commercial optoelectronic devices are made of direct band-gap group III-V alloys such as InAs, InSb, and GaAs. Costs of such materials are several times bigger than Si [64-73].

2.5.1 GeSn based infrared photodetection

GeSn became one of the most potential candidate for its adjustable band gap and probable direct band-gap structure [74-81]. An alloy of Sn and Ge improved the performances in the

infrared region associated with a lowering of the direct bandgap [82-99]. First-generation n/i-GeSn/p-Si (110) photodiode detector was reported based on a $\text{Ge}_{0.98}\text{Sn}_{0.02}$ active layer [29]. The GeSn thin film was grown on B-doped Si (100) substrate by ultrahigh vacuum chemical vapor deposition. A 150 nm thick SiO_2 was deposited on the surface of GeSn material for passivation and protection. The mesa of the device is defined by standard optical photolithography followed by reactive ion etching. 20 nm-Cr/200 nm-Au metal contact was deposited by electron beam evaporation associated with lift-off processes. The photoresponse of the devices was measured under the monochromatized light generated by a halogen lamp. The incident light was directed into the window of the device using an optical fiber. The highest device response was obtained at a bias voltage of 0.16V. The wavelength-dependent external quantum efficiency is plotted in Figure 2.9(b). Reasonable photoresponses in all optical communication up to 1750 nm (from O-U bands) region were observed.

Fig. 2.9 (a) Schematic structure of n-i-p GeSn/Si photodetector. (b) The external quantum efficiency of the device as a function of wavelength.

Another p-i-n hetero-structure photodetector was reported based on the GeSn alloy with Sn component increased to 4% [30]. It was fabricated with a solid source molecular beam epitaxial deposition. The 300 nm thick GeSn active layer was deposited on a Ge virtual substrate that was grown under 330 °C by MBE followed by a high-temperature thermal treatment. Responsivities of photodetectors with different Sn component as a function of wavelength and bias voltage was measured. The maximum responsivity of 181 mA/W was measured for GeSn photodetector with 2.8% and 4% Sn concentration (Figure 2.10). The optical response of GeSn photodetector with 4% Sn concentration at $\lambda=1600$ nm increased by more than a factor of 10 with respect to the reference Ge photodetector. Red shift was observed in the responsivity spectrum as a function of the increased Sn concentration. Similar works have also been reported in references [27, 28, 36, 100].

Fig. 2.10 Responsivity (A/W) spectrum of GeSn photodetectors with different Sn concentrations.

2.5.2 Lasing in GeSn alloy

Since the direct-bandgap GeSn alloy was achieved as we discussed in the previous session, GeSn laser was another feasible application[101-106]. An optically pumped GeSn microdisk laser was reported in the year 2016 [107]. The active GeSn epilayers were deposited on a Ge virtual substrate grown on Si (001) using a reactive gas source epitaxy process adapted to an industrial reduced pressure chemical vapor deposition reactor. The mesa of the device was defined by electron beam lithography followed by reactive ion etching using a Cl_2/Ar plasma. The virtual Ge substrate underneath the GeSn layer was selectively etched away by isotropic CF_4 dry etching, leaving GeSn microdisk adjoined to the Ge pillar. Biaxial compressive strain within the GeSn layer is partly relaxed in this way, enlarging the energy separation between the indirect L valley and direct Γ valley. The microdisk laser was optically pumped by a pulsed Nd:YAG laser with a center wavelength of 1064 nm. The energy of the photon being excited from the microdisk was around 0.5 eV as shown in Figure 2.11. The lasing threshold was observed at 200 kW/cm^2 after which output power increased significantly with rising input power. Light-in light-out (LL) curve was in an S-shape with a lasing threshold at approximately 220 kW/cm^2 . Saturation occurred at a high pumping level as a result of the heating effect.

Fig. 2.11 (a) Schematic fabrication process of GeSn microdisk laser by dry etching. (b) SEM images of GeSn microdisk laser. The radius of the microdisk is 3.6 micron. (c) PL spectrum as a function of optical excitation. The energy of the released photon is around 0.5 eV.

Typical Fabry-Perot structure GeSn laser was also reported in reference [102]. The active GeSn layer was grown by a reduced pressure chemical vapor deposition reactor. A 700-nm thick Ge buffer layer was deposited on a silicon substrate associated with in-situ annealing, followed by a 1000-nm thick GeSn epilayer with 9% of Sn concentration. On top of the GeSn layer was a 10-nm thick Ge cap. The wet chemical etching was used to define a ridge waveguide with 5 μm -width for the optical pumping characterization. It was carried out by a pulsed laser operating at 1060 nm with 45 kHz repetition rate and 6ns pulse width. The

performance was measured by the light-in light-out curve of the 600 μm -long devices operating at 10 K and 90 K. The threshold values were measured at 68 kW/cm^2 and 166 kW/cm^2 for 10 K and 90 K respectively as shown in Figure 2.12. Temperature-dependent photoluminescence measurement was conducted. The intensity increased significantly as the temperature decreased from room temperature to 10K, indicating a typical property of direct band-gap material. The blue shift of the PL peaks was observed.

Fig. 2.12 Light-in light-out curve of 600 μm -long devices operating at 10 K and 90 K. Insets are SEM image of the device and the temperature-dependent PL spectrum. Threshold power density is 68 kW/cm^2 at 10 K, and 166 kW/cm^2 at 90 K.

2.6 Summary

This chapter introduces important theoretical backgrounds on electronic band theory. The energy bands are formed by the splitting of the discrete energy states when oceans of individual

atoms are orderly arranged in a lattice. The most important two bands, conduction band, and valence band, which are the closest bands to Fermi level, determine most of the electronic and optoelectronic properties of a solid. An electron at an energy state (in a band) can be described by solving Schrodinger's equation in a periodic potential. The solution is in the form of Bloch wavefunction that can use in the k.p simulation model. By taking advantage of second-order perturbation theory, the E-k dispersion relation is revealed. The development of the GeSn alloy and its application are illustrated in the second half of this chapter. The research community has explored the potential of this material in photodetection and lasing, indicating that GeSn is likely the next-generation optoelectronic semiconductor material.

Chapter 3. Methods of growth and characterization

In this chapter, methods of realization and characterization involved in this project will be discussed. Magnetron sputtering deposition is used for the fabrication of GeSn alloy thin film. The crystallography and elementary composition of the sample are examined by HR-XRD associated with XPS. The optoelectronic properties are characterized by PL and FTIR measurements. Optical photolithography associated with etching and electron beam evaporation is used to define the pattern of the optoelectronic device. The performances of the devices are characterized by an integrated optoelectronic measurement platform.

3.1 Modified magnetron sputtering deposition system

Magnetron sputtering deposition is one of the widely used physical vapor deposition methods where plasma carrying positive charge is generated in the high-vacuum chamber and gets accelerated by an electric field on the negatively charged electrode (target) [108-110]. A strong electric field charged up the plasma up to hundreds or thousands of the electron volts, and drive them to bombard on the targets with sufficient kinetic energy. Atoms or atomic clusters of the target are ejected from the target surface and condense on substrates placed close to the sputtering cathode. The targets are made of materials that are going to be deposited on the substrate.

Conductive materials like metals can be mounted on a cathode using direct current (DC) power supply while less-conductive materials like semiconductor and insulators must be mounted on a cathode using radio frequency (RF) power supply. Traditional DC Sputtering is a cost-effective way to deposit metal but is limited when it comes to semiconductor or dielectric

materials. Polarized charges accumulated on the less-conducting materials slow down the incoming ions carried by plasma and finally stop the process completely. By exchanging the direction of the field with RF sputtering, the accumulated charges can be “wiped off” in each cycle. The power supply used in RF sputtering is a high voltage RF power normally fixed at 13.56 MHz. The blocking capacitor C placed in the circuit plays an important role in the impedance-matching network that provides the power transfer from the RF source to the plasma discharge.

The most widely used application in the early days for magnetron sputtering deposition is the production of hard disks. In semiconductor manufacturing, magnetron sputtering deposition is preferred as a physical deposition method for its low substrate temperature during fabrication processes such as the deposition of metal contacts for thin-film transistors, and the deposition of antireflection coating for optical applications. Materials with a very high melting point could be easily deposited by sputtering deposition comparing to evaporation. Many low-emissivity coatings that are used in double-pane window assemblies containing silver and metal oxides are fabricated by sputtering deposition. A large industry has developed around tool bit coating using sputtered nitrides like titanium nitride in order to make a hard coat with familiar golden color. The thin films deposited by sputtering deposition usually have much better adhesion than those deposited by evaporation due to the diffuse transport. This feature makes the thin films more compact, while on the other hand more difficult for structuring procedures like lift-off.

Fig. 3.1 Schematic configuration of the high-vacuum chamber during the co-sputtering process. Ge and Sn targets are installed on RF and DC power supply respectively. The in-situ thickness of thin film and deposition rate is being inspected by a build-in ellipsometer.

Our sputtering system could fulfill the requirement of sputtering four different materials at the same time in the chamber (only two targets are shown in the schematic) including two direct-current power supplies and two radio-frequency power supplies. To get better quality of sputtered semiconductor films, we designed a modified sputtering system. First, a cylinder metal cover is installed obliquely on each of the targets. It serves as the physical protection for targets from crossover contamination and also serves as the cluster selector, where large-sized or heavy atomic clusters were screened by the metal cover by the effect of gravity. Second, our system is equipped with an ellipsometer for in-situ thickness measurement and growth rate inspection. The third, the substrate is placed on a rotatable stage for better uniformity.

3.2 X-ray diffraction

X-rays are electromagnetic waves of high energy whose wavelength range is between 10^{-3} and 10^1 nm. The most common ways of generating X-rays used in laboratories are sealed tubes and rotating anodes. The principle of both methods is the same. The electrons generated from heating a tungsten filament in a vacuum are directed to a target after getting accelerated by a high potential electric field. Two types of X-rays are generated by the incident electrons: one is the emission of X-ray photons with a broad continuous distribution of wavelength by the deceleration of the electrons, and the other type comes from ejecting electrons from the inner shell and jumping back with releasing photons through the ionization of the impinged atoms. The energies of the photon from the second type have a discrete distribution which is determined by the energy difference between inner and out shells. Therefore, the radiation coming out of a sealed tube or a rotating anode is a superposition of two mechanisms. Generally, K_{α} radiation of the strongest intensity is used for XRD measurements, hence appropriate monochromators or filters are necessary to remove the remaining radiation and let pass the K_{α} radiation.

Fig. 3.2 X-ray spectrum generated by the sealed tube. K_{α} radiation is the most commonly used radiation source in the XRD measurements. The rest radiation in the spectrum is filtered[111].

The principle of the measurement is based on the constructive diffraction of X-rays by the periodical atomic planes and angles. The geometrical condition of having constructive diffraction is described by Bragg's Law as shown in Figure 3.3. d is the space between two adjacent atomic planes. θ is the angle of the diffracted beam in the unit of degree. n is the order of diffraction and λ is the wavelength of the light source. Different materials or different lattice planes have different constructive diffraction condition or intensities according to the crystal structure and space group of measured phases. As a result, each phase can generate a characteristic diffraction pattern for identification. When multiple phases are presented in one spectrum, the intensity of the diffraction peak is proportional to their amounts existing in the sample. Therefore, both qualitative analysis (present phases) and quantitative analysis (respective amounts) can be performed by XRD measurement. A ω - 2θ coupled scan is generally used for the qualitative and quantitative analysis where the angle ω between plane and incident light is always half of the angle 2θ between the plane and the detector during scanning. In order to achieve reliable phase analysis, high-quality diffraction patterns are required. The precision of patterns are determined by the scanning steps of ω in degree (the smaller, the better), and the rate of scanning in scans per second (the smaller, the better). The equipment that was used in this project is a Bruker D8 Discover High-resolution XRD.

Fig. 3.3 Bragg's Law. Constructive interference of diffracted X-ray occurs when the condition expressed by Bragg's Law is met.

3.3 Photoluminescence measurement

The photoluminescence measurement takes advantage of electron-hole pair generation and recombination and spontaneous emission. The generation and recombination of the electron-hole pair are the processes where carriers of charge (negatively charged electrons and positively charged holes) are generated or eliminated. This mechanism is related to the band structure of a semiconductor in the solid-state physics. The generation of an electron corresponds to the transition of an electron from valence bands to conduction bands by breaking an electron-hole pair with sufficient energy, while the recombination process corresponds to a reverse transition.

The distribution of the carriers in the bands of a semiconductor could be described following Boltzmann distribution as a function of Fermi level and the temperature of the electrons. At the absolute zero temperature, according to Boltzmann distribution, all the electrons remain below Fermi level as electron-hole pairs since no thermal energy could be provided to break the electron-hole pair. Above absolute zero temperature, some of the electrons are stimulated to jump to the conduction band. In intrinsic semiconductors, the Fermi

level is lying in the middle of the bandgap. The closest band below bandgap is the valence band which is almost fully occupied. The closest band above energy gap is the conduction band which is almost empty. Hence the conductivity of an intrinsic semiconductor is very low especially at low temperature because very few charge carriers could take part in the current flow. Typically the conductivity of an intrinsic semiconductor is enhanced for increasing the charge carriers in both valence band (holes) and conduction band (electrons) as described by Fermi-Dirac statistics. At thermal equilibrium, the rate of recombination and generation processes are balanced meaning that the density of charge carrier remains as a constant.

The generation and recombination processes always involve the interactions between electrons, holes, photons, and phonons (vibration of crystal lattice). These processes should always satisfy the conservation of both quantized energy and momentum. The energy created in the process of combination is released in the form of a photon (direct transition) or heat (indirect transition). Since the photon could not transfer momentum in relation to their energy, the vibration of the lattice takes part in the process, carrying the momentum and releasing heat. This leads to different types of recombination regarding the release of energy.

Shockley-Read-Hall (SRH) recombination also known as trap-assisted recombination is a process where the impurity-induced trap centers in the energy gap absorb the differences of carriers. The electrons in the conduction bands transit to trap states first to align the momentum and then recombine with the holes in the valence band. The energy released by this mechanism is in a form of phonon, a lattice vibration, which exchanges thermal energy with lattice. It is the typical non-radiative recombination in indirect band-gap materials such as Si and Ge.

In contrast, for radiative recombination, the energy released by recombination is in the

form of a photon which can carry no momentum. The electrons in the conduction band recombine directly with the holes in the valence band without any momentum exchange. This requires the conduction band minimum and valence band maximum align at the same k point in the reciprocal lattice (only for direct band-gap material). This kind of emission of photons is called spontaneous emission.

To quantitatively measure spontaneous emission and photoluminescence, we built a system as shown in Figure 3.4. A continuous 1064 nm solid-state laser is used as the light source for stimulating the electrons from valence band to conduction band. The light beam passes through a mechanical chopper to have a pulsed light source (310 Hz). This frequency is also used as an external reference of the lock-in amplifier for suppressing background noise. The beam gets reflected and focused by a reflective mirror and illuminates on the sample. The generated PL signals along with 1064-nm photons reflected by samples are focused by two focus lens. The focused beam goes through a 1300 nm long-pass filter which screens out 1064-nm photon from the light source and let pass the PL signals generated from samples, gets collected by a detector.

Fig. 3.4 The configuration of the photoluminescence measurement system. The mechanical chopper is used for generating pulsed source. The frequency of the pulses is fed back to the software so that low-frequency background noises (most of the noise are from daily lamps) could be screened out.

3.4 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy is a technique for measuring absorption or emission of a solid, liquid or gas in the infrared wavelength range. An enormous advantage of FTIR is its detectable signal that in a wide spectral range in comparison of a dispersive spectrometer.

To measure an absorption spectrum or a transmittance spectrum, the most simple and straightforward way is to illuminate sample by a monochromatic light source and collect the light absorbed or transmitted known as a dispersive spectrometer. As for Fourier-transform spectroscopy, instead of illuminating by monochromatic light, a beam of light that contains continuous wavelengths in a specified spectral range is used. The absorption or transmittance of the incident beam is measured. Combination of the frequencies in the incident light is

modified after the first measurement, and obtain the second data point. The similar process is repeated several times depending on the precision of the measurement. In the final stage, the computer deals with all the collected data and reveals the absorption or transmittance properties with respect to individual wavelength. The light beam is produced by a broadband light source containing a full spectrum of wavelengths to be measured. It is directed into a Michelson interferometer (shown in Figure 3.5(a)) for generating a different combination of the frequencies for every step when the mirror moves forward and backward. Since the incident light beam has a continuous spectral range, each wavelength has a particular constructive and destructive interference condition which results in distinguishing outcome spectrum. The raw data (interferogram) is measured from zero path difference to a maximum length that depends on the required resolution. The interferogram is “translated” to a spectrum by Fourier transformation which is a spectrum of series of discrete wavelengths. The range of the wavelengths is determined by the interval of the data points in the interferogram.

Fig. 3.5 (a) The Schematic configuration of a Michelson interferometer. (b) A typical interferogram spectrum measured from FTIR[112].

There are three main components in the optical path of FTIR spectrometers. Begin with the infrared light source. A silicon carbide element that heated to about 1200 K is commonly used for mid-IR measurement in the range of 2-25 μm whose output is like black-body radiation. For near-IR application in the range of 1-2.5 μm , a higher temperature source, typically a tungsten-halogen lamp is required. For the far-IR application, instead of a thermal source, a mercury discharge lamp gives higher output. The second part is the beam splitter in the Michelson interferometer that the incident light illuminates into. An ideal beam splitter divides

the light beam to half of reflected light and the other half of transmitted light. The spectral range in which the beam splitter is working is determined by the material of the splitter. To cover a wide spectral range, several beam splitters working in separate districts are needed. Beam splitter made of KBr with a germanium-based coating is usually used for mid-IR measurement, while CaF_2 is the material used in the beam splitter for near-IR measurements. The last part is the detector that converts optical signals to electric signals. Commonly used mid-IR detectors are pyroelectric detectors made of deuterated triglycine sulfate (DTGS) or lithium tantalate (LiTaO_3), or photoelectric detectors such as liquid nitrogen-cooled mercury cadmium telluride (MCT) for higher sensitivity or faster response. Uncooled indium gallium arsenide photodiodes or DTGS are the usual choices in near-IR systems. Liquid helium cooled silicon or germanium bolometers are used in far-IR measurements.

3.5 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy is an extremely surface sensitive method for the identification and quantifying of the chemical elements in the surface of a solid thin film and giving information on the binding state of the detected elements and their oxidation numbers or functionalities.

In the year 1905, Einstein explained the photoelectric effect and formulated the photochemical quantum equivalent Law:

$$h\nu = E_{\text{bind}} + E_{\text{kin}} + \Phi \dots\dots\dots (19)$$

in which the light must be considered as a flow of particles with a quantum energy $h\nu$ (h : Planck constant, ν : frequency of the photon). When photons with such energy hit a target, there

is a chance that electron could be ejected from its orbital. This photon energy must be high enough to overcome the binding energy E_{bind} , the energy difference between Fermi level (E_F) and the energy of the electron in the core level, and another small amount of energy Φ between the vacuum energy level (E_{vac}) and the Fermi level. The electrons jumping out from the surface of the material with certain kinetic energy (E_{kin}) provide useful information about the material. The value of binding energy is strongly related to the energy state distribution in the core and is distinguishable from each individual element which can be regarded as the “fingerprint” of an element. The elementary composition in this way can be identified.

Fig 3.6 The working principle of X-ray photoelectron spectroscopy. Through analyzing the kinetic energy of the ejected electron, the “fingerprint”-binding energy of an element could be measured[113].

Photoelectron spectrometer must consist of three basic units. A light source to generate photons that have well-defined energy equal to $h \cdot \nu$ is a must. Only ultra-violet light is suitable to provide sufficient energy for the electron at the core level. Core-shell electrons can be released by X-rays. An X-ray source emits a white spectrum which additionally contains intensive peaks of well-defined energies. Normally, $K\alpha_{1,2}$ radiation of magnesium

(1253.6 ± 0.35 eV) or aluminum (1253.6 ± 0.45 eV) is used in XPS. A crystal monochromator is required to block the remaining X-rays and only let out a part of $K\alpha_{1,2}$ radiation. The main purpose of the spectrometer is to measure the kinetic energy of the photoelectron escaped from the sample surface. The most common installation for this purpose is a hemispherical analyzer. After passing the electron-optics of the spectrometer, the photoelectrons introduce a slit between two hemispheres. The beam of photoelectrons is influenced by an electric field perpendicular to the moving direction, forcing the linearly moving photoelectrons to move on a circular path. The radius of the circular movement is determined by the strength of the electric field as well as the kinetic energy of the photoelectron. This means that only selected photoelectrons with certain kinetic energy matching radius of the hemisphere can pass the analyzer for a given electric field. Thus, the variation of the electric field strength separates the photoelectrons concerning their different kinetic energies. The field strength remains almost unchanged in practice. A slit plate with an adjustable electric potential slows the photoelectrons with high kinetic energies down in order to pass the hemispherical analyzer and arrive at the count unit. In this case, the voltage applied to the slit plate is a measure for the kinetic energy of the photoelectrons. The detector at the end of hemisphere counts the number of photoelectrons arrived, hence the unit of XPS spectrum is in *cps* (counts per second).

Figure 3.7 Typical build-up of a simple photoelectron spectrometer. When electrons are ejected from the sample, only those with certain kinetic energy could pass through the hemispherical analyzer[113].

3.6 Summary

This chapter introduces the magnetron sputtering deposition system as the growth method of GeSn thin film which can realize high-quality co-sputtering deposition. The quality of the thin film is characterized in two categories: crystallographic properties and optoelectronic properties. Several important characterization tools are introduced. X-ray related techniques (X-ray diffraction and X-ray photoelectron spectroscopy) are used for the analysis of the lattice structure of the samples. Photonics related techniques (photoluminescence measurement and FTIR spectroscopy) are for the electronic band structure of the samples.

Chapter 4. Theoretical study of GeSn/Ge quantum wells

This chapter presents a detailed theoretical study of a GeSn/Ge quantum well structure using the 6-band k.p method [114, 115]. The energy band lineup of the quantum well is calculated at first. Influences on the band structure induced by the temperature of the lattice and in-plane strain are taken into consideration. E-k dispersion relation in the quantum well is then calculated by solving Schrodinger's equation using the Hamiltonian that we discussed in Chapter 2 based on the energy band lineup. A discrete density of states reveals quantized energy states in the quantum well structure. Spontaneous emission rate spectrum and optical gain are also simulated which are the fundamentals of the optoelectronic properties of the quantum well structure. The effects of well width, lattice temperature, Sn component and in-plane strain are also examined.

4.1 Band structure lineup of GeSn/Ge quantum well

The calculation of the energy band lineup is the very first step for the simulation of the GeSn/Ge quantum well [116, 117]. It determines the well width, barrier height, and bandgap for different layers of the quantum well structure which are the key factors to determine the E-k dispersion relation. Our theoretical model simulates a sandwiched 3-layer quantum well structure [118], where the barrier layer is Ge and well layer is GeSn thin film. One particular feature of this model is that we included the interference of the indirect valley (L valley) into the calculation. As a so-called pseudo direct semiconductor material, there exists a small energy difference between the direct and indirect gap, hence the contribution of the indirect band to the spontaneous emission coming from L valley could not be neglected [119, 120]. It proved

that the contribution of the L valley had significant influences on the performance of the GeSn/Ge quantum well.

In this quantum well structure, all the energy states are relatively calculated referring to a ground state (0 eV). The average valence band energy ($E_{v,av}$) of Ge is defined as the ground state. Hence, we could determine the energy lineup of the barrier layer (Ge), and the valence band maximum and the conduction band minimum of Ge could be written as:

$$VBM(Ge) = E_{v,av}(Ge) + \frac{1}{3} \Delta(Ge) \dots\dots\dots (20)$$

$$CBM_{\Gamma}(Ge) = VBM(Ge) + E_{g\Gamma}(Ge) \dots\dots\dots (21)$$

$$CBM_L(Ge) = VBM(Ge) + E_{gL}(Ge) \dots\dots\dots (22)$$

where VBM is the valence band maximum, Δ is the spin-orbit energy, CBM_{Γ} is the conduction band minimum of Γ valley, CBM_L is the conduction band minimum of L valley, $E_{g\Gamma}$ and E_{gL} are energy gaps of Γ and L valleys respectively. We have two sets of valleys - Γ and L valley, determined by the direct and indirect band gaps separately. The valence band minimum of Ge could be defined as the sum of average valence band energy and one third of spin-orbit energy. Once valence band minimum is defined, the conduction band minimum of both valleys could be written as the sum of valence band minimum and energy gap. Note that the actual conduction band minimum of the material is determined by the one of smaller value.

Similar equations work for the calculation of the energy lineup of the $Ge_{1-x}Sn_x$ in which average valence band energy and spin-orbit energy of Ge should be substituted with GeSn alloy. The values could be estimated according to the elementary component of GeSn alloy, written as:

$$E_{v,av}(Ge_{1-x}Sn_x) = (1-x)E_{v,av}(Ge) + xE_{v,av}(Sn) \dots\dots\dots (23)$$

$$\Delta(Ge_{1-x}Sn_x) = (1-x)\Delta(Ge) + x\Delta(Sn) \dots\dots\dots (24)$$

The energy gaps of GeSn alloy could be presented by the linear superposition of gaps for two individual elements plus a parabolic bowing effect term, written as [121, 122]:

$$Eg_{\Gamma}(Ge_{1-x}Sn_x) = (1-x)Eg_{\Gamma}(Ge) + xEg_{\Gamma}(Sn) - x(1-x)b_f(GeSn) \dots\dots\dots (25)$$

$$Eg_L(Ge_{1-x}Sn_x) = (1-x)Eg_L(Ge) + xEg_L(Sn) - x(1-x)b_f(GeSn) \dots\dots\dots (26)$$

where b_f is the bowing factor of GeSn alloy. This factor is an experimentally fitted value which in the case of GeSn, it lacks corresponding reference meanwhile the component of Sn is rather small. Hence we use the bowing factor of Ge as a reasonable substitute.

Since we use GeSn as the quantum well layer, and Ge as the barrier layer, train effect should exist at the interface because of the different lattice constants of the two materials [123-125]. The interference of the strain is included in the calculation of the band structure (coupling between spin-orbit hole bands and light hole bands is considered) which is written as:

$$\delta E_c = a_c(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) = 2a_c(1 - C_{12}/C_{11})\varepsilon \dots\dots\dots (27)$$

$$\delta E_{HH} = -P_{\varepsilon} - Q_{\varepsilon} \dots\dots\dots (28)$$

$$\delta E_{LH} = -P_{\varepsilon} + \frac{1}{2}(Q_{\varepsilon} - \Delta + \sqrt{\Delta^2 + 2\Delta Q_{\varepsilon} + 9Q_{\varepsilon}^2}) \dots\dots\dots (29)$$

where

$$P_{\varepsilon} = -a_v(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) = -2a_v(1 - C_{12}/C_{11})\varepsilon \dots\dots\dots (30)$$

$$Q_{\varepsilon} = -b(\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz}) / 2 = -b(1 + 2C_{12}/C_{11})\varepsilon \dots\dots\dots (31)$$

$$\varepsilon_{xx} = \varepsilon_{yy} = (a_b - a_w) / a_b \dots\dots\dots (32)$$

$$\varepsilon_{zz} = -2\varepsilon_{xx} \cdot c_{12} / c_{11} \dots\dots\dots (33)$$

where δE_c , δE_{LH} , and δE_{HH} are the shift in the band edge for conduction band, light hole, and heavy hole respectively. a_c and a_v are the hydrostatic strain deformation potential constants for conduction band and valence band. b is the shear strain deformation potential constant. ε_{xx} , ε_{yy} and ε_{zz} are the strain component in X, Y and Z direction, where $\varepsilon_{xx}=\varepsilon_{yy}=\varepsilon$, and $\varepsilon_{zz}=-2C_{11}/C_{12} \times \varepsilon$. a_b and a_w are the lattice constant of barrier and well. C_{11} and C_{12} are the elastic stiffness constant. The shift of conduction band is expressed as the production the deformation potential constant for conduction band and the strain which is induced by the difference between the lattice constant differences between two layers. Parameters used are listed in Table I

Table I. The band parameters at 300K for α -Sn and Ge

	Ge	Sn
a (Å)	5.6573	6.4892
m_c (m_0)	0.038	-0.058
γ_1	13.38	-15
γ_2	4.24	-11.45
γ_3	5.69	-8.55
E_p (eV)	26.3	24.0
E_{gr} (eV)	0.664	0.092
E_{gL} (eV)	0.7985	-0.413
Δ (eV)	0.29	0.8
a_c (eV)	-8.24	-5.33
a_v (eV)	1.24	1.55
b_f (eV)	-2.9	-2.7
C_{11} (10 GPa)	12.853	6.9
C_{12} (10 GPa)	4.826	2.9
$E_{v,av}$ (eV)	0	0.69

The band structures and the performances of the GeSn quantum well at different temperature are going to be investigated, hence to precisely simulate this situation, influences induced by temperature on the band structure is also taken into consideration, which can be written as:

$$E_g = E_0 - \alpha T^2 / (\beta + T) \dots\dots\dots (34)$$

This equation is also known as Varshni's equation that describes the relationship between the bandgap and temperature. β and α as shown in Table II are experimentally fitted parameters, and E_0 is the bandgap at 0 K. This equation works for both indirect and direct valleys, hence it has two sets of parameters. Similarly, the Varshni parameters of GeSn are estimated to be the same as Ge's.

Table II. Varshni parameter for Ge

	Γ valley	L valley
α (meV/K)	6.842×10^{-4}	4.561×10^{-4}
β (K)	398	210

Now we plot the band diagram of the type I Ge/GeSn quantum wells regarding various settings in Figure 4.1. The energy band lineup of a relaxed 80Å/100Å Ge_{0.9}Sn_{0.1}/Ge quantum well at 300 K is plotted on the left side in the 4 groups of figures as the reference. In Figure 4.1(a), the component of Sn is raised to 0.15. The bandgap in both valleys of GeSn alloy is largely reduced from 0.448 eV to 0.291 eV which comes from the increased contribution from Sn. The valence band offset (VBO) also increases due to the increased spin-orbit (SO) energy. In Figure 4.1(b), the well width of the quantum well is increased from 80 Å to 100 Å while other parameters remain unchanged. This influences only the shape of the band diagram instead of changing the energy gap of the quantum well, and influences the distribution of the discrete energy levels if we consider the quantum confinement. Figure 4.1(c) shows the effect of environmental temperature on the band structure where it not only influences the bandgap of

GeSn layer but also influences the barrier layer. Hence band gaps of both materials changes. More specifically, both energy gaps should react to temperature differently as the temperature parameters of both materials are different. In our case, due to the fact that such parameters of GeSn lack experimental verification, we suppose the parameters of both materials are the same when the Sn component is not large. In Figure 4.1(d), a 1% tensile strain is introduced to the GeSn layer. As described in the energy shift of the bands by strain effect, a tensile strain increases the bandgap of the material through lifting up the conduction band minimum and pushing down valence band maximum. Hence the energy gap in the well region decrease from 0.448 eV to 0.268 eV.

Fig. 4.1 The energy band lineup GeSn/Ge quantum wells. The band lineup of a relaxed 80Å/100Å $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum well at 300 K is used as the reference in the left of each group. (a) Relaxed 80Å/100Å $\text{Ge}_{0.85}\text{Sn}_{0.15}/\text{Ge}$ quantum well at 300 K. (b)

Relaxed 100Å/100Å Ge_{0.9}Sn_{0.1}/Ge quantum at 300 K. (c) Relaxed 80Å/100Å Ge_{0.9}Sn_{0.1}/Ge quantum at 100 K and (d) 1% tensile-strained 80Å/100Å Ge_{0.9}Sn_{0.1}/Ge quantum at 300 K.

4.2 The E-k dispersion curves

By substituting the band structure into the Hamiltonian, we are able to plot the E-k dispersion relation of each quantum well. For holes in the valence band, E-k dispersion in the range from 0 eV to 0.400 eV is calculated. For electrons, the range is from 0.500 eV to 1.400 eV. The range of wavevector k is from $-10 \frac{2\pi}{L}$ to $10 \frac{2\pi}{L}$ with a step of $0.5 \frac{2\pi}{L}$ (L is the sum of the well width and barrier width). 10 electron-bands and 12 hole-bands in the Γ valley are plotted as shown in figure (including spin-up and spin-down). E-k dispersion in the L valley could be calculated using a similar method.

In Figure 4.2, each graph shows the E-k curves in both the conduction band and valence band corresponding to the quantum wells as we discussed in the previous paragraph. On the left side in each group of figures shows the E-k dispersion in the well region of a relaxed 80Å/100Å Ge_{0.9}Sn_{0.1}/Ge quantum well at room temperature. In conduction band, the lowest energy state is named as E1 state with energy eigenvalue of 0.719 eV at Γ point plotted as the purple curve. Second lowest one is named as E2 state with energy eigenvalue of 0.886 eV plotted as the red curve. Note that each of the curves actually represents two electron states which are spin-up electron and spin-down electron. In valence band, the highest energy state is the HH1 state with energy eigenvalue of 0.167 eV plotted as the orange curve. Following is the second-highest LH1 state that has a close energy eigenvalue (0.161 eV). The energy gap, in this case, equals to 0.552 eV (E1-HH1).

Fig 4.2 The E-k dispersion relation of GeSn/Ge quantum wells. The E-k dispersion relation of a relaxed 80Å/100Å $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum at 300 K is used as the reference at left of each group. (a) Relaxed 80Å/100Å $\text{Ge}_{0.85}\text{Sn}_{0.15}/\text{Ge}$

quantum at 300 K. (b) Relaxed 100Å/100Å Ge_{0.9}Sn_{0.1}/Ge quantum at 300 K. (c) Relaxed 80Å/100Å Ge_{0.9}Sn_{0.1}/Ge quantum at 100 K. (d) 1% tensile-strained 80Å/100Å Ge_{0.9}Sn_{0.1}/Ge quantum at 300 K.

As shown in Figure 4.2(a), in the Ge_{0.85}Sn_{0.15}/Ge quantum well, the whole conduction band and valence band shift closer to each other because the bandgap shrinks with higher Sn component. The bandgap now equals to 0.436 eV (E1 (0.655 eV) - LH1 (0.219 eV)). Another significant change observed in the E-k dispersion curve is the shape of the curves. This comes from the change of effective mass of electrons or holes by vary Sn component which affects the slope of E-k curves. Obviously effective mass in the quantum well with high Sn component is larger.

In Figure 4.2(b), well width slightly affects the distribution of the energy states in the conduction band and valence band without changes in the bandgap of energy lineup as we discussed before. When the well width is increased from 80 Å to 100 Å, the lowest energy state E1 in conduction band decreased from 0.719 eV to 0.698 eV. Meanwhile, the energy of the highest state in the valence band (HH1) increased from 0.167 eV to 0.172 eV. As a result, the bandgap decreased to 0.526 eV. The energy states become less discrete as described by Schrodinger's equation.

Figure 4.2(c) shows the temperature effect, where both band edges in the barrier and well regions are affected. Since Sn component in our case is rather small, we assume both materials have the same temperature parameters α , β in Varshni's relation. Hence the energy offsets in the conduction band and valence band remains unchanged because the energy gap in the well region and barrier region changes at exactly the same rate. By decreasing the temperature to 100K, E1 in well region is lifted to 0.79 eV, increasing the bandgap to 0.622 eV.

Strain effect is one of the most important factors for band engineering. As shown in Figure 4.2(d), with 1% tensile strain induced, the energy eigenvalue of the LH1 plotted by the orange curve is largely lifted up to 0.216 eV and that of E1 plotted by purple curve decreases to 0.658 eV as described by strain effect on the band edge in the previous session. As a result, the bandgap of the tensile-strained quantum well is 0.442 eV. On the contrary, if it with 1% compressive strain, the gap enlarges to 0.588 eV (which is not shown here). In that case, the highest energy state in the valence band will be a heavy hole instead, because heavy hole and light hole react differently to each strain type. The conduction bands and valence bands will shift to farther position comparing to a relaxed quantum well.

4.3 Density of states

After acquiring the E-k dispersion relation, the density of the states (DOS) could be calculated. This value describes the density of available state in a unit energy difference, or in other word, reflects the energy difference between adjacent two available energy states. The DOS in k-space is defined by:

$$\rho(E) = d\rho(k)/dE \dots\dots\dots (35)$$

where $\rho(k)$ is the density of states as a function of wave vector determined by the dimension of k-space. Typically, a two-dimensional k-space have a DOS in a step-like form:

$$\rho^{2D}(E) = m^*/\pi\hbar^2 \sum_n \Theta(E - E_n) \dots\dots\dots (36)$$

The concentration of the carrier is calculated by:

$$n = \int f(E)\rho(E)d(E) \dots\dots\dots (37)$$

m^* is the effective mass of the carrier. Θ is the step function. E_n is the eigenvalue for each

subband. $f(E)$ is the Fermi-Dirac probability distribution function.

4.3.1 DOS in the direct valley

As the reference, the DOS of $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum well and the concentration of electrons in the conduction band is plotted in Figure 4.3(a). The first state locates at 0.719 eV that corresponds to E1 calculated from E-k dispersion curve. The next state corresponds to E2 located at 0.886 eV. We calculated the first 10 electron states (including spin-up and spin-down), hence 5 states of DOS could be observed in the plot. The blue curve in the same plot demonstrates the total concentration of electrons as the function of Fermi energy level E . Figure 4.3(b) shows the DOS of $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum well and the concentration of holes in the valence band using the same model. The highest two levels correspond to the HH1 (0.167 eV) and LH1 (0.161 eV) calculated from E-k dispersion which is very closely located as shown in the figure. 6 states in total are observed in DOS of the valence band. Similarly, the total carrier density of holes as the function of Fermi energy is plotted by the curve.

Fig. 4.3 (a) Density of states and carrier concentration in the conduction band of a relaxed 80Å/100Å Ge_{0.9}Sn_{0.1}/Ge quantum at 300 K. (b) Density of states and carrier concentration in the valence band of a relaxed 80Å/100Å Ge_{0.9}Sn_{0.1}/Ge quantum at 300 K.

We use this method to calculate the DOS based on the different E-k relations. Since they share same theory and similar results, we take the tensile strained Ge_{0.9}Sn_{0.1}/Ge quantum well and relaxed Ge_{0.85}Sn_{0.15}/Ge quantum well as examples. Figure 4.4(a) and 4.4(c) shows the DOS spectra in the conduction band and valence band in the tensile-strained Ge_{0.9}Sn_{0.1}/Ge quantum well. The first state in the conduction band now locates at 0.658 eV corresponding to the eigenvalue of E1 as we calculated in the E-k dispersion curve of the strained quantum well. The first state in valence band now shifts to 0.216 eV accordingly. Also, we find that the DOS

spectrum in the valence band is spikier than that of the relaxed GeSn/Ge quantum well. This phenomenon derives from the deformation of the E-k dispersion curves at the Γ point shown in previous E-k plot. Instead of an ideally parabolic relation between energy and wave vector, a more complex E-k relation is observed. Hence the effective mass in the calculation of density of states will not remain as a constant as it is in the simple quantum well model. In a simple calculation model, the calculated DOS will be perfectly flat, however not accurate enough. In this model, we included a lot of mechanisms such as the interaction between holes in the valence band and electrons in the conduction band, the effect of temperature, etc. which will definitely influence the distribution of DOS. The spectrum becomes spikey but will be more accurate. An accurate DOS is the key to calculate the spontaneous emission rate.

Figure 4.4(b) and (d) are the DOS spectra of relaxed $\text{Ge}_{0.85}\text{Sn}_{0.15}/\text{Ge}$ quantum well in conduction band and valence band. Instead of strain effect, the increased Sn component is the major factor for bandgap engineering.

Fig. 4.4 Density of states and carrier concentration as function of Fermi level in (a) conduction band of tensile strained 80Å/100Å $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum at 300 K, (b) conduction band of relaxed 80Å/100Å $\text{Ge}_{0.85}\text{Sn}_{0.15}/\text{Ge}$ quantum at 300 K, (c) valence band of tensile strained 80Å/100Å $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum at 300 K, and (d) valence band of relaxed 80Å/100Å $\text{Ge}_{0.85}\text{Sn}_{0.15}/\text{Ge}$ quantum at 300 K.

4.3.2 DOS in the indirect valley

Similarly, the DOS in the indirect L valley is calculated using the same method. Parameters which we used for the Γ valley are substituted by those for L valley, including the band offsets in the conduction band and valence band, the effective mass of the electron (note that effective mass in L valley consists of two terms: transverse component and longitudinal component), the relative energy level regarding to our reference point. The DOS in L valley of relaxed $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum well is calculated as shown in Figure 4.5. Due to a very large longitudinal effective mass of electron in L valley (typically around $1.5 m_0$, while for an electron in Γ valley, it is no more than $0.038 m_0$), available electron states are densely

distributed and the energy difference between each state is very small. The carrier concentration rises very fast with the Fermi energy comparing to that in Γ valley.

Fig. 4.5 Density of states and carrier concentration as a function of Fermi level in conduction band at L valley of relaxed 80Å/100Å $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum at 300 K.

By adding the two parts of DOS in Γ and L valley, the influence of the indirect valley is included. Because the electron states in L valley is much densely distributed than those in Γ valley, once the indirect bandgap of GeSn alloy is smaller than its direct bandgap, the available states with the lowest energy are almost all in the indirect valley. As Fermi level increases, these states will firstly be occupied by electrons, leaving Γ empty. This mechanism appropriately simulates such type of semiconductor material whose band edge difference between two valleys is small. And based on it, optoelectronic properties of such materials could be estimated using this model.

4.4 Optoelectronic transition in GeSn/Ge quantum well

The optoelectronic transition of GeSn/Ge quantum well is based on the total density of

states in the conduction band (the contribution of the DOS in L valley is included in the DOS in Γ valley) and valence band. The optical transition matrix elements of momentum for transitions between the valence hole subbands and the conduction electron subbands are given by:

$$P_i^{n_c n_v} = \langle \psi_{n_c} | \hat{p}_i | \psi_{n_v} \rangle \dots\dots\dots (38)$$

i could be x, y or z-direction. Ψ is the real electron or hole wave function. p is the momentum operator. The spontaneous emission rate and the optical gain could be written as:

$$R_{sp}(E) = \frac{ne^2 E}{\pi m_0^2 \epsilon_0 \hbar^2 c^3} \sum_{n_c} \sum_{n_v} \iint \frac{Q^{n_c n_v}}{4\pi^2 l} f_c f_v \times \frac{1}{\pi} \frac{\hbar/\tau}{(E_{eh} - E)^2 + (\hbar/\tau)^2} dk_x dk_y \dots\dots\dots (39)$$

$$g(E) = [1 - \exp(E - \Delta F / k_B T)] \frac{\pi^2 c^2 \hbar^3}{n^2 E^2} R_{sp}(E) \dots\dots\dots (40)$$

E is the photon energy. ϵ_0 is the free-space dielectric constant. n is the refractive index. c is the light speed. $Q^{n_c n_v}$ is the squared optical transition matrix element. E_{eh} is the transition energy. τ is the intraband relaxation time. ΔF is the quasi-Fermi level separation dependent on the carrier density. k_B is the Boltzmann constant and T is the temperature. The mode of the light determines its composition of the square optical transition elements, that

$$Q_i = 2(P_i^{n_c n_v})^2 / m_0, \quad i = x, y, z \dots\dots\dots (41)$$

For TE mode and TM mode,

$$Q_{TE} = (Q_x + Q_y) / 2, \quad Q_{TM} = Q_z \dots\dots\dots (42)$$

The optical transition between the subbands should obey selection rule that transitions between

electron-hole pair which have the same index are allowed. For example, E1 to HH1 is allowed, while E1 to HH2 is not. And for the TM mode transition, there is not any contribution from heavy holes. From the expression of the spontaneous emission rate, we find that it is proportional to the integration between the wave functions of each electron-hole pair in reciprocal space. Hence a direct band-gap material (electron and hole subbands are aligned at the same k point) usually has much higher spontaneous emission rate than indirect band-gap material.

4.4.1 SERS of $\text{Ge}_{1-x}\text{Sn}_x/\text{Ge}$ quantum wells

Figure 4.6 shows the spontaneous emission rate spectrum (SERS) of a relaxed $\text{Ge}_{1-x}\text{Sn}_x/\text{Ge}$ quantum well with x ranges from 5% to 15%. Well width is 80 Å. Temperature is at 300 K. SERS for TE and TM mode are presented in the left and right figure respectively. In the TE mode SERS, the peak shifts from 0.457 eV to 0.700 eV as the Sn component decrease from 15% to 5%. This shift is caused by the change of the elementary composition that adjusts the bandgap in the well region, i.e. the term E_{eh} in the expression of R_{sp} . The intensity decreases with the reduction of the Sn component in the GeSn alloy because the contribution of the indirect L valley becomes more dominant in the alloy with lower Sn component. Because of a much more significant density of states in the L valley comparing to that in Γ valley, once electrons begin to occupy the states in L valley, they won't be able to occupy the states in Γ valley again unless the Fermi level is highly lifted which is almost unrealistic.

For $\text{Ge}_{0.85}\text{Sn}_{0.15}/\text{Ge}$ quantum well, the lowest energy state in Γ valley is at 0.655 eV while the lowest one in L valley is at 0.692 eV. Hence the effective energy gaps in Γ valley and L

valley with respect to valence band ($E_{hh1}=0.219$ eV) are 0.436 eV and 0.473 eV. In contrast, the two energy gaps for $\text{Ge}_{0.95}\text{Sn}_{0.05}/\text{Ge}$ quantum well are 0.685 eV and 0.607 eV. The excited electrons preferentially occupy the lowest available energy state in the conduction bands. Hence in the case of $\text{Ge}_{0.85}\text{Sn}_{0.15}/\text{Ge}$ quantum well, most of the contribution comes from the electrons that occupy the states in Γ valley, while with lower Sn component, it comes from those electrons been thermally stimulated into Γ valley, which results in the two-order difference in the significance of spontaneous emission rate. Furthermore, if the temperature is set to a lower level instead of room temperature, the spontaneous emission rate will be suppressed in the case of indirect GeSn alloy (this will be discussed in details in the following session). Similar analyses are applicable for TM mode transition, except that the contribution from heavy holes is forbidden.

Fig. 4.6 (a) TE mode transition spontaneous emission rate of relaxed $80\text{\AA}/100\text{\AA}$ $\text{Ge}_{1-x}\text{Sn}_x/\text{Ge}$ quantum well at 300 K. (b) TM mode transition spontaneous emission rate of relaxed $80\text{\AA}/100\text{\AA}$ $\text{Ge}_{1-x}\text{Sn}_x/\text{Ge}$ quantum well at 300 K.

The strain effect on the SERS of $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum well is investigated as shown in Figure 4.7. In-plane strain from -1% (compressive strain) to 1% (tensile strain) are applied on

a GeSn layer with 80 Å well width at 300 K. For both TE and TM mode, the peaks shift to lower energy and the intensity increases as the strain changes from compressive strain to tensile strain [126]. A tensile strain helps the band structure of GeSn alloy become more direct-like because the effective conduction band edge in Γ valley drops much faster than that in L valley (normally 4 times faster coming from a 4-times difference in the hydrostatic strain deformation potential constants between Γ point and L point). There will be a moment as the strain changes when the effective conduction band minimum at the Γ point becomes lower than that at L point. This explains the existence of not only the shift in photon energy but also the significant enhancement in the strength of spontaneous emission rate.

In the tensile strained quantum wells, a major peak in TE mode transition is split into two subpeaks. This originates from the separate LH1 state and HH1 state (main contribution to the SERS) as shown in the E-k dispersion relation of tensile strained GeSn/Ge quantum well (Figure 4.2(d)). These sub-peaks correspond to the transition of E1-LH1 and E1-HH1. In fact, a compressive strain will also separate the LH1 state and HH1 state, where a weak split subpeak could be observed in the SERS of compressively strained GeSn/Ge quantum wells. However, for its indirect dominant transition, those from the second energy level become a minority. As for the TM mode transition, this phenomenon disappears for transitions only from electron to light hole exist.

Fig. 4.7 (a) TE mode transition spontaneous emission rate of strained 80Å/100Å $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum well at 300 K. The major peak is split into two sub peaks under tensile strain. (b) TM mode transition spontaneous emission rate of strained 80Å/100Å $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum well at 300 K.

Figure 4.8 shows the temperature effect on the SERS of GeSn/Ge quantum well. Its influences reflect two main factors which are the strength of the emission rate and the photon energy. According to Varshni's equation, the energy band lineup of the GeSn/Ge quantum well is adjusted that causes the blue shift with rising temperature. In this case, the term E_{eh} in the expression of R_{sp} is affected. Another main effect of temperature is the term $k_B T$ in the Fermi-Dirac distribution equation f_c and f_v . It determines the total carrier in the valence band and conduction band while the product of f_c and f_v determines the magnitude of spontaneous emission rate. Therefore the intensity of the spontaneous emission increases under lower temperature.

Fig. 4.8 (a) TE mode transition spontaneous emission rate of relaxed 80 Å/100 Å $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum well at x K. (b) TM mode transition spontaneous emission rate of relaxed 80 Å/100 Å $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum well at x K.

Instead of changing the energy band lineup, the well width changes the effective energy gap by adjusting the distribution of electrons in the conduction band. According to the description of Schrodinger's equation, a narrower well width makes the energy states become more separated, hence the effective energy gap will be smaller, while for a wider well width it is the opposite. This is shown in Figure 4.9.

Fig. 4.9 (a) TE mode transition spontaneous emission rate of relaxed x Å/100 Å $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum well at 300 K. (b) TM mode transition spontaneous emission rate of relaxed x Å/100 Å $\text{Ge}_{0.9}\text{Sn}_{0.1}/\text{Ge}$ quantum well at 300 K

Among the mentioned parameters, the elementary composition of GeSn alloy and the in-

plane strain affect the spontaneous emission rate by adjusting the energy band lineup which is able to change the material from an indirect band-gap material to direct band-gap material. Temperature affects the emission rate to changing the total concentration of carriers involved in the emission process that occupy the conduction band minimum and valence band maximum. The well width help tune the effective energy gap in the quantum well.

4.4.2 Optical gain of $\text{Ge}_{1-x}\text{Sn}_x/\text{Ge}$ quantum wells

After acquiring the spontaneous emission rate spectra, the optical gain of the structure could be easily calculated, as written by [127-129]:

$$g(E) = [1 - \exp(-E - \Delta F / k_B T)] \frac{\pi^2 c^2 \hbar^3}{n^2 E^2} R_{sp}(E) \dots\dots\dots (43)$$

Figure 4.10 and 4.11 show the TE mode and TM mode optical gain of GeSn/Ge quantum wells. Basically, the optical gain corresponds to the spontaneous emission rate spectra that higher spontaneous emission rate results in a higher optical gain. The wavelength range where the gain reaches its maximum is consistent with the peak location in the SERS. We note that a low temperature significantly enhances the optical gain of the quantum well among other parameters. A low temperature not only increases the spontaneous emission rate as we discussed in the Fermi distribution in the previous session but also suppresses the possibility of thermal stimulation as shown in the term $1 - \exp(-E - \Delta F / k_B T)$. In this case, a three-order amplification is achieved by decreasing from room temperature to 50 K.

Fig. 4.10 TE mode transition optical gain of (a) relaxed 80 Å/100 Å Ge_{1-x}Sn_x/Ge quantum well at 300 K, (b) strained 80 Å/100 Å Ge_{0.9}Sn_{0.1}/Ge quantum well at 300 K, (c) relaxed x Å/100 Å Ge_{0.9}Sn_{0.1}/Ge quantum well at 300 K, and (d) relaxed 80 Å/100 Å Ge_{0.9}Sn_{0.1}/Ge quantum well at x K.

Fig. 4.11 TM mode transition optical gain of (a) relaxed 80 Å/100 Å Ge_{1-x}Sn_x/Ge quantum well at 300 K, (b) strained 80 Å/100 Å Ge_{0.9}Sn_{0.1}/Ge quantum well at 300 K, (c) relaxed x Å/100 Å Ge_{0.9}Sn_{0.1}/Ge quantum well at 300 K, and (d) relaxed 80 Å/100 Å Ge_{0.9}Sn_{0.1}/Ge quantum well at x K.

4.5 Room temperature enhanced SERS in GeSn/Ge quantum well

In the previous sessions, we discussed the influences of various parameters on the band structure, E-k dispersion relation, spontaneous emission rate, and optical gain.

We simulate a Ge_{0.95}Sn_{0.05}/Ge quantum well (0.7% of compressive strain is taken into consideration) to investigate its performance in a quantum well structure. GeSn alloy with such low Sn content remains as an indirect band-gap material where the conduction band minimum of L point is lower than the conduction band minimum of Γ point as shown in the band diagram in Figure 4.12. These three possible transitions (E1-HH1, E1-LH1, and E2-HH2) are the major contributors to light emission and optical gain.

Fig. 4.12 (a) Energy band structure of $\text{Ge}_{0.95}\text{Sn}_{0.05}/\text{Ge}$ at room temperature. (b) Electron and hole energy dispersion curves of $\text{Ge}_{0.95}\text{Sn}_{0.05}/\text{Ge}$ quantum well at 200 K.

The temperature and doping level dependence of spontaneous rate at the direct Γ point (without the interference of indirect L valley) is shown in Figure 4.13(a). At 200 K, 3 major peaks could be observed in the spontaneous emission rate, where each peak corresponds to one electron-hole recombination in the E-k dispersion at Γ point. It demonstrates a positive correlation between temperature and SERS. It is a typical phenomenon for a direct band-gap material because at this moment the influence of L valley is excluded. A higher temperature results in a larger proportion of free electrons at CBM getting excited onto upper energy states which is the reason for the SERS decreasing. A blue shift is observed when keep lowering the temperature. This is due to the negative correlation between temperature and energy gap where E_1 is pushed up when the temperature goes down. Figure 4.13(b) shows the effect of doping concentration on SERS. The temperature and injection electron-hole pair concentration are fixed at 200 K and $2 \times 10^{-18} \text{ cm}^{-3}$ while the doping level varies from 0 to $1 \times 10^{19} \text{ cm}^{-3}$. The transition of the higher levels is highly enhanced by doping comparing to the intrinsic one. The electrons of the donors first occupy the lowest E_1 level when doping is started. And after E_1 is

fully occupied, electrons begin to occupy the higher E2 levels when the doping level rises from $5 \times 10^{18} \text{ cm}^{-3}$ to $1 \times 10^{19} \text{ cm}^{-3}$.

Fig. 4.13 Low temperature enhanced TE mode transition spontaneous emission rate of Ge_{0.95}Sn_{0.05}/Ge quantum well without doping. (b). Doping enhanced TE mode transition spontaneous emission rate of Ge_{0.95}Sn_{0.05}/Ge quantum well.

Including the influence of the non-ignorable L valley, the temperature and doping dependence of spontaneous emission rate is shown in Figure 4.14. The position of the peak at 200 K is not shifted (same electron-hole recombination) while the intensity shows a 4-order descent because a large portion of electrons in the conduction band occupy the energy states in L valley. A room temperature enhanced SERS is observed, which is different from the result we got in the last session because we are now analyzing an indirect band-gap quantum well. A thermally stimulated electron in L valley now has a higher probability to occupy those energy state in the Γ valley with the interaction of phonon. Similar to direct transition, a higher doping concentration enhance the SERS as well.

Fig. 4.14 Room temperature enhanced TE mode transition spontaneous emission rate of $\text{Ge}_{0.95}\text{Sn}_{0.05}/\text{Ge}$ quantum well without doping. (b). Doping enhanced TE mode transition spontaneous emission rate of $\text{Ge}_{0.95}\text{Sn}_{0.05}/\text{Ge}$ quantum well.

Strain effect is one issue that prevents GeSn alloy from being useful for photoelectrical applications because the compressive strain caused by the lattice mismatch is unavoidable. The in-plane strain is defined by:

$$\varepsilon_{//} = \frac{a_{\text{sub}} - a}{a_{\text{sub}}} \dots\dots\dots (44)$$

a_{sub} is the lattice constant of the substrate, and a is the lattice constant of the GeSn alloy. This compressive strain greatly suppresses the spontaneous emission rate and the optical gain of the material. As shown in the Figure 4.15(a), no matter how much Sn is incorporated into the naturally strained GeSn alloy for the GeSn/Ge quantum well, the lowest energy state in L valley is always below that in Γ valley, i.e. it cannot transform to a direct band-gap material without strain engineering. We plot the effective band edge of Γ point in strained/relaxed GeSn alloy in GeSn/Ge quantum well. It is found that the accompanying rising compressive strain eliminates the contribution that is brought in by increasing Sn content.

Fig. 4.15 (a) The lowest electron energy levels at L and Γ points of the GeSn QW with different Sn composition at room temperature. (b) The strain effect of different Sn composition on the CBM at room temperature.

4.6 Summary

In this chapter, the author did theoretical research of $\text{Ge}_x\text{Sn}_{1-x}$ alloy in type I GeSn/Ge quantum well structure by a 6-band k.p method. We calculated the energy band lineup of GeSn/Ge quantum wells, E-k dispersion relations of each subband, the density of states, the spontaneous emission rate spectra and the optical gain in different types of quantum wells. By tuning the parameters (such as Sn component, well width, lattice strain, and temperature), modifications in the simulated optoelectronic performances were observed. In the last session, an abnormal temperature-dependent SERS that were found in the experiment was explained by our k.p model. This chapter gave detailed discussions on the roles of several important parameters in the optoelectronic transitions which also serves as theoretical guidance of following experimental realizations, where such modifications could be experimentally realized by corresponding changes in the process in the fabrication.

Chapter 5. Ge and Sn thin films fabricated by modified magnetron sputtering deposition

In this chapter, high-quality Ge thin films and Sn thin films are deposited on (001) Ge and GaAs substrates. The author would like to find out optimized deposition conditions for growing high-quality Ge and Sn thin films in preparation of GeSn alloy, which includes deposition rate, individual power on the target and chamber pressure. The quality of the thin films is characterized by analyzing surface average roughness and dimensions of the nanoparticles on the surface conducted by atomic force microscope and scanning electron microscope. The deposition rate is measured with the help of a surface profiler analyzer and a hard mask.

5.1 Ge thin film deposition on Ge substrate

Before we fabricated GeSn alloy using dual-target co-sputtering, we tried to fabricate Ge/Sn thin films using radio-frequency sputtering/direct-current sputtering to investigate the proper deposition environment for high-quality Ge/Sn thin films. Note that Ge and GaAs substrate are used for all the samples in these experiments and they have similar lattice structure.

The substrates were cleaned in acetone solvent / Isopropyl alcohol solvent by an ultrasonic cleaner for several minutes to remove all the possible organic and inorganic contaminant. They were dried in the oven at 105°C to get rid of the water residual. They were sent into the vented sputtering chamber after cleaning and were placed on to the rotatable stage in the chamber. High-purity Ge sputtering (99.99% from ACI Alloy USA) target was attached to the radio-frequency power supply. The chamber was then pumped by a molecular pump (running at 350 r/s) associated with a mechanical pump (for the security of molecular pump). During sputtering,

the mechanical pump was always operating at the same time to make sure that the no atmosphere would be in contact with the molecular pump. In order to have thin films with high quality, the chamber was pumped by the two-stage system for at least two hours. Normally, 9×10^{-7} Torr is the basic requirement before the thin film deposition.

Argon is the gas source as the plasma carrier. It was injected into the chamber before the deposition started for the generation of the plasma. There were two parameters to adjust the flow of plasma, pre-pressure and pressure that determine the gas pressure before/during deposition processes. Typically, pre-pressure was set to be 2 mTorr higher than pressure for the generation of plasma. Another purpose for this step is to stabilize the gas flow of Argon plasma in preparation for the following sputtering deposition. The Argon gas flow was sustainably injected through the system for 60 seconds and went down to the pre-set pressure during deposition and stabilized for another 30 seconds. The mechanically controlled shutters were then opened to let in the plasma that would be accelerated by the electric field generated by the power supplies. The initial kinetic energy of the plasmas was determined by the strength of the electric field controlled by the power from the power supplies. The atomic clusters would be ejected from the surface of targets as a result of the bombardment of the high-energy plasmas and deposited on substrates placed on the rotating stage.

In the process of deposition, two main factors (power and chamber pressure) control the deposition environment. We fabricated a series of Ge thin films on Ge substrate using a different combination of the power and chamber pressure (as attached in Table III) to investigate the morphology and quality of the Ge thin films.

Table III. Growth conditions of Ge thin films on Ge substrate

Name	Power (W)	Pressure (mTorr)	Name	Power (W)	Pressure (mTorr)
S1	60	2	S6	80	6
S2	60	4	S7	100	2
S3	60	6	S8	100	4
S4	80	2	S9	100	6
S5	80	4			

Figure 5.1 shows the AFM images of S1-S9 in a scanning area of $5 \times 5 \mu\text{m}^2$. The top three figures are samples grown under lower power (60 W) in comparing to the bottom figures for samples grown under 100 W. Figures in the left column are for the samples grown in lower Argon plasma pressure of 2 mTorr in comparing to figures in the right column grown under 6 mTorr. The largest maximum roughness (R_{max}) extracted from the images is 11.1 nm for S6 while the smallest maximum roughness is for S1 which is 7.2 nm. The largest average surface roughness (R_{ave}) is 1.87 nm for S9 while the smallest one is 0.87 nm for S1. In this batch of samples, R_{max} and R_{ave} are found to be irrelevant to deposition power because in each group of samples where the deposition power is varying (each column), those two values are similar. However, chamber pressure during deposition greatly influences the roughness that increases with pressure (each row in Fig. 5.1) for both R_{ave} and R_{max} . The pressure of the chamber, in other word, reflects the density of Argon plasma that has been accelerated and bombarded on the surface of the Ge target. In the flow of Argon plasma, it will become more crowded if chamber pressure is set to a relatively high level and as Argon plasma is in gas form but with charges, the interaction among the ionized gaseous substance becomes stronger. Collisions among these charged gas played a role in changing its momentum in the way towards the target

material. Therefore, the atomic clusters ejected by Argon plasma would be in various sizes if the initial momentum of plasma varies significantly (under high pressure). Based on this, there is a significant increment in the surface roughness from lower pressure to higher pressure as shown in the figure.

Fig. 5.1 AFM amplitude of samples (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4, (e) Sample 5, (f) Sample 6, (g) Sample 7, (h) Sample 8, (i) Sample 9 in area of $5 \times 5 \mu\text{m}^2$

We further examined the Ge clusters by SEM. Images are taken at electron high tension (EHT) of 5 kV, in a large magnification of 100 k times. Figure 5.2 shows typical SEM images,

where four samples (S1, S3, S7, and S9) are all densely and uniformly covered by Ge nanocrystals. The size of them is not sensitive to the growing power but to the pressure. The lateral dimension of the samples in the right group of figures is approximately two times of that in the left groups of figures, which is consistent with the previous analysis in AFM characterization.

Fig. 5.2 Surface inspecting of samples (a) Sample 1, (b) Sample 3, (c) Sample 7 and (d) Sample 9 by SEM.

5.2 Sn thin film deposition on Ge substrate

Similar growth method was applied for the deposition of Sn thin films on Ge substrates except that the high-purity Sn target (ACI Alloy, USA) was mounted on the direct-current power source. The deposition conditions are listed in the following table.

Table IV. Growth condition of Sn thin films on Ge substrate

Name	Power (W)	Pressure (mTorr)	Name	Power (W)	Pressure (mTorr)
S11	20	2	S14	20	6
S12	20	4	S15	20	2
S13	20	6	S16	20	4

AFM images of the Sn thin films are shown in Figure 5.3. Opposite to Ge thin films, the surface roughness of Sn thin film is more sensitive to growth power instead of the chamber pressure. The density of the bumps observed on the sample surface increased significantly as the sputtering power increased from 20 W (top figures) to 40 W (bottom figures). This comes from the nature of the Sn that is a malleable and ductile metal. Hence large clusters of Sn atoms may be ejected from target because it is softer. The smallest $R_{\max}$ is 11.8 nm for S12 and the largest is 47.1 nm for S15. For R_{ave} , the smallest one is 1.3 nm for S13 and the largest one is 7.7 nm for S15. There is a significant increment in both $R_{\max}$ and R_{ave} after raising the deposition power.

Fig. 5.3 AFM amplitude of samples (a) Sample 11, (b) Sample 12, (c) Sample 13, (d) Sample 14, (e) Sample 15, and (f) Sample 16.

Fig. 5.4 SEM surface inspecting of samples (a) Sample 11, (b) Sample 13, (c) Sample 14 and (d) Sample 16.

SEM images (Figure 5.4) taken at EHT of 5 kV in magnification of 100 k times give a clearer observation on the atomic clusters of Sn thin films. Not much difference is observed from S11 and S13 where Sn clusters on both samples are uniformly distributed. Note that there is a black frame in S13 caused by the long-time illumination of the electron beam from SEM. On S14 and S16, owing to the raised deposition power, the size of the clusters becomes obviously increased, resulting in large $R_{\max}$ and R_{ave} as we discussed previously.

5.3 Ge/Sn thin film deposition on GaAs substrate

Ge and Sn thin films were also tried to be deposited on GaAs substrate using the same technique. Deposition parameters are listed in the following table.

Table V. Growth condition of Ge/Sn thin films on GaAs substrate

Name (Ge)	Power (W)	Pressure (mTorr)	Name (Sn)	Power (W)	Pressure (mTorr)
S21	60	4	S27	20	4
S22	80	4	S28	30	4
S23	100	4	S29	40	4
S24	80	2	S30	30	2
S25	80	4	S31	30	4
S26	80	6	S32	30	6

Normally, magnetron sputtering deposition is considered as a physical vapor deposition method for polycrystalline semiconductor materials where the crystal structure of substrate gives less influence on the growth of thin films. However, when the substrate is changed to GaAs, the morphology of Ge thin film is changed a lot as shown in Figure 5.5. In these six samples, the $R_{\max}$ varies in a large range from 91.5 nm (S22) to 8.2 nm (S26), and R_{ave} in the range from 4.2 nm (S22) to 0.21 nm (S26). No apparent regularity between the growth environment and the roughness compared to the ones grown on Ge substrates.

Fig. 5.5 AFM height images of samples (a) Sample 21, (b) Sample 22, (c) Sample 23, (d) Sample 24, (e) Sample 25 and (f) Sample 26.

The deposition rate of the Ge thin films were characterized by measuring the height of the mesas defined by a hard mask technique. It is highly dependent on the growing power (Figure 5.6), while less dependent to chamber pressure.

Fig. 5.6 Deposition rate of Ge thin film.

For Sn films grown on GaAs substrate, $R_{\max}$ ranges from 17.7 nm (S27) to 360 nm (S32) and R_{ave} ranges from 1.15 nm (S27) to 27.2 nm (S32). Under the same growth circumstances, a lattice mismatch to the substrate causes non-uniformity, resulting in a significant increase in the maximum roughness and average roughness (Figure 5.7).

Fig. 5.7 AFM height images of samples (a) Sample 27, (b) Sample 28, (c) Sample 29, (d) Sample 30, (e) Sample 31 and (f) Sample 32.

Similarly, by measuring the height of mesa defined by the hard mask, we plot the deposition rate of Sn thin film by sputtering as a function of growing power and chamber pressure. The deposition rate of Sn thin films rises fast with deposition power (Figure 5.8).

Fig. 5.8 Deposition rate of Sn thin film.

5.4 Summary

In this chapter, the author explored the deposition conditions for growing high-quality unitary Ge and Sn films on Ge and GaAs substrates. Multiple combinations of deposition power and chamber pressure were tried, and the quality of the thin films was characterized through investigating morphology by atomic force microscope and scanning electron microscope. The average roughness and the size of the nanocrystal could be controlled by adjusting the growth conditions for thin films on Ge substrate but were less controllable for those on GaAs substrates. It turns out that the structure of thin films could be affected by the crystal structure of the substrate. Another important parameter is deposition rate which is highly dependent on the deposition power applied on the target.

Chapter 6. GeSn alloy films fabricated by modified magnetron sputtering deposition

In this chapter, multi-target magnetron co-sputtering deposition is used for growing high-quality GeSn alloy on Ge, GaAs and commonly used Si substrates. The quality of the GeSn thin film is characterized in morphology, crystallography, and elemental composition which are done by AFM, XRD, and XPS respectively. A diffraction phase that indicates the existence of the GeSn alloy is observed in the 2θ - ω scan spectrum measured by XRD. By analyzing the relative differences of Ge and Sn phases, the elemental composition could be calculated which is just in correspondence to the result got from XPS measurements. Temperature-dependent photoluminescence is measured. A negative correlation between temperature and photoluminescence strength with a shifted peak is observed. Transmittance spectra of the thin films are measured by FTIR which shows a dependence on the element composition. In the last session of this chapter, a metal-semiconductor-metal photoconductor is fabricated for characterizing the photo-electron conversion behavior.

6.1 Growth of the $\text{Ge}_{1-x}\text{Sn}_x$ thin films on various substrates

In the previous chapter, the sputtering growth conditions for the Ge/Sn thin films were discussed. In this chapter, co-sputtering deposition is applied to the growth of $\text{Ge}_{1-x}\text{Sn}_x$ thin films by sputtering the two targets simultaneously. We tried different types of intrinsic substrates, including the most common Si (001) substrate, Ge (001) substrate that has the closest lattice constant and the same crystal structure (diamond), and (001) GaAs substrate with a similar lattice constant and crystal structure (zinc blende).

The substrates were cut into square pieces in the size of $0.8 \times 0.8 \text{ cm}^2$ approximately. They were cleaned in the acetone solvent followed by isopropyl alcohol solvent by a standard ultrasonic cleaner for 5 minutes for each step. The power of the ultrasonic cleaner is set to 20 percent of full power in which the substrates get broken in the cleaner for group III-V GaAs substrates. Then, they were further washed in the de-ionized water by the ultrasonic cleaner to remove all the possible chemical residual. Before they were sent for thin film deposition, they were baked at 105°C in an oven. Despite all these common procedures, the Si substrates were required to be immersed into 5% HF solvent for removing the top SiO_2 layer in the beginning.

The chamber of the sputtering system was pumped before loading substrates into it. This procedure proved to be important as the dirt (from last sputtering process) and gas (H_2O and O_2) floating in the chamber could influence the quality of the thin films. Substrates were sent into the vented sputtering chamber after cleaning and were placed onto the rotatable stage at the bottom of the chamber. High-purity Ge and Sn sputtering (99.99% from ACI Alloy USA) targets were attached to the radio-frequency power supplies and direct-current power supply respectively. The vacuum chamber was pumped by a two-stage pumping system where the first stage is a vacuum pump and the second stage is a molecular pump. The chamber pressure was first lowered to a safe vacuum level which is approximately 9×10^{-3} Torr by a mechanical pump. Molecular pump running at 350 round per second would get damaged if it is operating in the atmosphere. Hence it was activated when the chamber pressure is low enough. During sputtering, the mechanical pump was also operating at the same time to ensure safe running environment. In order to get GeSn thin films of high quality, the chamber was pumped by the two-stage system for at least two hours before deposition. Normally, 9×10^{-7} Torr is the basic

requirement before the thin film deposition.

Argon was used as the carrier of plasma. In order to generate Argon plasma easily, the pressure of chamber before the deposition was set a higher value than that during deposition, typically 2 mTorr higher. This procedure could also help stabilize the strength of plasma flow in case of a sudden change in the pressure, especially in the starting phase of deposition. Two targets were isolated from the environment by metal covers with mechanically controlled shutters for prohibiting the possible cross-contamination. During the deposition process, the shutters were opened to let in the plasma that would be accelerated by the electric field generated by the power supplies. The initial kinetic energy of the plasmas was determined by the strength of the electric field that was controlled by the power applied. The target atomic clusters would be ejected from the surface of targets as a result of the bombardment of the high-energy plasmas, and deposit on the various substrates placed on the rotating stage.

Modifications, as shown in Figure 3.1 in Chapter 3, have been made to the sputtering system to be able to fabricate high-quality thin film that has smooth surfaces and good crystallinity. External long metallic covers were installed on each of the targets obliquely whose ends were directed to the substrate. Atomic clusters that were ejected from the surface would have different initial velocities depending on the size and mass. Large and heavy ones would have very low velocity and would not be able to get through the oblique metal cover and reach the substrate. Gravity would drive them to be attached to the inner surface of the metal cover. This mechanism made the metal covers to act as a size selector of the atomic clusters. Hence, only fine ones were able to be deposited on the substrates.

Referring to the growth condition for the individual target that has been discussed in the

previous chapter, a combined set of deposition parameters are used in the simultaneous co-sputtering of $\text{Ge}_{1-x}\text{Sn}_x$ thin films. In order to investigate how the lattice structure of the substrate would affect the formation of GeSn thin film, the GeSn thin films on different substrates were grown at the same time. Chamber pressure during deposition was set to 3 mTorr. The sputtering power was set to 100 W for Ge target and 20 W for Sn target, which gave 0.9 nm/min and 4.66 nm/min of deposition rate for Ge and Sn, respectively. The deposition time was fixed to 60 mins to obtain a thin film with a thickness of around 330 nm. Such parameters compromised for fair element composition ratio and the dimension of atomic particles for both targets.

6.2 Characterization of GeSn thin films

6.2.1 Morphologic and crystallographic characterization

Surface roughness measurement and morphology analysis were carried out by atomic force microscopy in an area of $5 \times 5 \mu\text{m}^2$ as shown in Figure 6.1 in which (a), (b) and (c) are $\text{Ge}_{1-x}\text{Sn}_x$ thin films deposited on Si, GaAs, and Ge substrate, respectively. There are a lot of “spikes” existing on the surface of the thin films which are the noises within the system, as the surface average roughness is below 1 nm that is close to the measurement limits of the tool. Figure 6.1 (d) is the zoom-in photo taken by scanning electron microscope, showing the nanoparticles on the surface. The lateral dimension of the clusters observed is in several tens of nanometers. Through the analysis software, the vertical average roughness (R_a), maximum roughness (R_{max}) and surface area difference are calculated as listed in Table VI. The average roughness is below 1 nm and the maximum roughness is below 10 nm.

Fig. 6.1 3-dimensional AFM images of $\text{Ge}_{1-x}\text{Sn}_x$ thin films grown on (a) Si, (b) GaAs, and (c) Ge substrates in $5 \times 5 \mu\text{m}^2$. Spikes on the surface are the noises within the AFM which means the roughness of the samples is as small as the amplitude of noises. d) Zoom-in SEM image of the surface.

Table VI. Surface roughness analysis of GeSn thin films by AFM

Name	Substrate	R_{average} (nm)	R_{max} (nm)
S1	Si	0.65	7.1
S2	GaAs	0.77	10.5
S3	Ge	0.71	9.1

X-ray diffraction measurement was carried out by a Bruker D8 high-resolution X-ray diffraction equipped with Cu-K α radiation operated at 40 kV and 40 mA in a parallel beam profile. The stage that holds the samples is equipped with a high-precision horizontal goniometer attached with Euler cradle including a three-dimensional X-Y-Z motion. The

strength and the focus of the X-ray beam could be adjusted by changing the types of the monochromators. In our case, a 2 mm slit was used. Two detectors were installed for different purposes. Scintillation 0D detector was commonly used for rapid scans such as sample alignment and rough measurement, while 1D Lynxeye detector was used for precise measurements such as coupled scan and reciprocal space mapping. The samples were fixed on the stage by an integrated vacuum system which fixed the substrate through the holes on the stage. Before XRD data capturing, sample alignment was necessary for thin film XRD, because it is orientation sensitive. The orientation of the substrate was used for it is typically the strongest signal in XRD measurement. 0 D detector was firstly used for a quick scan in the alignment process. Z scan was applied to adjust the height of the stage to let pass the half of maximum X-ray beam. A rocking curve scan was followed to adjust the tilt of the sample. These two procedures were repeated unless the optimized Z position and tilt was unchanged. Then the sample was driven to ω -2 θ position to align the substrate (note that the initial tilt measured by rocking curve scan and Z scan was included). The 2 θ position of Bragg peak for Si, Ge and GaAs substrates in the phase of (004) are 69.13 °, 65.99 ° and 66.07° respectively. The ω position equals to half of the 2 θ position plus the tilt. A combination of χ scan and rocking curve scan was used to align the (004) phase of the substrate by optimizing on the centroid of the parabola got from the scans. It was repeated several times until the θ and χ values remain almost unchanged. A repeated detector scan combined with 2 θ - ω scan was then used to optimize the position of the detector.

The coupled 2 θ - ω scan was carried out by a 1D detector for data collection. The increment of 2 θ was set to 0.005 degrees and the scan speed was set to 0.2 second/step. Such settings

certified a precise and detailed XRD spectrum. The raw XRD data with zoom-in GeSn phase (insert) was shown in Figure 6.2. In Figure 6.2 (a), the major peaks corresponded to the (004) phases of the substrates as mentioned before. The strong side peaks were induced by the Cu-K α radiation. As shown, we observed three constructive diffraction peaks related to the deposited thin film, which corresponded to β -Sn (004), GeSn (004) and Ge (004). The existence of Ge (004) and β -Sn (004) demonstrated that a portion of sputtered atomic clusters is not fully induced to form GeSn alloy but self-organized into single-crystalline islands inside the thin film. The GeSn peak is extracted from the envelope located at around 65.6 degrees close to the peak of β -Sn. In the case of the other samples shown in (b) and (c), because of the strong background intensity induced by the substrates, XRD phases that correspond to the Ge islands inside the GeSn thin films are covered. The GeSn (004) phases in this way could be extracted which are in the 2θ locations of 64.67, 64.69 and 64.58 degrees respectively.

Fig. 6.2 XRD spectrum of GeSn thin films deposited on (a) Si (001), (b) GaAs (001), and (c) Ge (001) substrates.

The relative difference in 2θ among the phases reflected the relative lattice constant. By substituting the θ value into Bragg's Law, we were able to calculate the lattice constant of the GeSn.

$$2d \sin(\theta) = n\lambda \dots\dots\dots (45)$$

where n is the order of diffraction which equals to 4 for the (004) phase. d is the distance between two nearby atomic layers. Considering the diamond lattice structure it has, d should be equal to lattice constant a . θ is half of the 2θ value of GeSn peak. λ equals to 1.54 nm for the wavelength of incident X-ray generated from Cu- $k\alpha$ radiation.

Hence Sn content that was introduced into GeSn alloy could be figured out with the help

of Vegard's Law.

$$a_{Ge_{1-x}Sn_x} = (1-x) \cdot a_{Ge} + x \cdot a_{Sn} \dots\dots\dots (46)$$

The in-plane lattice mismatch is defined by

$$Mismatch = (a_{epi} - a_{sub}) / a_{sub} \times 100\% \dots\dots\dots (47)$$

The lattice mismatch between GeSn and Si is calculated as 6.08%, and the Sn fraction in this sample is about 12.4%. The lattice mismatch between GeSn and GaAs is about 1.85% and the derived Sn fraction is about 12.6%. The lattice mismatch between the thin film and Ge substrate is 1.96%, and the Sn fraction rises to about 13.3% which is slightly higher than those in the films grown on Si and GaAs substrate. The lattice strain in GeSn on Si is the highest because of the large difference between lattice constants even though it has the smallest Sn content.

Figure 6.3 shows the XPS measurement of the sample. In the GeSn thin film. Scan on the Ge 3d orbit was used for the chemical bond analysis. Before the sample was loaded into the ultra-high-vacuum (UHV) analysis chamber, the surface of the sample was etched for 2 mins, which removed about 10 nm thick materials from the surface of the sample, in order to exclude the possible contamination and absorbed gas molecule. The envelope we got as shown by the raw data contained information related to all possible Ge related chemical bonds, which in this case can be Ge-Ge bond and Ge-Sn bond. By inputting the standard values of the peak location for Ge 3d orbit and the full width at half maximum (FWHM), which are 29.4 eV and 1.13 eV, respectively, the Ge 3d orbit envelope could be fitted by two component peaks using a standard XPS software (XPSPEAK41). The extracted minor peak shown as the green curve, corresponded to the Ge-Sn chemical bonds. The area ratio among these peaks can be regarded

as the element ratio in the thin films, and we observed about 13% of Ge-Ge bonds are replaced by Ge-Sn bonds. This result is consistent with the one we got from the calculation by Vegard's Law.

Note that the electron beam source in XPS could only penetrate into 10 nm at most from the surface, hence neither the type of substrate nor the lattice mismatch affects the XPS spectrum on Ge 3d orbit for a 300 nm thick thin film.

Fig. 6.3 XPS spectrum scanning on Ge 3d orbit. The raw data is fitted by software, and two subpeaks are extracted which are Ge-Ge bond and Ge-Sn bond.

6.2.2 Transmittance and photoluminescence spectra

In addition to the morphology and crystallography that is in our concern, the photonic properties are very important and need to be studied. The properties are highly dependent on the electronic structure of the material including the bandgap, and the energy difference between direct and indirect valleys.

To investigate the energy band gap and the electronic structure of the thin films, we measured the transmittance spectrum of the samples by FTIR. To eliminate the influence that the substrate may bring in, we used the sample grown on GaAs substrate whose bandgap (1.42

eV) is much larger than that of GeSn alloy (0.5 eV – 0.8 eV). We also fabricated a Ge thin film on the same GaAs substrate as a reference. Figure 6.4(a) shows the transmittance spectrum of the three samples (red curve: Ge thin film as the reference, black curve: substrate transmittance, blue curve: GeSn thin film). In the case of GaAs substrate, the absorption starts at 1.34 eV and cut off occurs at 1.40 eV with a steep drop (-8.5 eV^{-1}) which displays a typical transmittance spectrum of a direct band-gap characteristic. For Ge thin film, the absorption edge is located at 0.8 eV and the cut-off occurs at 1.39 eV with a drop rate of -1.1 eV^{-1} . This shrinkage of the slope can be considered as the consequence of narrower indirect L valley. A low efficiency indicates that only part of the photons with certain energy could be absorbed by the active Ge layer. As for $\text{Ge}_{1-x}\text{Sn}_x$ thin film, the absorption edge is further red-shifted to 0.5 eV and the cut-off is shifted to 1.12 eV. This observation indicates that the Sn atoms incorporated into the Ge lattice lower the CBM and the energy gap. The transmittance curve is divided into two parts. The first part is from 0.5 eV to 0.7 eV, where the slope is apparently steeper than the rest part of the curve. In comparison to Ge thin film, it increases to 3 eV^{-1} , suggesting that it is a direct gap dominated region where the role of Γ valley becomes significant and the two valleys have been crossed over. The region after 0.7 eV is similar to the Ge reference which is due to indirect band domination. The insert in the figure shows the change of the slope. The results reflect the influence of the electronic structure of the material on transmission.

Fig. 6.4 (a) Transmittance spectra of GeSn thin film, GaAs substrate, and Ge thin film. The inset shows the slope of the curves. (b) Tauc plot of GeSn thin film, GaAs substrate, and Ge lattice. (c) Tauc gaps of GeSn thin film, GaAs substrate and Ge lattice extracted from the intercept on energy axis from Tauc plot. (d) Temperature-dependent photoluminescence of GeSn thin film. A slight blue shift is observed under rising temperature. (e) Calculated electronic temperature-dependent band structure of GeSn thin film. (f) Comparison between the measured and calculated bandgap.

Tauc plot is used to estimate band gap of the thin films described by

$$(\alpha h\nu)^{1/m} \propto (E_g - h\nu) \dots\dots\dots (48)$$

where α is the measured absorbance (equals to $\log_{10}(T)/thickness$), $h\nu$ is the photon energy and E_g is the energy bandgap. m is a value that is dependent on the nature of the photon-electron transition ($m=0.5$ for direct allowed transition, $m=2$ for only indirect allowed transition). We plot the term $(\alpha E)^2$ as the function of photon energy $h\nu$ as shown in Figure 6.4(b). The energy gaps of three samples can be estimated by the interception of curves on the horizontal axis. Bandgap values, extracted from the intercepts are 0.56 eV for $\text{Ge}_{1-x}\text{Sn}_x$ thin film and 0.94 eV for Ge reference as shown in Figure 6.4(c). The observations clearly indicate that direct transmissions dominate in the $\text{Ge}_{1-x}\text{Sn}_x$ film.

Temperature-dependent photoluminescence measurement was carried out by a solid-state near-infrared 1064 nm laser. The laser beam was chopped into 350 Hz pulsed light source by a chopper, and illuminated on the sample attached on an adjustable sample holder by conductive silver glue. The holder was installed in a chamber that connected to a vacuum pump and air compressor. The compressor was for lowering the temperature of sample (lowest temperature: 4 K), and the vacuum pump was for getting rid of the water in the air that would congeal to ice on the window which might forbid the light to come in. The whole stage could move in X-Z dimension to aim the beam on the sample. The PL signals and the reflected light was focused by a series of convex lenses to form a light spot that had the highest intensity. It passed through a 1300 nm long-pass light filter to screen out the reflected 1064 nm source signal and to let the PL signals be collected by an infrared detector. The measured photoluminescence results are shown in Figure 6.4(d). We detected PL signals on $\text{Ge}_{1-x}\text{Sn}_x$ film grown on Ge substrate. As shown in the figure, the PL peak at 13 K is at about 0.58 eV which is consistent with the bandgap value extracted from Tauc Plot. The peak position is red-shifted with the increase of

temperature from 13 K to 50 K which can be described by the Varshni equation. This is a characteristic of direct bandgap emission. As expected, the peak intensity decreases significantly with the increase of temperature due to reduced excitation and band-to-band recombination efficiency at high temperature. When the measuring temperature increased to higher levels, no apparent PL signals could be observed. This may be due to the defects induced during deposition which would form traps (non-radiative recombination centers) where most of the stimulated electrons got captured instead of radiative recombination with the holes. This effect would be more significant at room temperature.

This temperature-dependent photoluminescence spectrum reflected the change of the electronic band structure with temperature. We simulated the situation using our k.p software and calculated E-k dispersion relation as shown in Figure 6.4(e). Y-axis corresponds to the energy. Relative "0" point of the level is set to the average valence band energy ($E_{v,av}$) of Ge. The X-axis corresponds to the coordinates in the reciprocal space. The major transition energy, heavy hole 1 (HH1 as green curve) to electron 1 (E1 as black curve) rises from 0.576 eV to 0.58 eV with temperature decreasing from 50 K to 13 K. A 2% compressive strain is taken into consideration for GeSn thin film has a larger lattice constant with respect to Ge substrate. A comparison of the theoretical energy gap and the measured gap from PL measurements shows that they are in good agreement as shown in Figure 6.4(f).

6.2.3 Sn/Ge ratio dependent optoelectronic properties

The amount of Ge atoms that have been replaced by the Sn atoms affects the band diagram of GeSn thin films according to our calculation in Chapter 3. This could be realized by adjusting

the ratio between the deposition rates for both targets during co-sputtering. In this case, we fabricated a series of $\text{Ge}_{1-x}\text{Sn}_x$ thin films on GaAs substrate based on different Sn fraction. From sample 1 to sample 5, the deposition power of the Ge target was fixed at 100 W while the power for Sn target was gradually raised from 8 W to 20 W.

Figure 6.5 (a) shows the transmittance spectra of the GeSn thin films, Ge lattice reference, and GaAs substrate. The absorption edge of the thin films is moving from long-wavelength range to short-wavelength range as the Sn composition is reduced (as shown in insert). Sample 5 has the response at the longest wavelength near $2.1\ \mu\text{m}$, while sample 1 responds at the shortest wavelength near $1.5\ \mu\text{m}$ which is slightly longer than the response of pure Ge lattice. In contrast to the transmittance spectrum of GaAs substrate which displays a typical transmittance spectrum with a sharp drop at the absorption edge, GeSn thin films including Ge lattice show a rather mild drop. The slope of the curves becomes smaller as the Sn composition is reduced. Comparing to the transmittance spectrum of Ge, the mechanism of photon-electron transition in GeSn thin films, especially with higher Sn composition, becomes more direct-gap dominated. The estimated Tauc bandgap shown in Figure 6.5 (b) verified this point that the bandgap of sample 5 already decreases to below 0.6 eV. Figure 6.5 (c) shows the Tauc gaps of the GeSn thin films of various Sn composition, Ge lattice and GaAs substrate. It is extracted from Tauc plot and shows a negative correlation between energy gap and Sn composition.

Fig. 6.5 (a) Transmittance spectra of Ge_{1-x}Sn_x thin films on GaAs substrate with the insert showing the change of absorption edge. (b) Tauc plot of Ge_{1-x}Sn_x thin films. (c) Estimated Tauc energy gaps of Ge_{1-x}Sn_x thin films.

6.3 A GeSn based MSM photoconductor

Photodetection related optoelectronic applications have been explored for Ge_{1-x}Sn_x alloys by the research community, and both Ge_{1-x}Sn_x related photoconductive and photovoltaic devices have been reported. Their excellent performance in photoelectric conversion shows the promising prospect for optoelectronic integration. To investigate the optoelectronic property of Ge_{1-x}Sn_x films grown by our modified sputtering system, we fabricated GeSn (S5) based photoconductors on GaAs substrate with a metal-semiconductor-metal configuration. The structure of the photoconductor is shown in Figure 6.6(a). The patterns of the photoconductors

are defined by a hard mask, followed by deposition of 30 nm Ti and 200 nm Au with an E-beam evaporation to form the metal contacts in the devices. The central gap of the device has a length of 100 μm and a width of 150 μm .

Fig. 6.6 (a) The structure of GeSn MSM photoconductor. The inset is the top view of photoconductor taken by an optical microscope. (b) I-V characteristics of photoconductor measured within -1 V to 1 V. The resistance of the photoconductor in the dark environment is around 27 Ω . (c) Photocurrent as a function of bias current at 456 mW as the power of the incident laser. (d) Photocurrent as a function of laser power at 3.6 mA as the bias current.

In experiments, a 1064 nm continuous laser was used to evaluate the photoelectric conversion of the photoconductor as it has much smaller photon energy than the bandgap of GaAs (1.43 eV). This eliminated the possible contribution brought by substrate. Many of the devices have been reported by other groups but they are based on Ge substrate. It has a very

similar response region and strength to GeSn thin film, hence is very hard to tell whether it is from GeSn. Our device entirely gets rid of such concerns because GaAs has no response to the light source being used. The laser beam was mechanically chopped into pulses of 300 Hz as the incident source to excite electrons and holes pairs (EHPs) in the $\text{Ge}_{1-x}\text{Sn}_x$ gap which form photocurrent under a bias. The photoelectric current signal was first amplified by a preamplifier and then recorded by a lock-in amplifier. The GeSn photoconductors on GaAs have a resistances of 27 Ω , as derived from the current-voltage characteristics shown in Figure 6.6(b). The linearity of the I-V indicates good ohmic contacts in the device eliminating the possible contribution of the metal-semiconductor junction. As evident from Figure 6.6(c) and Figure 6.6(d), the photocurrents increase linearly with the increasing bias current and output power of the source for both devices. They are in agreements with the theoretical expectation

$$I_{ph} = q\eta A\Phi_s R I_b \tau \mu_e / l^2 \dots\dots\dots (49)$$

in typical photoconductive detectors (where q is the element charge, η is the quantum efficiency, A is the area of the sensitive element, Φ_s is the incident photon flux, I_b is the bias current, τ is the lifetime of the carriers, μ_e is the mobility of the electrons, and l is the distance between metal contact). To evaluate the photoelectric conversion of the device, photocurrent responsivity $R_i = I_{ph}/p$ is used. For GeSn photoconductor on GaAs, by assuming a uniform distribution of incident power in the surface plane (with an area of $\sim 28 \text{ mm}^2$), the incident power on the device is 243 μW for the laser power of 456 mW. Therefore, at an applied bias of 3.6 mA, the photocurrent responsivity is $\sim 0.28 \text{ mA/W}$ at 1064 nm at room temperature. This responsivity value is comparable to that of the reported CVD grown GeSn photoconductors in Ref. [130].

6.4 Summary

GeSn thin films manufactured by a modified multi-target co-sputtering deposition have been characterized in two categories: morphology and crystallography. Roughness analysis conducted by AFM and SEM shows a smooth and uniformly distributed atomic clusters with an average roughness below 1 nm on the surface of the thin films. XRD measurements associated with XPS help confirm the formation of Ge-Sn phase in the symmetrical ω -2 θ scan and the elemental composition of the thin films. The maximum Sn fraction achieved is around 13% by adjusting the ratio of individual target power. Its photoluminescence response locates at 0.58 eV. Correspondingly, absorption edge observed in the transmittance spectrum of such material is at around 0.6 eV and goes up to 0.81 eV when Sn fraction is reduced to a minimum level. The GeSn thin film is further used for the fabrication of a metal-semiconductor-metal photoconductor. A hard mask process with E-beam evaporation defines the metal Ti/Au contacts. The dark equivalent resistance of the device is 27 Ω . The photocurrent responsivity is around 0.28 mA/W at room temperature with the illumination of 1064 continuous laser.

Chapter 7. GeSn/n-GaAs hetero-structure infrared photodetector

In this chapter, the theoretical analysis, device fabrication and device characterization of a GeSn/GaAs hetero-structure infrared photodetector is discussed. Similar techniques are used to characterize the performances of the GeSn thin films grown on GaAs substrate as discussed in previous chapters. The structure of the device is defined by standard optical photolithography associated with wet-etching procedures and electron beam evaporation. Dark current measurement shows good linearity in MSM structure of each layer, proving good ohmic contacts. Photocurrent responses of the devices are carried out by a wavelength-tunable laser and the spectral responsivity is analyzed. The hetero junction suppresses the dark current [131], hence a good sensitivity is acquired in the photodetector which is approximately 10 to 100 times larger than the devices reported by other groups.

7.1 Growth of intrinsic GeSn on n-type (001) GaAs substrate

The GaAs substrates that were used in this work are $0.7 \times 0.7 \text{ cm}^2$ pieces cut from a 2-inch n-type GaAs (001) wafer pre-doped to $2 \times 10^{12} / \text{cm}^3$. They were cleaned by acetone solvent in an ultrasonic cleaner for 5 minutes to remove organic residuals and dirt that were attached on the interface of the substrate. Isopropyl alcohol solvent was used for further deep cleaning in the ultrasonic cleaner for 3 minutes to get rid of the remaining contaminant. The vibration to the substrate induced by the ultrasonic cleaner could be hazardous hence the power of it should be carefully chosen. 20% of the full power is the upper limit for the cleaning of our substrate. HF solvent is used then to remove oxide layer. Post-baking is applied to remove

remaining moistures.

Substrates were sent into the vented sputtering chamber after the cleaning and were placed on to the rotatable stage at the bottom of the chamber. High-purity Ge and Sn sputtering (99.99% from ACI Alloy USA) targets were attached to a radio-frequency power supply and direct-current power supply respectively. Similar settings as discussed before is used. During sputtering, the vacuum pump was also operating at the same time to make sure that the no atmosphere would be in contact with the molecular pump. In order to get GeSn thin films of high quality, the chamber was pumped by the two-stage system for at least two hours. Normally, 9×10^{-7} Torr is the basic requirement before the thin film deposition.

The gas source that was used as the plasma carrier was Argon. It was injected into the chamber before the deposition started for the generation of the plasma. The chamber pressure during this process was set to a bit higher than that in the process of deposition, typically 2 mTorr higher, in order to inform plasma easily. Another purpose for this step is to stabilize the gas flow of Argon in preparation for the following sputtering deposition. Two targets were isolated from the plasma flow by shutters that were installed on them which prohibited the possible contamination. The Argon gas flow is sustainably injected through the system for 60 seconds and went down to the pre-set pressure during deposition and stabilize for another 30 seconds. The mechanically controlled shutters were then opened to let in the plasma that would be accelerated by the electric field generated by the power supplies. The initial kinetic energy of the plasmas was determined by the strength of the electric field that was controlled by the power applied to the power supplies. The target atomic clusters would be ejected from the surface of targets as a result of the bombardment of the high-energy plasmas, and deposit on

the GaAs (100) substrate placed on the rotating stage.

External long metallic covers were installed on each of the targets obliquely whose ends were directed to the substrate. Atomic clusters that were ejected from the surface would have different initial velocities depending on the size and mass. Large and heavy ones would have very low velocity and would not be able to get through the oblique metal cover and reach substrate. Gravity would drive them to be attached to the inner surface of the metal cover. This mechanism made the metal covers to act as a size selector of the atomic clusters. Hence, only fine ones were able to be deposited on the substrates.

Samples made of various Sn/Ge ratios were fabricated. The power of the radio frequency power supply was fixed at 100 W while the power of direct current power supply varied from 20 W to 40 W in order to adjust the elementary composition.

7.2 Characterization of the GeSn thin films on GaAs substrate

AFM was used for the analysis of the surface roughness. The quality of GeSn thin film was estimated by analyzing the average surface roughness (R_A), maximum roughness (R_{max}) and particle distribution. The thickness was measured by a thin film profiler. The samples are named as S1, S2, and S3, where the composition of Sn is gradually raised by increasing the deposition power of Sn target. The growth conditions with specs are listed in the following Table VII.

Table VII. Specifications of S1, S2, and S3

Name	Power	R_a	R_{max}	Diameter of	FWHM	Thickness
	(W)	(nm)	(nm)	particle (nm)		(nm)
S1	20/100	3.51	168	40	5	300
S2	30/100	0.53	57.9	28	2	325
S3	40/100	0.52	47.3	34	1.8	340

As the Sn component increased, the average roughness of the sample had a significant drop, from over 4 nm to 0.5 nm. This feature also reflected in the maximum roughness of the sample surface and the size distribution of the particles, where S1 had the largest $R_{\max}$ (168 nm) and the largest diameter of particle (40 nm). S2 had the smallest $R_{\max}$ (57.9 nm) and diameter (28 nm). The full width half maximum (FWHM) of the diameter distribution reflected the uniformity of the surface, where S1 had the largest (5 nm) and S3 had the lowest (1.8 nm). In the AFM images of these four samples, we found that in the case of S1, relatively large-sized atomic clusters (large white spots) were uniformly distributed on the surface of the sample, which excluded the possibility of the external contamination. The vertical dimension of these spots was much larger than that of the spots observed in the cases of S2 and S3. S2 and S3 have much smoother surfaces. In conclusion, the surface roughness is highly sensitive to the Sn/Ge ratio in the GeSn thin films. There would be a significant drop down in the roughness level when the ratio goes above 20/100. Three-dimensional AFM images as shown below gave a direct observation of GeSn thin films. Note that the vertical magnitudes were different.

Fig. 7.1 (a) AFM photo of Sample 1. (b) AFM photo of Sample 2. (c) AFM photo of Sample 3. (d) Surface roughness analysis of GeSn thin films through AFM.

We performed X-ray diffraction measurement on these samples to analyze the crystallography of them. The tool we used is a Bruker D8 high-resolution XRD. It is equipped with Cu-K α radiation operated at 40 kV and 40 mA of a parallel beam profile. It has various types of the attachable monochromators to adjust the focus and the strength of the X-ray and a high-precision horizontal goniometer attached with Euler cradle including an X-Y-Z motion. Two detectors for different applications are equipped, typically scintillation 0D detector for sample alignment and rough measurement, and Lynxeye 1D detector for precise measurement.

During sample alignment, the 0D detector was used. The sample was firstly attached on to the stage using double-tape. Z scan and rocking curve scan were applied to adjust the Z position and the tilt of the surface in order to receive the strongest X-ray. Repeat scans helped optimize the alignment by bisecting the beam. After that, the samples were aligned by finding the substrate peak. In our case, we use symmetrical (004) peak of GaAs which should be located 66.07degrees in the 2θ - ω scan. The goniometer was driven to 2θ and θ for the substrate's symmetrical Bragg peak where θ should be 33.03 degrees plus the tilt. A rocking curve scan was applied to align the accurate θ value by optimizing on the center of the parabola that defines the top half of the peak. A χ scan was followed to align the incident angle of the X-ray by optimizing on the centroid of the peak during rotating. These two steps were repeated several times until the θ and χ values remain almost unchanged. A repeated detector scan combined with 2θ - ω scan was then used to optimize the position of the detector.

The XRD data were collected by coupled 2θ - ω scan using 1D Lynxeye detector. The increment in of 2θ was set to 0.005 degrees and the scan speed was set to 0.2 second/step. Such settings certified a precise and detailed XRD spectrum. Raw XRD data of coupled 2θ - ω scan on sample 1 was shown as below. Strong peaks observed at 2θ of 31.6° and 66.1° represent the (002) phase and (004) phase of GaAs substrate. The peaks in between at 44.2° and 64.46° represent the (022) phase and (004) phase of GeSn thin film. By analyzing the d-spacing according to the standard XRD peaks of Ge and Sn, the content of Sn that was induced in the Ge lattice can be calculated with the help of Vegard's Law:

$$a_{A_xB_{1-x}} = x \cdot a_A + (1-x) \cdot a_B \dots\dots\dots (50)$$

which equals to 14.8%. The intensity of GeSn peaks is two-order lower than that of the GaAs

peak, indicating that the crystallinity of the GeSn thin film is not as good as substrate. We extracted the region where GeSn (022) phase lies in, zoomed in and compared the GeSn (022) phases of all the three samples as shown in Figure 7.2. A shift in the 2θ value is clearly observed as we expected. By increasing the power of RF power supply applied on Sn targets, S3 was supposed to have the highest Sn/Ge ratio among these three samples, reflected as the smallest 2θ value of centroid of GeSn peak in XRD spectra. Using the same calculation methods as we discussed above, the composition of Sn in the three samples is 14.8%, 15.6%, 16.4%, respectively. The consistency of the growth method was verified, where full width half maximum of the GeSn peaks are similar,

Fig. 7.2 (a) Full-range XRD scan on Sample 1 from 20 degrees to 75 degrees. Three major peaks from left to right are GaAs (002), GeSn (022), and GaAs (004) phases. (b) Zoom-in extracted GeSn (022) phase of Sample 1. (c) The shift of GeSn phase as a function of Sn composition.

We used FTIR to examine the electronic band structure of the GeSn thin films. The bandgap of the material determines the transmittance spectrum of it. Photons with energy smaller than the bandgap will be able to travel through the thin film without being absorbed,

while those with energy higher than the bandgap of the material would break the electron-hole pair, and stimulate the electron on to the conduction band. The energy of the photon will transform into the potential energy of the electron, which in another word is being absorbed. The material will be transparent to photons whose wavelength is larger than the characteristic wavelength of the material (dependent on the bandgap). Therefore, the absorption edge in the transmittance spectrum reflected the energy bandgap. Because we grew GeSn thin films on GaAs substrate, the energy gap of GaAs should also be considered. It has a large value (1.424 eV) than that of GeSn, thus is totally transparent to absorption range of GeSn and has no influence to our conclusions. The transmittance spectrum measured at room temperature of S1, S2, and S3 is shown in Figure 7.3 (a). The absorption edge of S1 (smallest Sn/Ge ratio) is the smallest, hence has the largest energy bandgap. In contrast, S3 has the largest absorption edge which means the smallest energy gap. The experimental results are in good agreement with our previous theoretical predictions.

Tauc plot is a very useful way to estimate the values of the energy gap through transmittance spectrum. It is written as:

$$(\alpha hv)^{1/m} \propto (E_g - hv) \dots\dots\dots (51)$$

where α (Figure 7.3 (b)) is the measured absorbance (equal to $-\log_{10}(T)/thickness$), hv is the photon energy and E_g is the energy bandgap. m is a value that is dependent on the nature of the photon-electron transition ($m=0.5$ for direct allowed transition, $m=2$ for only indirect allowed transition). We plot the term $(\alpha E)^2$ as the function of photon energy hv as shown in following Figure 7.3 (c). The energy gaps of three samples can be estimated by the interception of curves on the horizontal axis, which are 0.7 eV, 0.65 eV and 0.61 eV for S1, S2, and S3 respectively.

They are highly sensitive to the Sn/Ge ratios and a red shift is clearly observed as the content of Sn increased from S3 to S1.

Fig. 7.3 (a) Transmittance spectrum of GeSn thin films grown on GaAs substrate. (b) Absorbance spectrum of three samples. (c) Tauc plot of three samples to estimate the Tauc band gaps.

7.3 Fabrication of GeSn/GaAs hetero-structure photodetectors

GeSn/GaAs hetero-structure infrared photodetectors were fabricated based on samples with the largest bandgap (Sample 1) and the smallest bandgap (Sample 3) to investigate the optoelectronic responses as the function of band structure. The mesa of the hetero-structure photodetector was defined by standard optical photolithography associated with wet-etching

procedures. AZ 5214 photoresist was spin-coated on the surface of GeSn thin films at the rate of 3000 round per minute for 30 seconds. Such recipe gave us a 1.6 μm thick photoresist covering the whole surface. The sample was then baked at 105 °C for several minutes to harden the photoresist in preparation of the following procedure. It was exposed in a Karl Suss mask aligner. The exposure time was determined by an experimental relation: $t = 560 / I$, where I was the in-situ intensity of the light source in the mask aligner. It was developed in the AZ developer solvent (developer/DI water: 1/2) for 120 seconds and post-baked for 8 minutes to get rid of moisture. In this step, AZ5214 photoresist was applied as a positive photoresist.

The GeSn layer on the top of the sample was etched by hydrochloric acid/hydrogen peroxide solvent (15 mL 35% - hydrochloric acid, 15mL hydrogen peroxide, and 300 mL DI water) for 25 seconds. Such a solvent provided an etching rate of approximately 720 nm/min. The substrate was etched in citric acid/hydrogen peroxide solvent (15 mL citric acid, 15 mL hydrogen peroxide and 300 mL DI water) at a rate of 180 nm/min for 10 seconds. Afterwards, the remaining photoresist was removed by acetone solvent. The size of the mesa was 650×650 μm^2 .

The metal contacts of the device were fabricated by standard optical photolithography associated with electron-beam evaporation. Similarly, AZ 5214 photoresist was spin-coated on samples at the rate of 4000 round per minute for 30 seconds to have a thickness of approximately 1.4 μm and baked. Due to the design of our photomask, we used negative-photoresist characteristic of AZ 5214. The first exposure time was determined by relation: $t = 51 / I$. After being baked at 110 °C for 8 minutes, a flood exposure for $t = 255 / I$ was applied. The sample was developed in AZ developer solvent (1 developer/1 DI water) for 25S

and post-baked. Electron-beam evaporation with the help of the lift-off process formed the metal contacts as shown in the schematic cross-section in Figure 7.4 (b). The size of the window opened on the GeSn layer was $300 \times 300 \mu\text{m}^2$.

Fig. 7.4 (a) Configuration of the hetero structure photodetector. (b) Schematic cross-section of the device. (c) Top view of the device by an optical microscope.

7.4 Performances of GeSn/GaAs hetero-structure photodetector

Since GeSn thin film and GaAs substrate have different work functions, two different types of multi-layer metal contacts were needed for the hetero-structure photodetector. Contact barrier would be formed on either material if only one type of contact was used, which will have a significant influence on the performance characterization of the device with a junction. Ti/Au-structure was used for the top layer GeSn, where 20 nm -Ti acted as a binder between the 150 nm - Au layer and GeSn layer. A multi-layer Ni/Ge/Au/Ni/Au-structure associated with

post thermal treatment was used for the substrate layer GaAs. The thickness of each layer was 2 nm, 25 nm, 100 nm, 20 nm, and 200 nm. Ni served as a diffusion barrier between the Au/Ge and GaAs substrate and reacted with GaAs forming Ni_3GaAs during annealing. The thermal treatment also helped form a long-term stable Ni/Ge/Au/Ni/Au contact [2009 NiGeAu]. The effect of annealing temperature is shown in the following figure. 350 °C is a critical temperature that significantly decreases the resistance of the device. In order to verify that the Schottky contact barrier is fully eliminated using these two types of contact, we additionally fabricated MSM structure (as mentioned in Chapter 6) for both material and investigated their I-V characteristic as shown in Figure 7.5 (b). Instead of a typical rectification, good linearity in both layers was observed indicating no Schottky contact remained in the MSM structure. The dark current characteristic as a function of biased voltage of GeSn/GaAs hetero-junction photodetector measured from -1.5 V to +2 V is shown in Figure 7.5 (c). The non-biased dark current density is $1.6 \times 10^{-7} \text{ A} \cdot \text{cm}^{-2}$, and increased to $4.6 \times 10^{-4} \text{ A} \cdot \text{cm}^{-2}$ at -1 V. Obvious rectification is observed, demonstrating the formation of the hetero-structure diode.

Fig. 7.5 (a) Influences of the temperature on the I-V characteristic of the photodetector during RTP. 350 °C is the critical temperature to eliminate the Schottky barrier. (b) I-V characteristics of MSM structures of both layer (Ni/Ge/Au-GaAs and Ti/Au-GeSn) showing good linearity. (c) I-V characteristic of GeSn/GaAs hetero-structure photodetector showing rectification effect. (d) Absolute I-V characteristics in log scale.

Figure 7.6 shows the band diagram of GeSn/GaAs hetero-structure in thermal equilibrium. Due to the affinity energy difference between GaAs (4.07 eV) and GeSn (4 eV), the offset in the (CBM) conduction band minimum is 0.07 eV. The doping in the n-GaAs substrate is $2 \times 10^{15} \text{ cm}^{-3}$. Hence, the Fermi level in GaAs is 0.14 eV below CBM. The Fermi level of intrinsic GeSn is at the centroid of the bandgap. Weak built-in electric field points from n-type GaAs to intrinsic GeSn layer would be formed owing to relatively higher Fermi level in substrate. Reverse bias is defined when the positive voltage is applied on the n-GaAs side.

Fig 7.6 Energy diagram of the hetero-structure photodetector. The built-in electric field is pointing from substrate to absorption layer.

To evaluate the photoresponse of the GeSn/GaAs heterostructure, a wavelength tuneable continuous laser is used to measure the photocurrent response in the range of 900-1450 nm. In this case, possible photocurrent contribution from the GaAs substrate (with a bandgap of 1.434 eV/870 nm) could be excluded, since the photon with such wavelength was not able to stimulate the electron from the valence band to conduction band. In experiments, the incident light was first chopped at 310 Hz and illuminated vertically into the window of the photodetector. The photocurrent driven by the applied bias (integrated into preamplifier) was amplified and got recorded by a lock-in amplifier. The applied voltage bias varied from -0.1 V to -0.5 V. The increment for the wavelength of the incident light is 50 nm. The incident power was calibrated by a standard power meter and all the measured responses have been normalized to the power distribution. We fabricated two heterostructure photodetectors (Device A and Device B) based on GeSn materials with different Sn content (S1 and S3). Figure 7.7 (a) and (b) show the responsivity spectra of both photodetectors in the wavelength range of 900-1450 nm. For Device A (lower Sn composition), the responsivity reached its highest value of 3.5 mA/W at 1250 nm under a voltage bias of -0.5 V. A different spectrum was observed for Device B (higher Sn composition), where the responsivity increased continuously at larger wavelength

and reached its highest value of 0.6 mA/W at 1450 nm under a voltage bias of -0.5 V. Different electronic band structure induced by the different Sn/Ge ratios caused photodetection region of two photodetectors to lie in separate range. Apparently, the device with higher Sn content worked in the longer wavelength range consists of transmittance spectra measured by FTIR. The responsivity for both devices showed a linear relation as the function of voltage bias, indicating that the drifting of the photo-carriers generated in the GeSn was the main contribution of the photocurrent.

Fig. 7.7 (a) Responsivity and (b) detectivity of the GeSn/GaAs hetero-structure photodetector made of Sample 1. The bias voltage is from -0.1 V to -0.5 V. (c) Responsivity and (d) detectivity of GeSn/GaAs hetero-structure photodetector made of Sample 3.

As a figure of merit to estimate the final performance of a photodetector, specific

detectivity (D^*) reflects the sensitivity of the device with respect to noises. It is defined by

$$D^*(\lambda) = R(\lambda) / (2qJ + 4kT / (RA))^{1/2} \dots\dots\dots (52)$$

$R(\lambda)$ is the responsivity as the function of incident light wavelength. J is the dark current density. T is the temperature. RA is the product of resistance and the value of R is derived from the I-V characterization shown in the figure. At room temperature, thermal and dark current shot noises were dominated comparing to the photocurrent shot noise evaluated by RP/A which is two-order lower. The highest detectivity measured in Device A was $2.2 \times 10^9 \text{ cmHz}^{-1/2}\text{W}^{-1}$ at 1250 nm under voltage bias of -0.1V. By increasing the absolute value of reverse bias, the detectivity was found to be decreased owing to the increased dark current noise. As for Device B, the highest detectivity was $0.7 \times 10^7 \text{ cmHz}^{-1/2}\text{W}^{-1}$ measured at 1450 nm under voltage bias of -0.5 V. The detectivity of Device B showed an opposite correlation between bias and detectivity to Device A, owing to increased responsivity at higher voltage bias. The detection region (900 nm-1450 nm) is displaced with the theoretical detection region, hence the significant increase in the responsivity acted dominantly in comparison with the increase in the dark current noise when voltage increased. We compared our work with current state of art reported recently in Table VIII. The detectivity of our device is comparable to the others' measured at room temperature. Considering the simple magnetron sputtering that we used for growing GeSn, this device demonstrated great promise in the optoelectronic applications.

Table VIII. Typical performances of the GeSn based photodetectors

Device	Fabrication technique	Incident wavelength (nm)	Operating bias (V)	Detectivity (jones)
Ge_{0.9}Sn_{0.1} photoconductor [132]	CVD	1550	30	4×10 ⁹ (77 K)
Ge_{0.93}Sn_{0.07} photoconductor [133]	CVD	1550	10	1×10 ⁹ (77 K) 6×10 ⁸ (140 K)
Ge_{0.9}Sn_{0.1} photodiode [134]	CVD	1550	0.05	2.4×10 ⁹ (77 K) 2×10 ⁸ (300 K)
Ge_{0.89}Sn_{0.11} photoconductor [135]	CVD	900-1450	1	2×10 ¹⁰ (77 K) 5×10 ⁷ (300 K)
This work	sputtering	1250	0.1-0.5	2.2×10 ⁹ (300 K)

7.5 Summary

This chapter introduced the design, fabrication, and characterization of GeSn/GaAs hetero-structure photodetector. The performances of the detectors were mainly characterized by a tunable laser in the range between 900 nm and 1450 nm. Two types of photodetectors were made based on GeSn thin films with different bandgaps. They have different spectral responses as a result of different band structures where Device A with larger bandgap has strong responsivity and detectivity in the shorter wavelength range around 1200 nm, while Device B responds strongly in the longer wavelength range. 2.2×10⁹ jones is the highest detectivity measured from Device A at room temperature under -0.1 V. It is a comparable value to the performances of the photodetectors reported by other groups using different deposition methods.

Chapter 8. GeSn quantum dots and enhanced photodetection

In this chapter, the author first explores the fabrication of GeSn quantum dots (QDs) on GaAs substrate and then compare their photodetection properties with the thin film structures. Thin layer of GeSn quantum-dot sheets were fabricated on GaAs substrate. A two-times larger maximum responsivity and detectivity were achieved from the GeSn QDs/GaAs sample compared to GeSn thin-film photodetector owing to the enhanced photocurrent and reduced dark current [136-138]. We also fabricated a nano-scale metal structure, which was a 2-dimensional subwavelength hole array (2DSHA) in the absorption window, on the top of the GeSn QDs/GaAs structure for surface plasmon polariton enhancement (SPP) of photodetection [139-151]. Hole arrays of two different periods were fabricated and they showed the selective enhancement corresponding to their surface plasmon resonance (SPR) wavelength. A further 3 – 6 times enhancement of the maximum responsivity and detectivity was observed in the photodetectors of GeSn QD/GaAs with a subwavelength 2DSHA on top.

8.1 GeSn quantum dots on GaAs substrate

As mentioned in previous chapters, our modified magnetron sputtering system deposits very fine and uniform atomic clusters. Hence it could be very useful for depositing quantum-dot sheets if we could precisely control the thickness of the layer so that only several layers of clusters are deposited on the substrate to form quantum-dot sheet instead of thin films.

We used the same growth recipe of Sample 1 for the fabrication of the quantum-dot sheets except for limiting the growth time down to only 60 seconds. This will give us a roughly 20-nm thick GeSn quantum-dot sheet as shown in Figure 8.1 (a) by AFM. The clusters are firmly

and tightly bound with each other by chemical bonds, showing a very flat and smooth surface. High-temperature rapid thermal process (RTP) is applied to break the inter-connected chemical bonds to form separate dot-like structures. Figure 8.1 (b) and (c) shows the surfaces of the same sample after 30s RTP treatment under 500°C and 700°C. Under 500°C, the thermal energy is not sufficient to break the bonds, hence the surface of the sample remains smooth and flat. When it is increased to 700°C, the quantum-dot sheet is formed and could be clearly observed in the AFM image of the surface. The size of the dot is approximately 100 nm – 200 nm wide in the lateral plane, and about 20 nm – 30 nm thick in the vertical direction.

Fig. 8.1 (a) Surface roughness image of 20nm-thick GeSn thin layer taken by AFM. (b) Surface roughness image of 20nm-thick GeSn thin layer after 30s/500°C RTP treatment. (c) Surface roughness image of 20nm-thick GeSn thin layer after 30s/700°C RTP treatment. Quantum dot sheet is formed after high-temperature RTP treatment.

The transmittance spectrum for the three samples was measured using FTIR spectroscopy with an infrared light source. As shown in Figure 8.2 (a), the transmittance spectrum could reflect the absorption of the three samples in the infrared range from 1000 nm to 3500 nm. The transmittance curves for both samples without RTP (black curve) and with 30s/500°C RTP (blue curve) are quite similar and have almost 100% in the full wavelength range. A very small

part of the incident light could be absorbed by the absorption layer as the thickness of the absorption layer is extremely thin (around 20 nm). Meanwhile, GaAs substrate could not interact at such spectral region, and most of the light will just pass through the sample and get collected by the detector. For the sample with 30s/700°C RTP (red curve), due to the existence of GeSn quantum-dot sheet, the incident light will be scattered back and forth by the rough surface. A large part of the incident light (10% - 30 %) below 2500 nm is able to be absorbed by the quantum dot sheet. Half of the light ingredients pass through the sample, and the rest 20% - 40% are scattered away. Absorbance spectrum derived from transmittance,

$$\alpha = -(1/d) \times \ln(T) \dots\dots\dots (53)$$

is shown in Figure 8.2 (b) where d is the thickness of the absorption layer, T is the transmittance. The quantum-dot sheet formed by RTP significantly enhances the absorbance of the absorption layer.

Fig. 8.2 (a) Normalized transmittance of the 20 nm-thick GeSn thin layers without RTP, with 30 s/500 °C RTP, and with 30s/700°C RTP. About 40% decay in the transmittance is observed after 30 s/700 °C RTP. (b) Corresponding absorbance spectrum of three samples derived from transmittance.

8.2 GeSn QDs/GaAs hetero-structure infrared photodetector

To test the photodetection properties of the GeSn quantum dots, the GeSn quantum dots/GaAs hetero-structure infrared photodetector was fabricated, as shown in Figure 8.3. A GeSn thin layer was firstly deposited by the modified magnetron sputtering deposition system. The power during the deposition process is set to 100 W for Ge target and 15 W for Sn target. The other parameters remained the same as the ones used for GeSn thin-film hetero-structure photodetector. The deposition time was strictly fixed at 60 s. To ensure the flow of Ar plasma stable and steady, the preparation time before the deposition was set to 2 mins during which the Ar ion kept bombarding on the target surface while the clusters are prohibited from falling on to the substrate by the shutters. After the deposition process was finished, the samples immediately underwent for RTP at 700 °C for 30 s to form the GeSn quantum-dot sheet.

The mesa of the photodetector was defined by standard optical photolithography associated with 2-step wet-etching process. The solvent for GeSn QD sheet is hydrochloric acid/hydrogen peroxide solvent (15 mL 35% - hydrochloric acid, 15mL hydrogen peroxide, and 600 mL DI water), and the etching time is 5 s. The substrate was etched in citric acid/hydrogen peroxide solvent (15 mL citric acid, 15 mL hydrogen peroxide and 300 mL DI water) at a rate of 180 nm/min for 10 seconds. The metal contact on the GaAs substrate is Ni/Ge/Au/Ni/Au multilayer structure (2 nm/10 nm/ 80 nm/ 10nm/ 150 nm) deposited by E-beam evaporation and thermally treated in RTP at 350 °C for 30 s. On top of GeSn QD sheet, we deposited Ti/Au (10 nm/150 nm) as the contact. The devices were bound to package using a wire-binding process.

Fig 8.3 Schematic configuration of GeSn quantum dot/n-GaAs hetero-structure infrared photodetector.

The optoelectronic performance of the GeSn QDs photodetectors was characterized by the same tuneable laser system working in the range of 900 nm to 1450 nm. The incident source was chopped into 310 Hz pulses by a chopper and fed back to the lock-in amplifier in order to eliminate the environmental noises. The photocurrent was generated by the vertically illuminated laser and was driven by the bias voltage using a build-in supply. The bias voltage in the case of QDs photodetectors was applied from -4.5 V to 4.5 V. Figure 8.4 (a) shows the responsivity spectra of the GeSn QDs photodetector in comparison to the GeSn thin-film photodetector A. The responsivities of the GeSn QDs photodetector is about 3-6 time better than those of the GeSn thin-film photodetector for wavelengths greater than 1200 nm. The largest responsivity is 13 mA/W measured at 1400 nm (the largest detectivity of the GeSn thin-film photodetector is 3.5 mA/W measured at 1250 nm as discussed in previous chapters). We also notice an improvement in the spectral region before 1000 nm, owing to the largely reduced active absorption layer thickness. A part of the light of certain wavelength (~900 nm) passes through the very thin GeSn quantum-dot sheet and generate electron-hole pairs in the GaAs substrate near the interface. This part is also driven by the bias voltage and contributes to

photocurrent.

The specific detectivity (D^*) of the photodetectors defined by:

$$D^*(\lambda) = R(\lambda)/(2qJ + 4kT/(RA))^{1/2} \dots\dots\dots (54)$$

is shown in Figure 8.4 (b). For the quantum-dot sheet, the term $4kT/(RA)$ is small enough comparing to the term $2qJ$ which can be neglected. The largest detectivity measured from GeSn QD photodetector is 4.7×10^9 Jones at 1400 nm, which is about two times larger than that measured from the GeSn thin-film photodetector (2.2×10^9 Jones at 1250 nm).

Fig 8.4 (a) Responsivity of GeSn QD photodetector and GeSn thin-film photodetector measured from 900 nm to 1450 nm. (b) Specified detectivity of GeSn QD photodetector and GeSn thin-film photodetector.

8.3 SPP enhancement in photodetection

On the surface of a metal, collective excitations of the electron density lead to the formation of surface plasmon polaritons, which are infrared or visible-frequency electromagnetic wave along a metal-dielectric interface. For a photon to excite an SPP, both must meet the requirement of energy conservation and momentum conservation. However, for a given wavelength, a free-space photon has less momentum than an SPP because of different

dispersion relations. This is the reason that the light in the visible to near-infrared range does not couple to surface plasmons on a smooth metal-dielectric interface, but a periodic metal structure allows the optical probing of the surface plasmon dispersion. Optical properties of metallic hole arrays display extraordinary zero-order transmission spectra at wavelengths larger than the array period (subwavelength), due to the coupling of light with plasmons on the surface of the periodically patterned metal thin film. It is found that the position of the peaks is mainly determined by the periodicity of the arrays, independent of types of metal. The width of the peaks is strongly dependent on the aspect ratio (depth divided by diameter) of the holes. Such structures can be manipulated to allow selectively enhanced transmission in a direction which is normal to the plane of the thin film [149, 152, 153]. The very high transmission efficiencies make these structures attractive for possible application in the enhancement of infrared photodetection [145, 154-157].

The 2-dimensional subwavelength hole array GeSn quantum dot/GaAs hetero-structure infrared photodetector was designed and fabricated based on the GeSn/GaAs hetero-structure photodetector.

For the 2DSHA, the interaction between light and the surface plasmon obeys momentum conservation given by [158]

$$k_{spp} = |k_x \pm G_{i,j}| = |k_0 \sin \theta \pm iG_x \pm jG_y| \dots\dots\dots (55)$$

where $k_0 \sin \theta$ is the in-plane incident vector and $G_x = G_y = 2\pi / p$ are the reciprocal lattice vectors. k_{spp} is the wave vector of the SPP at the interface between the metal structure and the dielectric, which is expressed as

$$k_{spp} = k_0 \sqrt{\epsilon_m \epsilon_d / (\epsilon_m + \epsilon_d)} \dots\dots\dots (56)$$

When light is normally incident into the window, for the gold 2DSHA with a hole period p , the surface plasmon resonance wavelengths are given by

$$\lambda_{ij} = \frac{p}{\sqrt{i^2 + j^2}} \text{Re} \left\{ \left[\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d} \right]^{1/2} \right\} \dots\dots\dots (57)$$

where (i, j) is the set of integers denoting the mode orders in x- and y-directions, and $\epsilon_m(\epsilon_d)$ is the permittivity of the metal (semiconductor). The permittivity of GeSn in the wavelength range of interest is around 4.5, while the permittivity of gold is expressed by the Drude model as

$$\epsilon_m(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\omega_\tau)} \dots\dots\dots (58)$$

where $\epsilon_\infty=1$ is the high-frequency dielectric constant, ω_p and ω_τ are the plasma frequency and collision frequency got from the software. Derived from these two equations, the 2DSHA structures in period 400 nm/ 350 nm result in 1400 nm/ 1100 nm as the surface plasmon resonance for the fundamental mode at normal incidence. The confinement of surface plasmon polariton waves in the dielectric layer can be described as the SPP penetration depth

$$\delta_d = \frac{1}{k_0} \left| \frac{\epsilon_m' + \epsilon_d}{\epsilon_d^2} \right|^{1/2} \dots\dots\dots (59)$$

where ϵ_m' is the real permittivity of gold, ϵ_d is the permittivity of GeSn QD sheet, and k_0 is the wave vector in the free space. The penetration depth of the structure is found to around 1000 nm.

The configuration of the SPPs enhanced photodetector is shown in Figure 8.5. On top of

GeSn QD sheet, we deposited Ti/Au (10 nm/150 nm) as the contact. 2D subwavelength hole array was in the center of the window. The pattern of the hole array was defined by E-beam lithography and fabricated by E-beam evaporation with the lift-off process. The thickness of the 2DSHA is around 55 nm, including 5 nm Ti for adhesion and 50 nm Au[159].

Fig 8.5 Schematic configuration of 2DSHA GeSn quantum dot/GaAs hetero-structure infrared photodetector.

We fabricated two types of hole array structure of different periods on the same GeSn QDs/GaAs hetero-structure photodetector. Figure 8.6 shows the top view of the 2D subwavelength hole array taken by SEM. Figure 8.6 (a) and (b) show the top view of the devices with 2DSHA pattern in 400 nm period (named as QD 1) and 350 nm (named as QD 2) period respectively. The duty cycle of both patterns was set to 0.8. A few tens of microns were left between the 2DSHA and Ti/Au contact as shown in Figure 8.6 (c).

Fig 8.6 (a) Zoom-in top view image of 2DSHA in 350 nm period taken by SEM. (b) Zoom-in top view image of 2DSHA in 400 nm period taken by SEM. (c) Zoom-out top view image of 2DSHA fabricated in the center of the window taken by SEM. (d) Hole arrays manufactured by EBL.

With the 2DSHA integrated with the QD photodetector, an enhancement factor of 2 to 4 times in the responsivity is observed with respect to bare QD photodetector (Figure 8.7 (a) and (b)). The largest responsivity values are 52 mA/W at 1400 nm for P400 QD 1 photodetector, and 21 mA/W at 1150 nm for P350 QD 2 photodetector, which occurred near the surface plasmon resonance wavelength of 1400 nm and 1200 nm, respectively. The largest detectivities for these two photodetectors are 19.4×10^9 Jones measured at 1400 nm, and 7.4×10^9 Jones measured at 1150 nm, respectively.

Figure 8.7 (c) shows the enhancement factor as a function of wavelength for the two photodetectors. Without considering the photocurrent generated by the substrate (below 1000

nm), the largest enhancement factor of P400 QD 1 photodetector is about $4\times$ at 1450 nm while the largest enhancement factor of P350 QD 2 photodetector is about $3\times$ at 1150 nm. This phenomenon comes from the different SPR wavelength as circled in Figure 8.7 (d). SPR occurs at 1400 nm and 1200 nm for the 2DSHAs with different periods. It should be noted that minor error between the experimental results and simulation is tolerable.

Fig 8.7 (a) Responsivity of QD photodetectors with 2DSHA, measured from 900 nm to 1450 nm. Bare QD photodetector is included as references. (b) Specified detectivity of QD photodetectors with 2DSHA and bare QD photodetector. (c) The enhancement factor of the QD photodetectors with 2DSHA structure with respect to the bare QD photodetectors. (d) The theoretically calculated transmittance and reflectance with 2DSHA structure.

To gain insights into the enhanced electrical field, we plot the numerical simulations

(FDTD) for the 2DSHA structures as shown in Figure 8.8. Images in the left column are the electric field distribution in the X-Y plane, and images in the right columns are the electric field distribution in the X-Z plane. Figure 8.8 (a) and (b) are for P400 QD 1 photodetector with incident light at 1400 nm. Figure 8.8 (c) and (d) are for P350 QD 2 photodetector with incident light at 1200 nm. Figure 8.8 (e) and (f) are for bare QD photodetector. With 2DSHA structure, the electric field of certain frequency will be confined at the interface between the nano metallic structure and the quantum dot sheet instead of propagating through freely like the bare device. It enhances the photo-electron transition within the active GeSn QD sheet and increases the amount of electron-hole pairs. Since the quantum dot sheet is extremely thin (~20 nm), the electric field of SPP is also overlapped with the substrate, therefore the electron-hole pairs that are generated by the GaAs substrate are also increased and so is the photocurrent.

Figure 8.8. Electric field distribution of device with/without 2DSHA structure. (a) E-field distribution at the interface between 400 nm-period 2DSHA and GeSn QD sheet in the X-Y plane. (b) E-field distribution under 400 nm-period 2DSHA in X-Z plane. (c) E-field distribution at the interface between 350 nm-period 2DSHA and GeSn QD sheet in the X-Y plane. (d) E-field distribution under 350 nm-period 2DSHA in X-Z plane. (e) E-field distribution at the surface of the bare device in the X-Y plane. (f) E-field distribution under the surface of the bare device in X-Z plane.

8.4 Summary

We took the advantage of the modified magnetron sputtering deposition associated with rapid thermal treatment to fabricate GeSn quantum dot sheet. We also fabricated GeSn QDs/GaAs photodetector whose responsivity is 3 to 6 times of that of the GeSn thin-film/GaAs

detector. 2DSHA metallic structures on the GeSn QD sheet made by electron-beam lithography is integrated with the GeSn QDs/GaAs photodetector for enhancing photodetection, and 2 to 4 times enhancement at designed wavelength range for different 2DSHA periods are achieved. The final specific detectivity of the 2DSHA GeSn quantum dot/GaAs hetero-structure infrared photodetector reaches a considerable high value of 2.3×10^{10} jones.

Chapter 9. Conclusions and future works

9.1 Conclusions

The Ph.D. project focuses on GeSn alloys and their application for photodetection. The electronic band structures and spontaneous emission rate are studied using an 8-band k.p method. GeSn thin films are fabricated by modified magnetron sputtering deposition. MSM GeSn photoconductor and GeSn/GaAs hetero-structure infrared photodetector are fabricated on the basis of GeSn thin films. GeSn quantum dots were also fabricated by the modified sputtering system and photodetection performance is studied. In addition, enhancement of photodetection using 2DSHA metallic structures is also explored. The conclusions of the work are listed below:

1. A comprehensive calculation of electronic band structure and simulation of performances on GeSn is carried out. All the parameters that could affect the band structure and the performance are well studied. The density of states, as a function of Sn composition, is proved to be more densely distributed when Sn fraction rises. By introducing the density of states in the indirect L valley, the total density of states, spontaneous emission rate spectrum and optical gain for both indirect and direct band-gap GeSn alloy could be calculated. A GeSn/Ge quantum well structure is studied using this model. Considering the compressive strain and the quantum confinement, a room-temperature enhanced spontaneous emission rate is observed in the GeSn quantum well.

2. Ge and Sn thin films are fabricated on different substrates by a modified magnetron sputtering deposition system. The morphology of the sample surface is mainly characterized

by atomic force microscopy. It is found that two environmental parameters – chamber pressure and deposition power are the key factors to control the surface roughness and the size of target atomic clusters. It serves as the preparation work for following binary GeSn thin film deposition using the co-sputtering technique.

3. GeSn thin films are fabricated by a modified magnetron sputtering deposition system using co-sputtering deposition technique. Different combinations of individual power and chamber pressure are tried. X-ray diffraction measurements have shown the shift of constructive interference as the function of Sn composition, suggesting the change of lattice constant with different composition. Accordingly, the transmittance spectrum also shows the shift in the absorption edge, indicating the change in the bandgap when Sn fraction varies. A peak at around 0.58 eV in the temperature-dependent photoluminescence spectrum was observed. Such value matches well with the bandgap that is calculated in our theoretical model. A metal-semiconductor-metal GeSn photoconductor is fabricated to examine its photodetection performance. Its responsivity at 1064 nm under negative bias is 0.28 mA/W.

4. A GeSn/n-GaAs hetero-structure infrared photodetector is fabricated by standard optical photolithography on GeSn thin film grown on n-type GaAs substrate. Possible internal Schottky barrier potential is successfully eliminated by depositing different metallic contacts on individual layers. The device is bound to the package through wire-bonding technique. The responsivity and detectivity are measured through a wavelength-tuneable laser from 900 nm to 1450 nm. Devices based on different Sn composition are fabricated in the same environment. Differences in the spectral response are observed, showing that the device with larger Sn fraction has its maximum responsivity and detectivity in the longer wavelength. The maximum

detectivity is 2.2×10^9 jones observed at 1250 nm under -0.1 V for bias voltage in the device with smaller Sn fraction.

5. GeSn quantum dots was obtained by rapid thermal annealing of the GeSn layer deposited using the modified sputtering system. GeSn QDs/GaAs photodetector was fabricated. The responsivity and detectivity were found 3 to 6 times of that of the GeSn thin-film/GaAs detector. 2-dimensional subwavelength hole array is fabricated in the absorption window on the top of the GeSn QD/GaAs detectors, and 2 to 4 times enhancement on the responsivity and detectivity are achieved. The maximum detectivity is 2.3×10^{10} jones measured at 1450 nm with the 400 nm-period 2D subwavelength hole array structure.

9.2 Future works

GeSn alloy is a prospective candidate as a photoelectric semiconductor material. Its advantages, such as adjustable energy band gap, spectral response wavelength, and probability in Si-base integration, could make it remain to be a hot topic in the near future. Some future works that could be done on the basis of present works are listed as follows:

1. The integration of the GeSn related devices on Si substrate. To overcome the large lattice mismatch, a high-quality buffer Ge layer could be firstly epitaxially grown on a Si substrate. It matches better to the GeSn layer while left the dislocations caused by the strain onto the interface between the Si substrate and Ge buffer layer. Such a configuration could guarantee the crystal quality of the GeSn alloy.

2. The fabrication of p-i-n GeSn photodetector. The doping in intrinsic GeSn thin film fabricated by magnetron sputtering deposition system is worth trying. The p-i-n structure could

largely enhance the responsivity by the intrinsic GeSn absorption layer while reduce the dark current by the built-in electric field. Such a device could possibly boot the detectivity up to at least 10 times owing to the highly increased photocurrent and small dark current.

3. The fabrication of 2-dimensional GeSn photodetection array imaging system. After successfully achieving high-detectivity single GeSn photodetector, 2-dimensional GeSn photodetection array imaging system could be fabricated on one chip. It should work with a digital external circuit for the collection of the current, and a current processing circuit for process the imaging. This kind of product has potentials in both commercial or military infrared imaging applications.

Publications

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