

REPORT DOCUMENTATION PAGE				Form Approved OMB NO. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 27-01-2023		2. REPORT TYPE Thesis or Dissertation		3. DATES COVERED (From - To) -	
4. TITLE AND SUBTITLE MBE-Grown GaAsSb Nanowire-Based Core-Shell n-i-p Heterojunction Photodetector up to 1.5 μ m.				5a. CONTRACT NUMBER W911NF-19-1-0002	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 106012	
6. AUTHORS Priyanka Ramaswamy				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES North Carolina A&T State University 1601 East Market Street Greensboro, NC 27411 -0001				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSOR/MONITOR'S ACRONYM(S) ARO	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) 72457-RT-REP.16	
12. DISTRIBUTION AVAILABILITY STATEMENT 2 Approved for public release; distribution is unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Shanthi Iyer
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 336-285-3710

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Continuation for Block 13

Proposal/Report Number: 72457.16-RT-REP

Report Title: MBE-Grown GaAsSb Nanowire-Based Core-Shell n-i-p Heterojunction Photodetector up to 1.5 μm .

Report Type: Ph.D. Dissertation

Publication Type: Thesis or Dissertation

Institution: North Carolina A&T State University

Date Received: 27-Jan-2023

Completion Date: 5/3/22 3:19AM

Title: MBE-Grown GaAsSb Nanowire-Based Core-Shell n-i-p Heterojunction Photodetector up to 1.5 μm .

Authors: Priyanka Ramaswamy

Acknowledged Federal Support: Y

MBE-Grown GaAsSb Nanowire-Based Core-Shell n-i-p Heterojunction

Photodetector up to 1.5 μm .

Priyanka Ramaswamy

North Carolina A&T State University

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department: Electrical and Computer Engineering

Major: Electrical Engineering

Major Professor: Dr. Shanthi Iyer

Greensboro, North Carolina

2022

The Graduate College
North Carolina Agricultural and Technical State University

This is to certify that the Doctoral Dissertation of

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has met the dissertation requirements of
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Dedication

To

Amma, Daddy,

Sisters, Abikutty and Saisri,

Brothers, Rakesh and Srivatsan.

Acknowledgments

Firstly, I would like to thank my advisor, Dr. Shanthi Iyer, for molding me into a better person professionally and personally. I am grateful for giving me a fantabulous opportunity to work in this highly motivated group. I want to express my sincere gratitude for your endless support and for pushing the boundary of my capabilities beyond my imagination. Thanks, Dr. Shanthi Iyer, for giving freedom to explore various advanced characterization tools.

I would like to thank my committee members Dr. John C Kelly, Dr. Numan S. Dogan, and Dr. Zhijian Xie from the Department of Electrical and Computer Engineering, North Carolina A &T State University, Dr. Lewis Reynolds Jr. from the Department of Materials Science and Engineering, North Carolina State University for their advice on structuring my research and valuable comments on my experiments. In addition, I would like to thank Dr. Ling Xu for accepting to serve on the doctoral dissertation committee as the Graduate College faculty representative. Finally, I would like to thank Dr. Abdullah Eroglu, the chairperson of the Department of Electrical and Computer Engineering, North Carolina A &T State University, for his great support throughout my academics at NCAT.

I would like to extend my sincere gratitude to Dr. John Kelly, Dr. Numan S. Dogan, Dr. Zhijian Xie, Dr. Robert Li, Dr. Jung H Kim, and Dr. Clinton Lee of the Department of Electrical and Computer Engineering, North Carolina A &T State University for their immense support throughout the graduate course work. Also, Dr. Shyam Aravamudhan, the director of JSNN core facilities, Nanoengineering Department, for his strong support and allowing access to the incredible facilities in the department.

Dr. Iyer's group is the perfect example of the proverb, "If you want to go fast, go alone. If you want to go far, go together." Each and everyone have contributed to my Ph.D. dissertation in

some way or the other. A special thanks to Dr. Jia Li, Post-doctoral researcher, for his endless support in successfully running the MBE lab and optics lab. I would like to acknowledge Dr. Manish Sharma and Dr. Prithviraj Deshmukh for training me on various equipment. I would like to thank Dr. Surya Nalamati for his tireless encouragement and assistance in the working of C-AFM. My sincere thanks to my fellow labmates, Mehul for the fabrication process, Rabin for COMSOL simulations and MBE, Shisir for his valuable input on the research, and MBE, Hirandeep for Raman measurements and supporting me with the PL, and Kendall for Raman measurements, COMSOL and device fabrication. Thank you, Sean, for the I-V analysis, and I always enjoyed discussing the Physics aspect of the device with you.

My profound thanks to Dr. Kyle Nowlin of JSNN for the equipment training and valuable suggestions on various techniques, Keith Jones and Ryan Fuierer of Asylum research for their collaboration and strong support of the C-AFM/SKPM characterization technique. Fred Stevie, Analytical Instrumentation Facility, North Carolina State University, for his collaboration and valuable guidance on XPS/UPS technique.

I would like to thank Dr. J. Hemalatha, Professor, Department of Physics, NIT, Trichy, who taught me that even a negative result is a result that paves the path toward successful optimization and to see problems in different dimensions.

I am forever grateful to my beautiful family for their constant motivation. Without their love and support, this is not possible. Thanks to the technology for the video calls, I visited my family in India four years after coming to the US in 2017, but nothing has changed. Amma always sends homemade snacks so that I don't have any homesickness. I am thankful to my friends, who always kept my spirits high.

I would like to acknowledge the financial support through the U.S. Army Grant Number W911NF-19-1-0002 under the DoD HBCU/MI program and monitored by the Air Force Office of Scientific Research. The National Science Foundation also supported a part of this work under grant# ECCS-1832117. This work was performed at the Joint School of Nanoscience and Nanoengineering, a member of the Southeastern Nanotechnology Infrastructure Corridor (SENIC) and National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the National Science Foundation (ECCS-1542174).

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List of Publications

Journal publications

1. **Ramaswamy, P.**, Parakh, M., Devkota, S., Kuchoor, H., Dawkins, K., and Iyer S. Passivation efficacy study of Al₂O₃ dielectric on self-catalyzed molecular beam epitaxially grown GaAs_{1-x}Sb_x nanowires. *Nanotechnology*, (2022) Under Review.

(Ramaswamy, P. and Parakh, M., are the first authors)

2. **Ramaswamy, P.**, Devkota, S., Pokharel, R., Nalamati, S., Stevie, F., Jones K., Reynolds, L. & Iyer, S. A study of dopant incorporation in Te-doped GaAsSb nanowires using a combination of XPS/UPS, and C-AFM/SKPM. *Scientific Reports* 11, 8329 (2021).

<https://doi.org/10.1038/s41598-021-87825-4>

3. **Ramaswamy, P.**, Pokharel, R., Parakh, M., Jones K., Li, J., & Iyer, S. Be-doping assessment in Self-Catalyzed MBE Grown GaAs Nanowires, *Conference on Lasers and Electro-Optics, OSA Technical Digest*, SW2F.7 (2021). https://doi.org/10.1364/CLEO_SI.2021.SW2F.7

List of relevant publications as co-author

1. Pokharel, R., **Ramaswamy, P.**, Devkota, S., Parakh, M., Dawkins, K., Penn, A., Cabral, M., Reynolds, L. & Iyer, S. Epitaxial high-yield intrinsic and Te-doped dilute nitride GaAsSbN nanowire heterostructure and ensemble photodetector application. *ACS Appl. Electron. Mater.* 2(9), 2730-2738 (2020). <https://doi.org/10.1021/acsaelm.0c00450>

2. Devkota, S., Parakh, M., Johnson, S., **Ramaswamy, P.**, Lowe, M., Penn, A., Reynolds, L., & Iyer, S. A study of n-doping in self-catalyzed GaAsSb nanowires using GaTe dopant source and ensemble nanowire near-infrared photodetector. *Nanotechnology* 31, 505203 (2020).

<https://doi.org/10.1088/1361-6528/abb506>

3. Parakh, M., Johnson, S., Pokharel, R., **Ramaswamy, P.**, Nalamati, S., Li, J., & Iyer, S. Space charge limited conduction mechanism in GaAsSb nanowires and the effect of in situ annealing in ultra-high vacuum. *Nanotechnology* 31, 025205 (2019).

<https://doi.org/10.1088/1361-6528/ab47aa>

Conference Proceedings

1. P Ramaswamy, et al., Electrical and surface characterization of Ga-assisted MBE grown Be-Doped GaAs nanowires and Te-Doped GaAsSb nanowires for infrared photodetector application, October 14-15, 2021 - *Nanoscientific Symposium Latin America, virtual*.

2. P Ramaswamy, et al., Doping assessment of Ga-assisted MBE grown Be-doped GaAs and Te-doped GaAsSb nanowires, September 06-09, 2021 - *21st International Conference on Molecular Beam Epitaxy, virtual*.

3. P Ramaswamy, et al., Electrical characteristics and surface analysis of Ga-assisted MBE grown Be-doped GaAs nanowires and Te-doped GaAsSb nanowires for infrared photodetector application, August 24-26, 2021 - *ICTN-KLC Conference, virtual*.

4. P Ramaswamy, et al., Doping assessment of Ga-assisted MBE grown Be-doped GaAs and Te-doped GaAsSb nanowires for infrared photodetector application, June 23-24, 2021 - *63rd Electronic Materials Conference, virtual*.

5. P Ramaswamy, et al., Be-doping assessment in self-catalyzed MBE grown GaAs nanowires, May 9-14, 2021 - *CLEO, OSA, virtual*.

6. P Ramaswamy, et al., Surface characterization of self-catalyzed MBE grown Be-Doped GaAs nanowires and Te-doped GaAsSb nanowires for infrared photodetector application, April 17 - 23, 2021 - *MRS Spring Meeting, virtual*.

Abbreviations

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AFM	Atomic force microscopy
ALD	Atomic layer deposition
Al ₂ O ₃	Aluminium oxide
at. %	Atomic percent
Be	Beryllium
BEP	Beam equivalent pressure
Bi ₂ Se ₃	Bismuth(III) selenide
C-AFM	Conductive atomic force microscopy
CdS	Cadmium sulfide
CdTe	Cadmium telluride
CNT	Carbon nanotubes
C-S	Core-shell
Cu	Copper
CVD	Chemical vapor deposition
EDS	Energy-dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscopy
FWHM	Full-width half maxima
GaAs	Gallium arsenide
GaAsSb	Gallium arsenide antimonide

GaAsSbN	Gallium arsenide antimonide nitride
GaN	Gallium Nitride
GaSb	Gallium antimonide
GaTe	Gallium telluride
Ge	Germanium
HgTe	Mercury telluride
HgCdTe	Mercury cadmium telluride
HRTEM	High resolution transmission electron microscopy
i-	intrinsic
IE	Ion exchange
InAs	Indium arsenide
InAsSb	Indium arsenide antimonide
InGaAs	Indium gallium arsenide
InGaSb	Indium gallium antimonide
InAsP	Indium arsenide phosphide
InP	Indium phosphide
InSb	Indium antimonide
IR	Infrared
ITO	Indium tin oxide
I-V	Current-voltage
LEC	liquid encapsulated Czochralski
LPE	Liquid phase epitaxy
LWIR	Long-wave infrared

LFN	Low-frequency noise
LO	Longitudinal optical
MBE	Molecular beam epitaxy
MLG	Monolayer graphene
MOCVD	Metal-organic chemical vapor deposition
MWIR	Mid-wave infrared
NIR	Near-infrared
NIRPD	Near-infrared photodetector
NW	Nanowire
O ₂	Oxygen
PbSnTe	Lead tin telluride
PD	Photodetector
PL	Photoluminescence
PMMA	Polymethylmethacrylate
Pt	Platinum
Pt/Ir	Platinum/Iridium
QD	Quantum dots
QW	Quantum wells
RIE	Reactive ion etching
RMS	Root mean square
RT	Room temperature
SEM	Scanning electron microscopy
Si	Silicon

SiO ₂	Silicon dioxide
SKPM	Scanning Kelvin probe microscopy
SLG	Single-layer graphene
SnS	Tin (II) sulfide
SnSe	Tin (II) selenide
SNW	Single nanowire
SRV	Surface recombination velocity
STEM	Scanning transmission electron microscope
SWIR	Short-wave infrared
Te	Tellurium
TEM	Transmission electron microscopy
TI	Topological insulator
TO	Transverse optical
UPS	Ultraviolet photoelectron spectroscopy
VLS	Vapor-liquid-solid
VS	Vapor-solid
XPS	X-ray photoelectron spectroscopy

Abstract

In the past few years, $\text{GaAs}_{1-x}\text{Sb}_x$ nanowire (NW) has attracted tremendous attention for the near-infrared photodetector (NIRPD) applications, as it covers important telecommunication wavelengths (1.3 μm and 1.55 μm). This dissertation reports on the successful fabrication of high-performance core-shell (C-S) n-i-p heterojunction-based GaAsSb NWs on n-Si (111). For realizing advanced high-performance NW-based IRPD, the assessment of dopant incorporation is essential. Therefore, we investigated on the variation in carrier concentration of Te-doped GaAsSb NWs and Be-doped GaAs NWs as a function of GaTe and Be cell temperatures using a combination of contactless, non-destructive techniques X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), conductive-atomic force microscopy (C-AFM), and scanning Kelvin probe microscopy (SKPM).

C-S n-i-p GaAsSb NWs provide an ideal platform for the high-performance NIRPD. Therefore, a systematic and detailed device study has been carried out to design different C-S architectures to improve device performance and increase the cutoff wavelength. These studies have successfully led to the growth of C-S n-i-p GaAsSb NWs with a high responsivity of 190 A/W and detectivity of 1.1×10^{14} Jones at -1 V bias up at the wavelength of 1.1 μm . However, to further redshift the device operational wavelength, a novel hybrid axial C-S n-i-p GaAsSb PD has been bandgap engineered with higher Sb% ($\text{GaAs}_{0.70}\text{Sb}_{0.30}$), which exhibits responsivity of 18 A/W and detectivity of 1.1×10^{13} Jones extending up to 1.5 μm . The successful demonstration of room temperature hybrid axial C-S n-i-p GaAsSb NWs NIRPD thus paves the way to realize high-performance PD beyond 1.5 μm , and the novel design structure can expand to other designs that have not been conceived yet for the next-generation optoelectronic devices.

CHAPTER 1

Introduction

1.1 Background

In the last few decades, various low dimensional semiconductor systems, namely 0 D quantum dots (1, 2), 1D nanowires (NWs) (3-8), and 2D quantum wells (9-13), have been the subject of extensive investigation. Among these, semiconductor NWs have attracted a great deal of interest in various fields due to their size-induced quantum confinement effect, superior photon harvesting function compared to thin films, high surface-to-volume ratio, sub-wavelength diameter, unique anisotropic geometry, and high refractive index (14). The small footprint of NWs supports a highly strained heterogeneous material system, which is not possible in planar film form without the creation of misfit dislocation (15). Semiconductor NWs have exhibited unique capabilities where different architectures of NWs, namely core-shell(C-S) (16), axial (17), insertion of quantum dots (QDs) (18), and quantum wells (QWs) (19), can be bandgap engineered using compound semiconductor materials on the wide choice of substrates for the realization of desired application as optoelectronic devices. Further, the light-trapping properties are much superior to the thin films, though orientation-dependent. In the horizontal NWs, it is observed that the leaky-mode resonances or the Mie-resonances facilitate the efficient coupling with incident light and play a significant role in determining the absorption property of horizontal NWs (20, 21). While in the case of an array of vertical NWs, waveguiding effect and resonance absorption effect provide outstanding light-trapping properties, which enhances the total absorption significantly compared to the horizontal NWs lying on the substrate (22). Because of the reasons mentioned above, NWs are being pursued for various optoelectronic applications, namely, energy-efficient photovoltaic converters, infrared photodetectors (IRPD),

gas detectors, industrial and pollution monitoring devices, light emitting diodes (LEDs), lasers, single-photon sources, wavelength shifters, and high electron-mobility transistors (23-30). They also offer unique properties, such as the ability to grow highly lattice-mismatched NWs on Si directly. Furthermore, the superior properties of NWs compared to their bulk counterparts, low voltage operation, low cost, and the versatility of direct integration of NW IR sensor with Si for the application in image read-out and processing circuitry have made them an ideal candidate for the next generation near-infrared photodetectors (NIRPD) (31).

Semiconductor NW-based NIRPD is the main focus of this dissertation. In this chapter, we briefly discuss the working principle and role of IRPD in numerous applications, namely thermal imaging, telecommunication, environmental, medical, industry, and defense-related applications. Then, we review a wide range of semiconductor NW-based IRPD in detail and also discuss their advantages and disadvantages, followed by the motivation for selecting GaAsSb material system and C-S n-i-p junction configuration for the application of NIRPD.

1.2 IRPD

IRPD plays a crucial role in detecting and sensing IR radiation in various applications, namely night vision, military missile tracking, medical imaging, industry defect imaging, environmental sensing, and exoplanet exploration (32). The IR radiation is generally divided into four different categories, namely near IR (NIR) region (0.75-1 μm), short-wave IR (SWIR) region (1-2.5 μm), mid-wave IR (MWIR) region (3-5 μm), and long-wave IR (LWIR) region (8-12 μm). Depending on the bandgap of materials used in the active region, IRPD can detect light in different regimes. SWIR wavelength of 1.3 μm and 1.55 μm is considered to be important wavelengths for telecommunication applications, while MWIR and LWIR (also known as thermal IR) are for blood/breath monitoring, thermal imaging, free-space communications, and

astronomy-related applications such as night vision, locating landmines during aircraft landing, and missile tracking for military applications as the high transparency of the atmosphere at these wavelengths allow transmission without significant signal loss. Since IRPD supports non-contact, non-destructive techniques, it is widely used in industrial and medical applications as well.

In this dissertation, we concentrate on the area of NIR and SWIR applications, as it provides an opportunity to explore a wide range of IR spectrum applications such as industry (non-destructive process control), transport (automotive), space (earth observation), and defense and security (night vision, active imaging) (33). In addition, due to the attenuated Rayleigh scattering of light at longer wavelengths, the SWIR camera provides imaging advantages over other visible and thermal bands, as it offers intuitive visible-like images, better imaging in adverse environments, and also can see through any weather conditions, including haze, dust, smoke, and fog. In addition, it was found that most of the materials used to make parts of the visible camera, namely windows, lenses, and coatings, can be used for SWIR cameras as well, to cut down the cost (34).

1.3 IRPD Applications

IRPD is classified as thermal detectors and photon detectors. The output signal of the thermal detectors depends on the change in the temperature of the detector element and is not selectively sensitive to photons. In photon detectors, the incident light is converted into an electrical signal proportional to the number of photons and, hence, wavelength-dependent. The advantages of a photon over thermal detectors are high sensitivity (high signal-to-noise ratio) and high response speed. In order to achieve this, cryogenic cooling is required to prevent the thermal generation of charge carriers, which makes non-cooled devices very noisy.

To date, a wide range of semiconductors, namely Si, Ge, carbon nanotubes, hybrid perovskites, group II-VI and III-V compounds, and organic semiconductors, have been exploited for the IRPD application (35). However, the conventional Si-based PDs suffer from crosstalk between the adjacent pixels that require high-temperature processing. In addition, the cut-off wavelength of 1100 nm related to the 1.12 eV bandgap of Si is considered a fundamental shortcoming for the detection of wavelengths beyond 1100 nm. Hence, to realize extended wavelength capabilities for the application of a wide range of IRPDs, rapid advances were made in developing narrow bandgap semiconductors (high optical absorption coefficient, high electron mobility, and low thermal generation rate). In the mid-1950s, InSb, the newly discovered narrow bandgap III-V semiconductor compound, was developed, but its operating wavelength spectral region is limited to MWIR. Therefore, the need for LWIR PD led to the development of various narrow-gap ternary alloy materials, namely HgCdTe, PbSnTe, InAsSb.

1.3.1 HgCdTe IRPDs. HgCdTe, an II-VI alloy, holds the most important position in the IRPD family and has inspired four generations of IRPD (36). HgTe is a semimetal, while CdTe is a semiconductor with a bandgap of 1.5 eV. Thus, the direct bandgap tuning, a high absorption coefficient, a moderate thermal coefficient of expansion, and a moderate dielectric constant of HgCdTe give the potential to use this material system in the application of detection of SWIR, MWIR, and LWIR regions. However, the challenges associated with the fabrication of high-quality HgCdTe related to the need for high mercury vapor pressure, high defect densities, non-uniformity in yield of detectors, surface instability, and mercury toxicity have been major drawbacks. Furthermore, HgCdTe alloys suffer from a high Auger recombination rate, reducing the signal-to-noise ratio and not supporting bias-tunable multicolor detection capabilities

compared to other QWIRPDs and QDIRPDs (37). Also, the imaging arrays based on HgCdTe use expensive CdZnTe substrates, limiting them to military applications rather than civilian ones.

1.3.2 III-V IRPDs. Over the last decade, III-V NWs have paved the way for the development of nanoelectronics and nanophotonics-based devices due to their excellent physical properties. One of the advantages of the 1D geometry of NW is implementing different architectures. Besides, NW structures induce elastic strain relaxation, enabling monolithic integration of III-V semiconductor-based devices on the Si platform. A plethora of studies have been reported on a wide range of NW structures, namely core/shell (C-S) (38, 39) and axial (17, 31), with the desired composition through specific dopants incorporation and optimization of growth parameters. The possibility of achieving high photoconduction in NWs has attracted researchers to work on the potential application of NWs, such as photo-sensing elements in highly integrated optoelectronic devices, transceivers, and optical interconnects (40). The most promising candidate amongst the semiconductors is considered to be the III-V semiconductor because of the excellent transport properties, high optical absorption coefficient, and ease of doping. Further, the bandgaps of III-V NWs can be tuned by changing their composition to achieve the desired operating wavelength for the application of high-performance and high-speed optoelectronic devices. Extremely high photoconductive gain is observed in III-V semiconductor NWs because of the short carrier transit time, further attributed to the high mobility in high-quality and defect-free single-crystalline NWs (41). Due to the high sensitivity and quantum efficiency achieved in III-V semiconductor NWs, significant development has been made in PD devices (41).

Binary III-V compounds: Among binary III-V NWs, InSb, InAs, and GaSb have the potential for broadband photodetection ranging from visible to IR region ascribed to their narrow

bandgap. In general, III-V photodiodes are fabricated by molecular beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), liquid phase epitaxy (LPE), impurity diffusion, and ion implantation techniques. As an alternative technology to HgCdTe, the attention has shifted towards III-V semiconductors due to their superior bond strength, well-behaved dopants, material stability, and high-quality III-V substrates. From the early 1990s, InSb detectors have been extensively studied by national agencies of several countries like the U.S., Germany, and France. They have found diverse applications in the space and defense industry (42). The significant advantages of a thinned InSb are that it requires no substrate and also respond from the near UV to $5.5\ \mu\text{m}$ at 80 K. The exciton Bohr radius of InSb NW is around 65 nm, which is more than ten times greater than that of silicon, provides more flexibility for the fabrication of NWs with different band gap energies. When the diameter of InSb NW is greater than 65 nm, the bandgap energy (0.17 eV) remains the same as the bulk material due to the absence of quantum confinement. When the diameter is in the range of 30 nm to 65 nm, the bandgap energy of InSb NWs varies from 0.17 to 0.2 eV. It further increases to 1.2 eV when the diameter decreases from 30 to 5 nm (43). In InSb NW-based PDs, a high signal-to-noise ratio can be obtained with a prolonged photocarrier lifetime and shortened carrier transit time due to the high surface-to-volume ratio of NWs.

In comparison with InSb, the formation and purification of InAs are more complex, as it is necessary to keep the arsenic (As) from disappearing due to its high vapor pressure near the melting point. It is to be noted that using the high-pressure liquid encapsulated Czochralski (LEC) technique, InAs single crystals up to 100-mm diameter are being grown commercially (44). InAs NWs have been explored for their application in high-speed and high-frequency electronics due to high carrier mobility. Despite low electron-effective mass, InAs NWs suffer

from significant leakage current due to a small bandgap (45). Miao et al. (46) reported the first RT single InAs NW NIRPD of 5.3×10^3 A/W photoresponsivity with detection wavelength spanning up to $\sim 1.5 \mu\text{m}$. One of the earliest insights into the graphene-InAs based NW vertically stacked heterojunction IRPD with a large photoresponsivity of 0.5 A/W and $I_{\text{light}}/I_{\text{dark}}$ ratio of 5×10^2 was demonstrated by Miao et al. (47). In the following section, various As-based and Sb-based ternary III-V alloys IRPD are described.

As-based ternary III-V alloys: Among III-V ternary alloys, $\text{In}_x\text{Ga}_{1-x}\text{As}$ ternary alloy has been of great interest for the SWIR PD, low-cost detector applications, as it is a direct bandgap semiconductor material that is tunable between 900 nm and 1700 nm. From a commercial aspect, it is a mature material manufactured in mass for the application of fiber optic receivers at 1.3 and $1.55 \mu\text{m}$. It is also observed that the wavelength of $\text{In}_x\text{Ga}_{1-x}\text{As}$ can be extended up to $2.6 \mu\text{m}$ by increasing the Indium (In) content to $x = 0.82$, and the electron mobility can be increased from ~ 1000 to $6000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (48).

Zhou et. (49) demonstrated the growth and compositional characteristics of MBE-grown Au catalyzed C-S InGaAs NWs on GaAs $\{111\}_B$ substrates using a high In/(In+Ga) ratio of ~ 0.85 . The photoresponsivity of SNW was estimated to be 5.75 A/W at a gate voltage of 40 V with the illumination at 1550 nm at 77 K and was found to be higher than the commercial large-area planar InGaAs PDs (0.88 A/W at 1550 nm). Tan et al. (50) reported an RT $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ NW PD, grown by chemical vapor deposition (CVD), with a high responsivity of 6.5×10^3 A/W and EQE of $5.04 \times 10^5 \%$ over a spectral range of 1100 nm to 2000 nm. Zhang et al. (51) fabricated $\text{In}_{0.51}\text{Ga}_{0.49}\text{As}$ NW RT IRPD using a novel two-step CVD method, which exhibited responsivity of 7300 A W^{-1} , a specific detectivity of 4.2×10^{10} Jones, and an EQE of $5.84 \times 10^6 \%$ under 1550 nm illumination for an SNW, whose rise and decay time constants were found to

be 480 μs and 810 μs , respectively. Chiba et al. (52) demonstrated a 20-fold increase in photocurrent density of axial p-i-n InGaAs ensemble NWs with InP as a passivation shell under 1.55 μm wavelength radiation.

InAs_xP_{1-x} is the ternary alloy of InAs and InP, with bandgap tunability ranging from NIR to MIR region. Ren et al. (53) showed a complete compositional tunability spanning from 700 nm to 3500 nm in InAs_xP_{1-x} NWs using a novel two-step growth combination of the VLS mechanism and ion exchange (IE) process. As a result, a responsivity of 3833 A/W at a peak response wavelength of 1200 nm was obtained for InAs_{0.25}P_{0.75} NW PD, while a high responsivity of 5417 A/W at 1700 nm was achieved for a higher As incorporation in InAs_{0.52}P_{0.48}, which further confirmed the successful bandgap tuning of InAs_xP_{1-x} (53).

Sb-based ternary III-V alloys: InGaSb and GaAsSb are other ternary III-V alloys that operate at 1550 nm wavelength. Li et al. (54) fabricated flexible non-epitaxial growth of RT In_{0.28}Ga_{0.72}Sb NWs IRPD using the CVD method exhibiting responsivity of 1520 A/W and ultrafast response speed below 20 μs at 1550 nm illumination, a record-high performance among all flexible NIRPDs. Ma et al. (55) demonstrated a single GaSb/GaInSb p-n heterojunction NW with a responsivity of 10³ A/W, EQE of 10⁴ %, and a short response time of 2 ms at the wavelength of 1550 nm. Li et al. (56) synthesized Au catalyzed metalorganic vapor phase epitaxy (MOVPE) grown GaAs_{0.56}Sb_{0.44} NWs and demonstrated an RT IRPD with a responsivity of 2.37 and 1.44 A/W at 1.3 and 1.55 μm telecommunication wavelengths, respectively. C-S GaAsSb/InP NWs exhibited enhanced device performance due to the in-situ passivation shell attributed to its low surface recombination velocity (SRV), enhanced carrier mobility, and carrier concentration (57). Ahmad et al. (17) and Sharma et al. (58) from our group were the first ones to demonstrate axial p-i-n GaAsSb NWs using Te as n-dopant and axial p-i GaAsSb NW

Schottky barrier based IRPD, respectively. Sharma et al. (58) reported MBE-grown p-i GaAsSb/AlGaAs ensemble NWs with high responsivity, EQE, and detectivity of 311 A/W, $6.1 \times 10^4 \%$, and 1.9×10^{10} Jones at 633 nm, respectively and also showed good spectral response up to a wavelength of 1.1 μm , which was attributed to post-growth in-situ annealing of NWs in the ultra-high vacuum. Deshmukh et al. (39) demonstrated coherently strained GaAsSbN shell with higher Sb concentration grown on non-nitride GaAsSb core with 4K photoluminescence (PL) emission in the SWIR wavelength spanning up to 1.4 μm . Devkota et al. (59) demonstrated ensemble Te-doped GaAsSb NW PD of improved responsivity of 580 - 620 A/W and detectivity of 1.2×10^{12} - 3.8×10^{12} Jones and showed a broad spectral response up to 1.2 μm of wavelength. Pokharel et al. (60) reported Te-doped GaAsSbN NW Schottky-based PD on both SNW and ensemble NW with a responsivity of 5 A/W at 860 nm and 3800 A/W at 1100 nm, respectively, with a detectivity of 3.2×10^{10} Jones.

1.3.3 IV and IV-VI IRPDs. Si, the second most abundant group IV semiconductor on earth, has a narrow indirect bandgap of 1.12 eV and superior transport properties that are fabricated using various oxide-assisted growth and CVD techniques (61, 62). Si NW-based PDs exhibit excellent photoresponse and detect IR light with high sensitivity. However, they are limited to low-temperature operation only. NIRPD plays a crucial role because of its large absorption coefficient in the NIR region, high mobility, and offers excellent compatibility with the conventional Si processing technology. However, most of the Ge NW IRPD suffers from a very low responsivity due to the diffraction limit of the light. Carbon nanotubes (CNTs) also play an essential role in NIRPD applications due to their broadband optical absorption in the NIR regime, direct structure-dependent bandgap, low heat capacity, and unique 1D van Hove singularities (63).

Zeng et al. (64) demonstrated a photovoltaic type IRPD based monolayer graphene (MLG)/ Ge heterojunction with peak sensitivity at 1400 nm with responsivity and detectivity of 51.8 mA/W and $1.38 \times 10^{10} \text{ cm Hz}^{1/2} \text{ W}^{-1}$, respectively and the fast light response speed of 23 μs . Lu et al. (65) fabricated a high-performance Ge nanoneedle NIRPD using single-layer graphene (SLG) modified with non-metal plasmonic indium tin oxide (ITO) nanoparticles, which promote localized surface plasmon resonance under NIR irradiation. The responsivity, detectivity, on/off ratio, and response speed were 185 mA/W, $2.28 \times 10^{13} \text{ cm Hz}^{1/2} \text{ W}^{-1}$, 5×10^4 , and 450/460 ns, respectively, under 1550 nm illumination. In addition, Lu et al. (66) successfully demonstrated graphene/MWCNT nanohybrid IRPD, resulting in the detectivity of $1.5 \times 10^7 \text{ cm Hz}^{1/2} \text{ W}^{-1}$.

Binary IV-VI semiconductors, SnS, and SnSe are the narrow bandgap materials with a direct bandgap of 1.0-1.2 eV and 1.30-1.55 eV and an indirect bandgap of 1.2-1.5 eV and 0.90-1.12 eV, respectively, that offer great potential in the application field of PDs. Zheng et al. (67) fabricated p-type SnSe and SnS NWs via CVD. Both of these SnSe (SnS) NW IRPDs exhibited good responsivity of $1.0 \times 10^4 \text{ A/W}$ ($1.6 \times 10^4 \text{ A/W}$), detectivity of $3.3 \times 10^{12} \text{ Jones}$ ($2.4 \times 10^{12} \text{ Jones}$) at 3V bias with rise and fall times of 460 and 520 μs (1.2 and 15.1 ms), respectively, under 830 nm illumination. The CVD-grown SnS NW IRPD showed responsivity of 267.9 A/W and EQE of $3.12 \times 10^4 \%$, with the rise and decay time of 4.5 and 0.7 s, respectively, under 1064 nm IR radiation has been reported by Shen et al. (68).

1.3.4 Chalcogenide IRPDs. In addition to IV, IV-VI, and III-V groups, compound semiconductors, namely chalcogenides, have attracted considerable attention towards the application of IRPDs. Bi_2Se_3 , a topological insulator (TI), is said to have unique electronic properties as the surface states form a single Dirac cone inside a large bulk bandgap (69). The

origin of the photocurrent of such TI is a complex phenomenon, and it is still at the early stage of research. In_2Te_3 (bandgap of 1.19 eV) is beneficial to fabricate IRPDs due to its excellent ambient stability, high absorption coefficients as large as $1 \times 10^5 \text{ cm}^{-1}$, and suppressed thermally excited carriers; hence, high photo-dark current ratio (63). Sharma et al. (69) successfully demonstrated topological insulator Bi_2Se_3 SNW as NIRPD with a responsivity of 300 A/W, EQE of $3.4 \times 10^4 \%$, and detectivity of 7.5×10^9 Jones, respectively, at a constant bias of 150 mV at 1064 nm wavelength illumination. Wang et al. (70) reported the first CVD-grown In_2Te_3 with a broad light detection spanning from 350 nm to 1090 nm.

The NW-based IRPD discussed in this chapter section has its advantages and disadvantages. The disadvantage of HgCdTe-based IRPD is the toxic nature of Hg, high Auger recombination rate, non-uniformity in the yield of detectors, and instability. Thus the challenge is faced during the fabrication of large-area PD for civilians, thereby restricting its application to military services only. In the case of IV-VI semiconductor materials, very high thermal expansion coefficients and large permittivity are found to be detrimental to IRPD application. Also, the chalcogenide TI-based PDs are still in their early research stage, and only SNW has been examined so far. Another major disadvantage is that most of the semiconductor materials discussed above cannot be integrated directly into current Si technology because of the high lattice mismatch. They also require cryogenic cooling and expensive lattice-matched substrates for the application of IRPD (31). Hence, the III-V semiconductor is the right choice for the IRPD application, as it shows the potential to overcome the above challenges.

Among ternary III-V based semiconductor NWs, it is observed that GaAs-based systems, GaAsSb, and InGaAs exhibit the emission wavelengths at the telecommunication wavelength region from 1300 nm to 1550 nm and are considered promising building blocks for the

application of IRPDs due to their tunable narrow bandgap in the near- and mid-IR spectral region (71). Furthermore, GaAsSb is superior to InGaAs in many ways, as the large difference in In and Ga diffusion rates affects the compositional homogeneity in InGaAs NWs (72). In addition, GaAsSb offers superior carrier mobility, longer electron lifetime, suppressed auger recombination, less dependence of the electronic structure on its alloy due to the presence of a single group-III element, the superior crystal quality offered by the surfactant nature of Sb, and freedom to tailor the desired crystal structure (28). Hence, these features make GaAsSb a better semiconductor material for further improving the IRPD device performance.

1.4. Growth of NWs

Various advanced techniques have been developed to fabricate high-quality NWs, which offer good control over the dimensions, position, composition, and impurity doping. Top-down and bottom-up are the different approaches to synthesize NWs. In the case of the top-down method, various patterning and etching are used to fabricate semiconductor NWs from the bulk material, which is limited by the resolution of the lithography system and the etching techniques, for instance, e-beam lithography, colloidal lithography, metal-assisted wet chemical etching, or reactive ion etching (RIE). In addition, the growth of heterostructure NWs of highly lattice-mismatched semiconductor materials is restricted in the top-down method. These limitations can be overcome by the bottom-up approach in which the formation of NWs is due to the epitaxial layer-by-layer growth. In the bottom-up approach, the NWs have formed from the vapor phase via metal catalyst in the vapor-liquid-solid (VLS) mechanism, while in the case of solid particles, growth is supported by the vapor-solid-solid (VSS) mechanism (73). This approach allows precise growth control under highly reproducible conditions, and also, different heterostructure NWs can be grown as the small footprint of the NWs effectively accommodates strain relaxation.

1.4.1 VLS mechanism. VLS mechanism is a commonly used method for the formation of well-controlled NWs using MOVPE and MBE, in which supersaturated liquid droplet initiates and controls NW growth (39, 58, 74, 75). VLS growth mechanism facilitates the fabrication of uncommon ternary alloy NWs and lattice-mismatched heterostructure, which is ideal for monolithic integration for attaining high-performance optoelectronic devices based on Si technology (76-80). The induced strain due to lattice-mismatched heterostructure is relieved elastically in a few monolayers due to a small contact area and large-surface-to-volume ratio over a few monolayers of thickness growth (81). In the VLS mechanism, the metal droplets act as a catalyst, are introduced at a constant vapor pressure, promotes mass transfer from the vapor phase, and condense into a liquid droplet form. With continuous overpressure of vapor onto the substrate surface, supersaturation of metal droplets occurs, which leads to precipitation of crystalline layer under the liquid metal droplet. Hence, with a continuous supply of the growth species at a constant vapor pressure, NW growth subsequently occurs from the nucleated liquid metal droplet at the liquid-solid interface. It is observed that the diameter and the orientation of the NW depend on the size of the droplet, oxidation thickness of the substrate, growth temperature, growth species, and growth flux. Conventionally, gold (Au) was used as a metal catalyst due to its inert nature and ability to form alloys at low temperatures (82). However, the presence of foreign material like Au, a fast diffusing metal, contaminates the NWs by inducing deep-level traps, affecting charge-carrier lifetime and unintentional III-V NWs doping by the Si dissolved in the catalyst droplet (83). In order to mitigate the contamination from the foreign catalyst, Au was replaced by one of the constituents of the NW itself. Self-catalyzed NW growth demonstrated a high degree of homogeneity in axial and radial directions (84, 85) and was found to be promising and successful, despite the versatility of Au-catalyzed growth. Over the past

decade, researchers have succeeded in the self-catalyzed III-V NW growth on Si substrate (80, 86-91).

1.4.2 GaAs_{1-x}Sb_x NIRPD. The focus of this dissertation is the fabrication of MBE-grown n-i-p GaAs_{1-x}Sb_x NWs for the NIRPD application. GaAs_{1-x}Sb_x is considered the most desirable semiconductor compound for application in optical telecommunication, NIR sensing, etc., due to their capability of bandgap tuning between 870 nm and 1700 nm. Ma et al. (92) fabricated the IRPDs based on GaAsSb NWs, which showed a broadband response with a high response peak at 1.31 μm , whose responsivity, external quantum efficiency, and short response time is $1.7 \times 10^3 \text{ A/W}$, $1.62 \times 10^5 \%$, and 60 ms, respectively. Huh et al. (93) reported GaAsSb based PDs owing to the high local electric field for a reverse-biased Schottky barrier whose responsivity at -3V is around 1463 A/W under an illumination intensity of 20.7 mWcm^{-2} and is found to be 2500 times higher than GaAs/AlGaAs C-S NW and 48,000 times higher than GaAs NW based PD. Our group, Pokharel et al. (60), Devkota et al. (59), and Nalamati et al. (94), successfully demonstrated self-catalyzed MBE grown Te-doped GaAsSbN, Te-doped GaAsSb, and GaAsSb NWs, respectively, for the NIRPD application.

1.4.3 N-I-P junction PD. P-I-N or N-I-P junction semiconductors are widely used structures in IRPD due to the high impedance under reverse bias. These IRPDs are utilized as mode amplifiers in Si read-out integrated circuits for the application in IR imaging.

In n-i-p, as the name suggests, an intrinsic layer is sandwiched between n and p- doped regions, and the Fermi levels of the n and p- doped regions must be aligned at the same level. The potential difference across the intrinsic layer (built-in potential) is the main driving force to separate photon-generated electrons and holes to n and p regions for collection, respectively (95). When the junction is connected to the external circuits, the accumulated charge carriers

contribute to the current flow. N-I-P junction is superior to n-p or p-n junction as the intrinsic region can be modulated according to the application. An increase in width of the intrinsic region provides a large volume for absorbing more light, and thus more photogenerated carriers, and also reduces the junction capacitance. However, transit time is increased due to the decrease in RC delay, which can be overcome by reducing the intrinsic region width. Hence, a trade-off between the quantum efficiency and transit time exists due to the thickness of the intrinsic region. In an n-i-p junction PD, diffusion current is the major contribution of the dark current, which is defined as the gradient of minority carriers in the two quasi-neutral regions. The boundary conditions further define the gradient of minority carriers at each end, which can be varied by optimizing SRV. It is to be noted that boundary condition plays a critical role in the short p-n junction diode, with one of the region widths being small compared to the minority carrier diffusion length. Hence, the length of the p/n- region determines the diffusion current density rather than the minority carrier diffusion length. As a result, the diffusion current density of the short diode is larger than that of the long diode. Furthermore, the minority carrier concentration follows a linear function, thereby generating a constant diffusion current density (96).

The surface recombination limits the minority carrier diffusion length and carrier lifetime, which is detrimental to the IRPD. However, the non-radiative surface recombination can be suppressed by large bandgap surface passivation layers that are chemically inactive to prevent further formation of surface states leading to an increased carrier lifetime (97-99). Hence, the device performance largely depends on the excess carriers, which are also influenced by the surface (96, 100).

In the last few years, many researchers have demonstrated axial and C-S heterostructure NWs with a p-n or p-i-n junction. Compared to axial, C-S is said to be advantageous due to the following reasons. In the case of the C-S NW p-n junction device, light is absorbed along the whole NW, whereas the photogenerated carriers are separated along the radial direction. Hence, for the C-S, light absorption and carrier extraction are decoupled. High efficiency is achieved in radial structure, as the distance that carriers must travel across the NW radially is small compared to the minority carrier diffusion length, which leads to low non-radiative recombination. Furthermore, compared to the axial devices, the radial device has a large junction area, which increases the charge separation efficiency. In addition, the above advantages facilitate us to use lower-purity, less-expensive materials to fabricate C-S NWs, which can significantly reduce the device cost. In contrast, the axial structure suffers from mid-gap surface states, which are detrimental due to (a) non-radiative recombination that can affect the carrier lifetime, diffusion length, and material gain, (b) generation of carriers may cause high leakage current in reverse bias, and (c) depletion of the core NW will generate high series resistance and space-charge limited transport (101-103).

Christesen et al. (100) compared the axial and radial n-i-p NW structures and showed that the latter is insensitive to surface recombination. As the depletion region of the axial device is exposed to the surface, it requires SRVs to be as low as 10^3 - 10^4 cm/s to achieve internal quantum efficiency of 95%, whereas, in the radial device, even high SRVs of 10^5 cm/s will generate the similar level of performance. So far, very few studies have been demonstrated on the III-V C-S IRPDs. Dai et al. (104) demonstrated RT C-S NW PD with a responsivity of 0.57 A/W and detectivity of 7.2×10^{10} cmHz^{1/2}/W at a wavelength of 855 nm. Gallo et al. (38) fabricated high-speed time response C-S GaAs/AlGaAs NWs of 10 ps full-width half maximum

(FWHM) with an estimated corrected value of less than 5 ps, and Li et. (105) showed IR photodetection at RT in C-S InAs/AlSb NW. Recently, for the first time, Wang et al. (106) reported visible-IR p-n C-S GaAs_{1-x}Sb_x/InAs NW photodetector with a responsivity of 0.12 A/W at $V_{ds} = -0.3$ V at 1310 nm and a high response up to 1800 nm with an on/off ratio of 2.5. Wang et al. (107) demonstrated antimony-rich GaAsSb NWs passivated by organic sulfides for NIRPDs whose responsivity and detectivity are 5.4×10^4 A/W and 2.5×10^{10} Jones at $V_{ds} = 2$ V for 1550 nm light irradiation. It is to be noted that the research work on C-S GaAsSb NW has not yet been fully explored, and it is still in the initial stage despite the development of III-V NIRPD. To the best of our knowledge, there has been no report on the fabrication of the C-S n-i-p GaAsSb NW configuration, which is known for suppressing the dark current and improved device performance as opposed to axial configuration. Furthermore, the C-S NW configuration provides more freedom for device design, which is vital for realizing RT NIRPD and extending the wavelength of operation.

1.5 Challenges

The main objective of this dissertation is the fabrication of an RT C-S n-i-p GaAsSb NW-based PD with detectivity in the 10^{13} Jones range for wavelength approaching 1.5 μm . Following are the growth and processing challenges faced by C-S n-i-p devices.

- Most of the research work related to the growth of III-V NWs has been mainly focused on the p-type Si substrate (39, 59, 60, 108). There is no work on the study of vertical growth of GaAsSb NWs on n-type Si substrate. As the NWs can grow in four different possible directions on Si substrate, careful optimization of oxide thickness parameters is necessary for the growth of vertical NWs.

- Fabrication of ensemble C-S NWs is quite challenging due to the shadowing effect of NWs, which leads to non-uniform shell thickness.
- To realize NW-based devices, controlled and effective dopant incorporation is essential (109). However, the assessment of dopant incorporation in NWs is more strenuous compared to thin films due to their small footprints. Therefore, in recent years, various sophisticated characterization tools, namely atom probe tomography and Hall measurements were used and are found to be destructive, while other optical methods, namely PL, Raman spectroscopy, involve uncertain empirical relations (110).
- It is also observed that the knowledge obtained from previous thin-film studies cannot be transferred directly to NWs (95). Firstly, the p-, i-, and n-layers are considerably thin compared to the bulk, and a large surface-to-bulk volume ratio of NWs makes it quite susceptible to surface states, which can trap many charge carriers, thereby lowering the effective doping concentration. Hence, the carrier density in the p and n regions, which leads to difficulty in the formation of the n-i-p junction and the formation of crystal structural defects at the core/shell interface.
- Evaluation of the junction quality of NWs also poses a problem due to its nanoscale. Hence, there is still a lack of systematic study on fabricating high-quality junctions.
- The i- GaAsSb (undoped) is found to be slightly p-type, as the nominal concentration is in the range of 10^{16} cm^{-3} , exhibits p-type behavior, and displays non-excitonic residual acceptor impurity such as Ga vacancy-related defects and Ga antisite defects ($V_{\text{Ga}}\text{GaSb}$) (111).
- In the past decades, C-S NWs such as GaAs/AlGaAs, ZnO/ZnS (112) have been easily fabricated for the application of ultraviolet and visible light photodetection due to their

large bandgap. Whereas it is found to be a great challenge to produce RTIRPDs with high performance due to the large dark current.

- The intrinsic (active region) is closer to the top metal contact, and also, the cross-section area of the junction is small. Hence, the depletion of a significant portion of the junction is possible due to the band bending at the metal-semiconductor interface formed by trap states or a Schottky barrier.
- In addition, fabrication of electrical contacts for ensemble NW devices also causes the problem, as it has limitations such as the shell of the NWs can be over-etched during the etching process, and the NWs may bend during spin coating of polymer.

1.6 Objectives and Results

The main objective of this dissertation is the study of dopant incorporation in GaAsSb NWs and a systematic and detailed study of the n-i-p junction to achieve a high-performance C-S n-i-p GaAsSb NW device for the RT NIRPD application approaching 1.5 μm . This dissertation addresses all the issues mentioned above to demonstrate RT MBE-grown C-S n-i-p GaAsSb NW for NIRPD application. In this work, we use n-type Si substrate, as both Te and Be dopants are surfactants, and in addition, i-GaAsSb shows slightly p-type behavior. Hence, it is advisable to grow an n-type core followed by an i- shell, which will eliminate the diffusion of Be into the i- region. Also, it is to be noted that the diffusion of Te from n-core (if any) will compensate for the p-type nature of the i-region and will not be as detrimental as in the case of p-core. Following systematic studies were undertaken to realize high device performance C-S n-i-p NW NIRPD. successfully

(a) The challenge of determining the carrier concentration of doped NWs was addressed by the use of a combination of non-destructive characterization tools, namely X-ray photoelectron

spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), conductive-atomic force microscopy (C-AFM), and scanning Kelvin probe microscopy (SKPM).

(b) Investigation of ex-situ passivation technique using atomic layer deposition (ALD) for the suppression of surface states effect on NWs.

(c) Optimization and demonstration of the conventional and hybrid axial C-S based n-i-p GaAsSb SNW and ensemble NW IRPD at the wavelength emission of 1.5 μm .

1.6.1 A study of dopant incorporation in Te-doped GaAsSb NWs and Be-doped GaAs NWs using a combination of XPS/UPS and C-AFM/SKPM. We investigated the effect of different GaTe and Be cell temperatures on Te and Be dopant incorporation and electronic properties of MBE grown Te-doped GaAsSb and Be-doped GaAs NWs, respectively, using several surface analytical characterization techniques tools, namely XPS/UPS and SKPM along with C-AFM.

Statistical analyses of all four measurement techniques have provided evidence for confirmation of Te and Be dopant incorporation in these GaAsSb and GaAs NWs, respectively. Furthermore, the values of electron density from UPS concur very well with the values of electron density determined from C-AFM. Hence, these surface analytical tools without contact fabrication are found to be a very powerful tool for direct measurement of the dopant incorporation and doping levels in NWs. These are the first results of the study of doping assessment in Te-doped GaAsSb NWs with variation in GaTe cell temperature and Be-doped GaAs NWs with variation in Be cell temperature. This work has been published in Scientific Reports, 2021.

1.6.2 Study of passivation efficacy of thermal ALD Al₂O₃ dielectric layer on self-catalyzed GaAs_{1-x}Sb_x NWs. Surface states play a major role in the degradation of electrical and

optical properties of NWs, as these act as non-radiative recombination centers. It is found that the high density of surface states is detrimental to the efficiency, sensitivity, and speed of the NW devices. The native oxide formation on the NW sidewalls and the un-passivated dangling bonds arising from the sharp termination of material growth radially led to the formation of surface states. Therefore, we examined the efficacy of the ALD deposited Al_2O_3 passivation layer to mitigate the surface states on GaAsSb NWs using surface and optical characterization tools.

*The study showed that ALD deposited Al_2O_3 passivation layer on GaAsSb NWs is not as effective as AlGaAs/GaAs due to optical degradation. The XPS spectral analysis indicated that precleaning with sulfur treatment before Al_2O_3 ALD deposition effectively removed III-V native oxides formed on the NW surface, thus ruling out the effect of native oxides on optical degradation. Raman characterization suggested that the defect creation at the NW/dielectric interface of Al_2O_3 ALD deposition is very likely responsible for the optical degradation in the Al_2O_3 passivated GaAsSb NWs. **This work has been submitted to Nanotechnology, 2022 (under review).***

1.6.3 C-S n-i-p GaAs_{1-x}Sb_x NWs for IRPD application. The following is the list of tasks undertaken to fabricate C-S GaAsSb n-i-p NW devices for the application of NIRPD at a wavelength approaching 1.5 μm .

- Electrostatic mapping from COMSOL simulation - The electrostatics mapping of the C-S n-i-p junction NW using COMSOL Multiphysics Modeling Software by varying thickness and dopant concentration of n-, i- and p- layer were performed.
- Firstly, the oxidation time was optimized for the vertical uniform growth of Te-doped GaAsSb on an n-type Si substrate. Then, a low-frequency noise (LFN)

measurement was carried out to determine the noise spectra of the device as well as the quality of the grown NWs.

- The substrate temperature for the initial growth of GaAs stem/GaAsSb was optimized for the dense vertical growth of NWs without using any sophisticated instruments like e-beam lithography (EBL) and nanoimprint lithography (NIL).
- To suppress the accumulation of Be and the enhancement of Be incorporation, the effect of the V/III ratio on the p- shell was examined.
- To compensate for the p-type nature of GaAsSb, the pulsing of Te, which is an n-type dopant during the growth of the intrinsic shell, is employed. The success of this technique was demonstrated by enhanced detectivity, rectification ratio, and on-off ratio from the I-V characteristic of the ensemble PD device. In addition, LFN measurement was carried out to provide better insight into the generation-recombination (G-R) noise components arising from the G-R centers.
- Sb% composition in the n-i-p layer was optimized to form a heterojunction, which creates an energy barrier. The energy barrier confines the injected charge carriers, thereby reducing the series resistance in the intrinsic region, the insertion loss compared to the homojunction, and suppressing the dark current (113, 114). A wide-bandgap p⁺ shell (Be-doped GaAs_{0.90}Sb_{0.10}) acts as a window for the light to enter the intrinsic region ((i- GaAs_{0.75}Sb_{0.25}). The wide-bandgap material of the n-i-p window determines the short-wavelength cut-off, while the small-bandgap of the intrinsic region decides the long-wavelength cut-off of the photoresponse (115).

- The variation in the intrinsic region width was investigated to realize the high-performance C-S n-i-p GaAsSb NW IRPD. The device performance and the junction quality were investigated using I-V, LFN, and C-V measurements.
- This work provided a better insight into the series resistance and device performance of conventional C-S n-i-p junction configuration (Figure 1(a)), and their feedback was used to design a novel C-S structure to fabricate a high-quality C-S n-i-p junction (Figure 1(b)). Further, it was observed that the optical absorption and ohmic contact formation depends on the p- and i- segment thickness and dopant concentration of p- and n- segment.

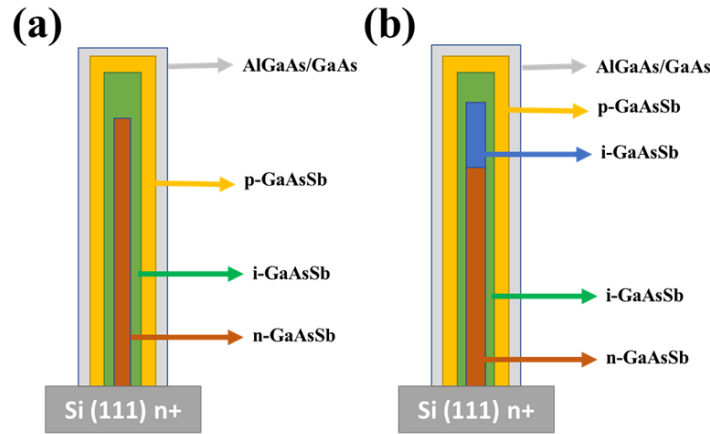


Figure 1. Schematic of (a) conventional and (b) hybrid axial C-S n-i-p GaAsSb NW structure.

- The following steps were undertaken to fabricate novel high-quality RT C-S n-i-p GaAsSb NW-based PD.
- The structure of the C-S n-i-p GaAsSb was redesigned in which a small segment of i-GaAsSb is grown on the core Te-doped GaAsSb, to improve the light absorption volume for an enhanced device performance, as shown in Figure 1(b)

and to eliminate the possible effect of over-etching of p- and i- shell during metal contact fabrication.

- To eliminate the shunt current path, the NW growth is initiated with GaAs stem for 3 mins followed by Te-doped GaAs for 2 mins.
- In this work, intrinsic shell Sb% is optimized for the emission at wavelength 1.5 μm and was determined to be of $\text{GaAs}_{0.70}\text{Sb}_{0.30}$ composition, while a wide-bandgap $\text{GaAs}_{0.90}\text{Sb}_{0.10}$ is grown as n-core and p-shell.
- In-situ vacuum annealing after the growth of each n-, i-, p- segment for the formation of a uniform junction. C-V measurement and LFN measurement were carried out to verify the junction quality and to determine the device performance of the hybrid axial C-S NW.

These are the first report on C-S n-i-p GaAsSb NW achieving a PL emission of 1.5 μm . A low dark current of 4 nA, an improvement in rectification ratio of 122, and comparatively low series resistance of 3×10^4 ohms are attributed to the formation of the high-quality and high-performance novel design of n-i-p junction in C-S NW geometry. The RT C-S n-i-p GaAsSb PD shows responsivity of 18 A/W and detectivity of 1.1×10^{13} Jones for the 1.5 μm illumination wavelength. Also, high responsivity and detectivity of 190 A/W and 1.1×10^{14} Jones at -1V, respectively, were estimated for the illumination of 1.1 μm wavelength for the conventional C-S n-i-p GaAsSb NWs, which is on par with the best InGaAs PD device metrics of the planar configuration currently in the market (116-119).

1.7 Dissertation Outline

This dissertation is organized into five chapters, and the brief content of each chapter from chapter 2 is provided below.

Chapter 2 provides experimental details on the fabrication of NWs using the MBE growth technique. The morphological and topography of NWs were characterized using SEM and C-AFM, respectively. Optical characterization of NWs was performed using RT, low-temperature 4K-PL, and Raman spectroscopy. XPS and UPS are the surface analytical tools used for determining the atomic concentration and work function of NWs. Finite element method simulations of I-V were carried out using COMSOL Multiphysics software. Ensemble I-V characteristics using a two-probe Keithley system, LFN measurement, and C-V measurement were performed for determining the electrical characteristics, the figure of merits of the NW IRPD, and charge carrier transport mechanisms. In addition, the doping profile of the Te-doped GaAsSb NWs was measured using Scanning Kelvin probe microscopy (SKPM).

Chapter 3 describes the methodology developed to assess the Te dopant incorporation in GaAsSb NWs and Be dopant incorporation in GaAs NWs. For the first time, Te and Be dopant incorporation was studied using a combination of non-destructive techniques, namely XPS, UPS, C-AFM, and SKPM. This work has been published in **Scientific Reports and OSA Technical Digest, 2021.**

Chapter 4 describes the efficacy of the ALD deposited Al_2O_3 passivation layer on self-catalyzed GaAsSb NWs. The effect of the Al_2O_3 passivation layer is examined using XPS and Raman characterization. This work has been submitted to **IOP Nanotechnology, 2022.**

Chapter 5 discusses the first report on the fabrication of RT hybrid axial C-S n-i-p GaAsSb NWs IRPD with PL emission up to $1.5\ \mu\text{m}$. In this work, the effect of various parameters, namely, Be and GaTe cell temperatures, Te compensation, and p- and i- segments variation, were investigated, emphasizing the fabrication of better RT-IRPD device performance. Furthermore, the C-S n-i-p junction device metrics were determined from SNW and ensemble

NW I-V characteristic, C-V, and LFN measurements. Based on these results, a new design involving an axial and C-S configuration hybrid were developed and fabricated. This work demonstrates how the properties of axial and C-S can be suitably tailored to improve the device performance.

Chapter 6 summarizes the systematic doping and device study that led to the significant achievements at each stage, ultimately leading to the successful high-performance RT-PD device fabrication at 1.1 μm , which is comparable to the device metrics of commercial PDs. The novel hybrid design constituting both the axial and C-S resulted in high responsivity and detectivity in the NIR wavelength region up to 1.5 μm . This chapter concludes with the scope of future work.

CHAPTER 2

Experimental Details

In this chapter, various tools used for the fabrication of molecular MBE-grown and material characterization C-S n-i-p GaAsSb NWs are presented in detail. The surface morphology of NWs was characterized using a scanning electron microscope (SEM), whereas Raman spectroscopy for finding the structural information. The RT and 4K Micro-photoluminescence (μ -PL) were used for the optical characteristics of the NWs. Tools utilized for the surface analytical characterization were XPS and UPS for determining the atomic concentration and work function of Te-doped GaAsSb NWs. Finite element method simulations of I-V were carried out using COMSOL Multiphysics software. Ensemble I-V characteristics using a two-probe Keithley system, LFN measurement, and C-AFM to determine the electrical characteristics of single and ensemble NWs, the figure of merits of the NW device, and charge carrier transport mechanisms. The doping profile of the Te-doped GaAsSb NWs has been carried out using SKPM.

The following is a brief description of the growth process and characterization of MBE-grown NWs, fabrication processing, and various characterization tools utilized for MBE-grown C-S n-i-p GaAsSb NW devices used in this dissertation.

2.1 MBE

MBE is an epitaxial technique in which the deposition of the cluster of atoms or atomic beam is generated by heating desirable source elements in Knudsen cells on a heated substrate in an ultra-high vacuum (UHV) ambience. As it is kinetically driven, MBE is an essential and versatile deposition technique for the growth of highly crystalline semiconductor materials of compositions away from thermal equilibrium conditions.

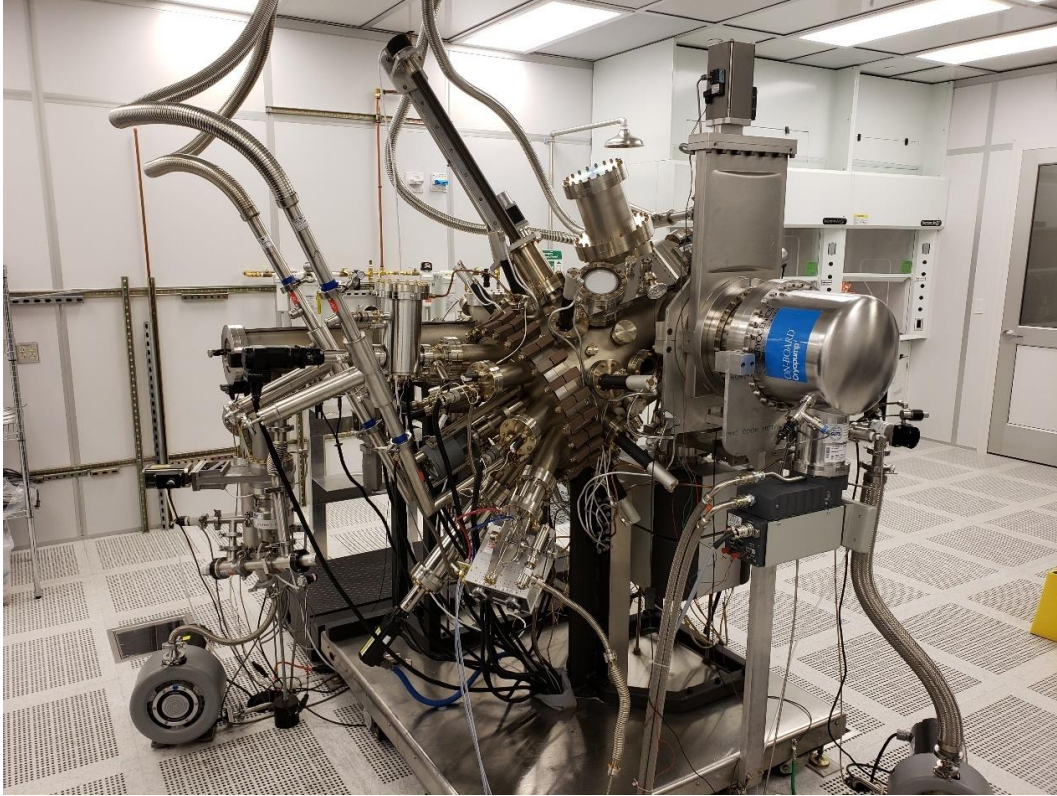


Figure 2. Veeco EPI 930 solid source MBE system.

In this project, Veeco EPI 930 solid source MBE will be used to grow III-V NWs, as shown in Figure 2. The MBE system is dedicated to the growth of III-V materials (group-III elements - Ga, In, and Al and group-V elements - N, As, and Sb). It consists of 5 Knudsen effusion cells, one SUMO cell, two-valved crackers, and a UNI-Bulb plasma nitrogen source. A SUMO cell was used for the Ga source, which supports dual filament in a hot lip configuration, thereby giving most of the power to be fed to the tip filament. Hence, the tip operates at a higher temperature than the primary (base) filament. In this configuration, the oval defects are reduced, limiting Ga droplet formation in the crucible. Group-III species such as In, Al (a high purity solid material) is evaporated as monomers through resistive heating in effusion cells. Effusion cells are used for dopants like Beryllium (Be), Tellurium (Te), and Silicon (Si). Valved cracker cells are used for group-V species such as As and Sb, which control the number of tetramers, dimers, and

monomers by varying the cracker temperature. Also, an automated needle valve positioner present in the valved cracker cells provides accurate control over the flux. The Substrate temperature is controlled by the thermocouple, which is fixed to the back of the sample holder and monitored by the pyrometer.

2.1.1 Growth of C-S n-i-p GaAsSb NWs. Si (111) n-type substrate was chemically treated to remove organic impurities using piranha solution for 10 mins and native oxide using 5% HF solution for 12 secs; the cleaned sample is left in the ambient atmosphere to grow native oxide at RT for 120 mins prior to loading in the MBE chamber.

Self-catalyzed Te-doped and Be-doped $\text{GaAs}_{0.90}\text{Sb}_{0.10}$ and intrinsic $\text{GaAs}_{0.75}\text{Sb}_{0.25}$ (shell) NWs were grown on heavily doped n-type Si (111) substrate (chemically treated using Piranha/HF) at a constant group-III beam equivalent pressure (BEP) of 6×10^{-7} Torr and valved group V As and Sb cracker sources using MBE EPI 930 system.

In chapter 5, we mainly discuss three MBE grown C-S n-i-p GaAsSb NW PD. Two NW sample structures follow conventional C-S n-i-p configuration (Figure 1(a)), whose intrinsic segment growth times are 25 mins and 30 mins, will be referred to as I-25 and I-30 samples hereafter, respectively. The third sample, referred to as MI, is the hybrid axial C-S configuration of the n-i-p structure, as shown in Figure 1(b).

Firstly, the oxidation time of the n-Si substrate was optimized. Four MBE-grown samples, C-S n-i-p GaAsSb NWs of oxidation time 50 mins, 90 mins, 120 mins, and 220 mins, will be referred to as I-50, I-25, I-120, and I-220 samples. The growth process of the I-25 sample is explained below in detail and is considered a reference to simplify the growth description of these many samples. Hence, with the I-25 sample as a reference, the growth process of the remaining samples is explained. For instance, in the case of I-50, I-120, and I-220, the only

difference between these samples and I-25 is the duration of oxidation time. The effect of the V/III ratio on Be incorporation was investigated using two NW samples, I-10 and I-25. It is to be noted that the only difference between these two samples is the V/III ratio of the i-p shell of the I-10 NW sample is 10, while for I-25, the V/III ratio was 11. The effect of a substrate temperature of 615 °C and 620 °C were studied, whose samples will be referred to as I-615 and I-620, respectively; in this case, only the core of the I-25 sample is grown. Finally, the effect of Te compensation is examined; the sample in which no Te compensation is carried out will be referred to I-R, while the Te-compensated sample will be referred to I-120, hereafter.

For the I-25 sample, the Ga shutter was opened for 9 secs before opening As flux and Te to grow the Te-doped GaAs stem with As₄ beam equivalent pressure (BEP) of 6×10^{-6} Torr at 615 °C for 8 mins. The growth temperature was further reduced to 590 °C for the growth of Te-doped GaAs_{0.90}Sb_{0.10}, resulting in the formation of $\sim 2 \mu\text{m}$ in length NW. During the core growth, the V/III ratio was maintained at 10, while for the shell, it was kept at 11. The Ga droplet on top of the NW was consumed by simultaneously shutting off Ga, Sb, and Te shutters and reducing the temperature to 550 °C while keeping As shutter open. The i- GaAs_{0.75}Sb_{0.25} (shell) NWs have been grown around the n-GaAsSb core at 550 °C with an opening of Te for 2 sec for every 2 mins of intrinsic shell growth, achieving a thickness of $\sim 40 \text{ nm}$ for the growth time of 25 mins. The growth of Be-doped GaAs_{0.90}Sb_{0.10} was initiated by opening Be for 5 secs in 30 sec for the first 2 mins of the growth, followed by in-situ annealing for 5 mins, whose thickness was 40 nm. Finally, the passivation shell of AlGaAs/GaAs was grown for 3 mins/2mins respectively, followed by 5 mins of vacuum annealing.

In the case of the MI sample, the following are the changes that have been implemented.

- The oxidation time was increased to 120 mins to reduce the parasitic growth and noise.
- Initially, GaAs stem was grown for 3 mins followed by 2 mins growth of Te-doped GaAs.
- Core Te-doped $\text{GaAs}_{0.90}\text{Sb}_{0.10}$ is grown at 590 °C for 5 mins. The i- $\text{GaAs}_{0.90}\text{Sb}_{0.10}$ was subsequently grown for 10 mins with an opening of Te for 2 sec for every 2 mins.
- The temperature was decreased to 465 °C for the droplet consumption, where the droplet was consumed by keeping As shutter alone open.
- Shell growth of i- $\text{GaAs}_{0.70}\text{Sb}_{0.30}$ was initiated at 550 °C for 35 mins, followed by in-situ annealing for 5 mins, during which the growth is paused.

2.2 Characterization Techniques

The following are the techniques that are used for the characterization of nanowires.

2.2.1 SEM. Carl Zeiss Auriga-BU FIB FESEM Microscope equipped with Bruker EDS used field emission gun for electron emission, was used to determine the morphology of the NWs. Typical accelerating voltages of 5 kV and a working distance of around 5 mm were used to obtain good quality SEM images.

2.2.2 μ -PL spectroscopy. The μ -PL measurements were conducted to determine the optical characteristics of the nanowires. In this system, 633 nm He-Ne laser was used as the excitation source. After excitation, the resulting PL signal is dispersed using a 0.32 m double-grating monochromator and detected using an InGaAs detector using a conventional lock-in

technique. Variations in PL characteristics of NW samples were studied for 4K and RT. The details of the PL instrument are provided elsewhere (120).

2.2.3 Raman spectroscopy. Raman spectroscopy was carried out at RT to determine the vibrational characteristics and hence, the quality of the nanowires using Horiba Jobin Yvon LabRam ARAMIS with a He-Ne laser of 633 nm excitation source.

2.2.4 XPS and UPS. XPS/UPS measurements were performed using monochromated Al K α X-rays source ($h\nu = 1486.6$ eV) and He-I photon source (21.21 eV), respectively, with a Thermo ESCALAB 250 Xi. The base chamber pressure is kept in the 10^{-9} mbar range at RT, and the diameter of the analyzed area is about 300 μm . From XPS spectra, the atomic concentration of the NW samples was determined, and UPS spectra were used to obtain the work function of the NW samples (121).

2.2.4.1 XPS. XPS characterization tool provides analysis of elements present in the sample (all elements except hydrogen and helium) and also the chemical state information of those elements (122). XPS is a surface-sensitive analytical technique based on the photoelectric effect with a probing depth of ~ 10 nm. The kinetic energy of emitted electrons from the surface due to the bombardment of soft x-rays is measured as described in equation (1) (122). The result of the complete transfer of the x-ray energy to a core level electron is the emitted photoelectron, as shown in Figure 3.

$$h\nu_{\text{x-ray}} = \text{BE} + \text{KE} + \Phi_{\text{spectrometer}} \quad (1)$$

where $h\nu_{\text{x-ray}}$ is the energy of the x-ray, BE is the binding energy of the electron, KE is the kinetic energy of the electron that is emitted, and $\Phi_{\text{spectrometer}}$ is the spectrometer work function.

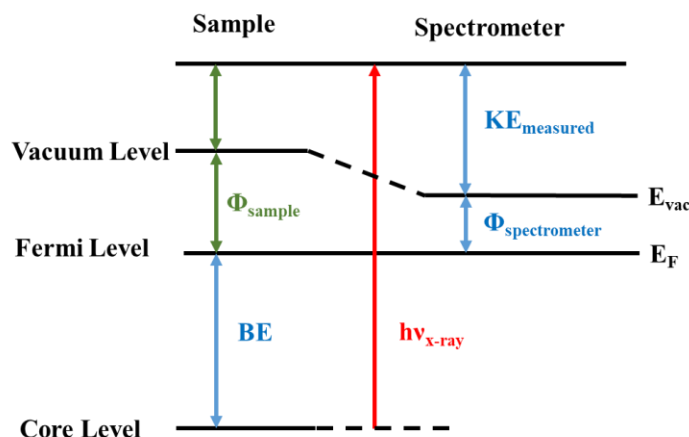


Figure 3. Schematic energy level diagram depicting working of XPS.

Avantage software analysis provided by ThermoFisher Scientific, NIST XPS database, reference books, and research papers can be used to identify each element based on the BE (123-126). It is to be noted that the BE is the material property and the corresponding photoelectron peaks are the fingerprints of the elements independent of the x-ray source used to eject the electrons. All photoelectron peaks emerge from the core-level orbitals, namely s, p, d, and f. It is to be noted that except s-orbital, all other orbitals exhibit doublet peaks due to spin-orbit coupling. The intensity ratio of the doublet plays an important role in distinguishing overlapped peaks of different elements, O1s and Sb 3d_{5/2}, for instance (121). The relative intensity of doublet states is characterized by $2j+1$, where $j = l \pm \frac{1}{2}$ quantum number. Therefore, the intensity ratios of p whose $l=1$ is $1:2 [(2(l-\frac{1}{2})+1) : (2(l+\frac{1}{2})+1)]$, while for d and f- doublets is calculated to be 3:2 and 4:3, respectively (122). In addition, the separation of the doublets is always constant for each element which depends on the angular momentum and principal quantum number.

Peak fitting is one of the crucial aspects of analyzing XPS spectra data. The first step to fitting is to select the appropriate background (BG) subtraction method to remove BG signals from the scattered electrons, thereby ensuring accurate peak intensity measurement. There are several BG subtraction methods, namely linear, Shirley, smart, simple, and tougaard (127).

Among these, smart BG is recommended as it is based on Shirley BG but with an additional constraint such that the intensity of BG should not be greater than the actual data. Following is the mixed G-L product function ($f(x)$) (equation (2)) that was used to analyze the peak after the subtraction of a non-linear BG from the spectra.

$$f(x) = \frac{H}{[1+M(x-x_0)^2/\beta^2] \exp [(1-M) [\ln 2 (x-x_0)^2]/\beta^2]} \quad (2)$$

where H is the peak height, M is the mixing ratio which takes the value of 1 for a pure L and 0 for a pure G peak, x is the BE, x_0 is the peak BE, and β is the parameter that is approximately half of FWHM. The atomic concentration (%) of each element is calculated as (100 x normalized area of a peak)/ (sum of normalized areas of all the peaks) (121).

2.2.4.2 UPS. The technique of UPS is as same as XPS but irradiated with a UV source. The UV source's low energy compared to the x-ray source is capable of ejecting electrons from the valence band only (Figure 4), thereby making it surface-sensitive with a probing depth of 2-3 nm (122). Hence, one should be mindful of surface contamination. The work function of the samples can be found from equation (3),

$$\Phi_{\text{sample}} = h\nu - (E_{\text{cut-off}} - E_F) \quad (3)$$

where Φ_{sample} is the work function of the sample, $h\nu$ is the energy of the He-I source, $E_{\text{cut-off}}$ is the cut-off energy, and E_F is the Fermi energy.

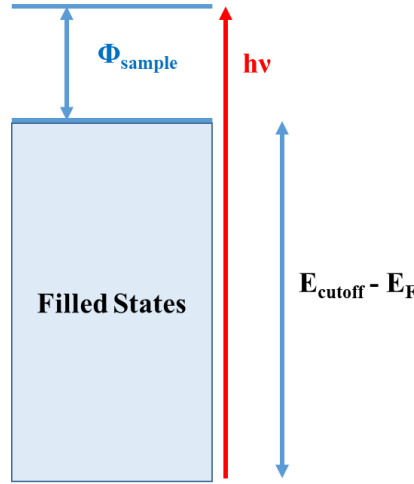


Figure 4. Schematic energy level diagram depicting working of UPS.

2.2.5 Simulations. The fine element method was executed using Comsol Multiphysics software to obtain the parameters such as charge mobility, and charge concentration from the I-V fitting (equations 4 and 5) (96). Electric field simulation of C-S n-i-p NW structure was performed using COMSOL finite element analysis, solver, and multiphysics simulation software.

$$J_n \times n = \frac{-A^* T^2}{N_c} \left(n - \left[N_c e^{-q\Phi_B/k_B T} \right] \right) \quad (4)$$

$$J_p \times p = \frac{A^* T^2}{N_v} \left(p - \left[N_v e^{-q(E_g - \Phi_B)/k_B T} \right] \right) \quad (5)$$

where J_n and J_p are electron and hole current density, n and p are the electron and hole carrier density, N_c and N_v are the effective density of states in conduction band and valence band, A^* is the effective Richardson constant, T is the temperature, k_B is the Boltzmann constant, q is the magnitude of the electron charge, Φ_B is the Schottky barrier height, E_g is the bandgap of the material.

2.2.6 Ensemble NW IRPD device fabrication. For ensemble PD, NWs samples were spin-coated with an insulating and transparent SU-8 photoresist, which served as a protective layer and filler for NWs. NW core tip from SU-8 was exposed using reactive ion etching (RIE). Metal contacts for the NW device consisted of silver NWs and silver paste were deposited for top contact and bottom contact, respectively.

2.2.7 I-V measurement of the ensemble NWs. I-V performance of ensemble NWs was assessed for various wavelengths ranging from 633 nm to 1500 nm at room and low temperature using Keithley 4200 characterization system by the two-probe method. The I-V measurement, the top contact, and bottom contact are silver NW and silver paste, respectively.

2.2.8 LFN measurement. LFN measurement was conducted to determine the noise characteristic of NWs. The top and bottom contacts are dc-biased using the low-noise amplifier's input terminal. The output was fed to the dynamic signal analyzer, in which a cross-correlation technique was used to process the data into power spectral density. It is to be noted that higher resolution of the frequency shows lower cut-off frequency and vice-versa. Hence, a standard resolution needs to be used to compare different data.

2.2.9 Capacitance-voltage (C-V) measurement. C-V characteristic was performed from the frequency range of 1 kHz - 1 MHz in reverse bias voltage between 0 and -3V, using Hewlett Packard LCR meter.

2.3 Characterization of SNW using C-AFM and SKPM

2.3.1 C-AFM. An important technique used to characterize the photoresponse of a single nanowire (121). During the current imaging scan, a DC bias was applied between the Ti/Ir conductive tips with a spring constant of 2 N/m and tip radius of 25 nm and the sample substrate,

in which the cantilever was grounded. Laser of wavelength 860 nm, and power of 1 mW, were used to illuminate the nanowire. This technique is described in detail in the following section.

2.3.1.1 Theory and background of C-AFM. Contact mode AFM is the frequently used imaging mode in AFM. In the AFM imaging technique, the tip tracks the topography of the sample by monitoring the cantilever deflection, as demonstrated in Figure 5.

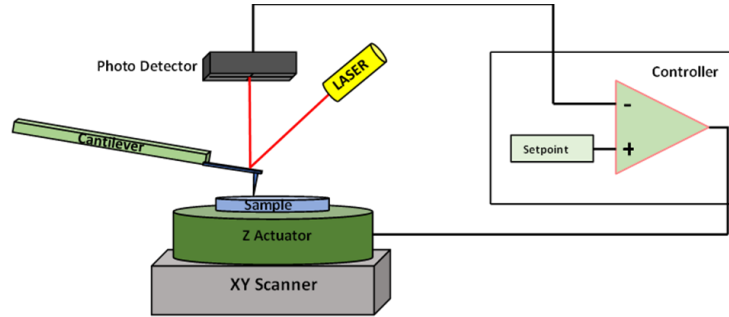


Figure 5. Tracking of topography using the tip.

Tracking of topography using tip: Let us consider that the tip is above the sample surface in the air by a few microns without Z feedback, and the Z actuator is fully retracted. Therefore, the lever is in a relaxed position. The alignment of the photodetector is done by centering the laser beam. Lever deflecting away from the relaxed position marks as a non-zero voltage - positive for bending away and negative for bending towards the sample. Corresponding to the deflection, a setpoint voltage is chosen. Figure 6 shows the cantilever deflection versus the Z sensor.

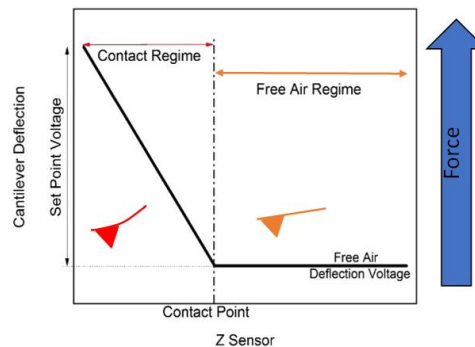


Figure 6. Cantilever deflection versus Z sensor.

The Z feedback loop controls the Z actuator, maintaining the fixed setpoint voltage. The Z actuator extends if the measured deflection voltage is less than the setpoint voltage. Otherwise, the Z actuator retracts if the measured deflection is greater than the setpoint voltage. The Z feedback maintains the deflection constant while the scanner is rastered along the X and Y direction. According to the feedback, when the cantilever moves over the sample, the voltage applied to the z actuator changes. Since the Z actuator is a piezoelectric material that acts linearly over a small range distance, the voltage received by the Z actuator is an accurate measurement of the topography of the sample, as shown in Figure 7.

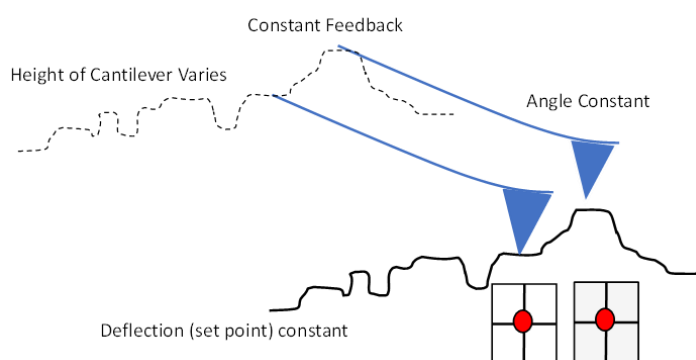


Figure 7. Tracking of the surface using Contact Mode.

C-AFM is a technique in which the electrical current passes through the tip, and the sample is recorded (128). The electrical characteristics will be investigated with C-AFM MFP-3D Origin (Asylum) in ambient conditions, operating in the contact mode.

In CAFM, the following measurements can be taken as depicted in Figure 8:

- A current map of the surface of the sample at a given bias gives us a single slice of the conductivity of the sample.
- Current-Voltage (I-V) spectra of the sample.

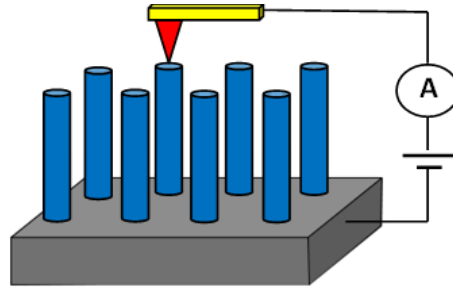


Figure 8. I-V Characterization of single NW using C-AFM.

2.3.2 SKPM. SKPM scanning of the samples was carried out using lift mode, which uses two separate passes per scan line. The sample topography was measured in the first pass, while the surface potential was measured in the second pass.

2.3.2.1 Theory and background of SKPM. SKPM is a non-contact mode technique based on detecting electrostatic tip-sample forces between sample and tip. The working of SKPM in which the probe tip is electrically driven with an AC bias. Thereby causing the probe to oscillate mechanically due to the potential difference between the tip and the sample. Further, these oscillations are nullified by the feedback loop on the bias. Hence, the voltage required to cancel the oscillations is recorded as the surface potential (121).

An AC bias is applied between the tip, and the sample generates an electrostatic force between the tip-sample. For simplicity, let us consider the sample and tip as parallel plate capacitors. Hence, the force between the two plates of the capacitor (F) is proportional to the square of the applied voltage (V). Therefore, the potential difference between the probe and the sample is the sum of applied DC voltage (V_{DC}), the potential difference between the probe tip and the sample (V_{sp}), and the applied AC bias (V_{ac}).

$$F = \frac{1}{2} \frac{\partial C}{\partial z} V^2 \quad (6)$$

$$V = (V_{DC} - V_{sp}) + V_{ac} \sin(\omega t) \quad (7)$$

Squaring equation (7),

$$V^2 = (V_{DC} - V_{sp})^2 + 2 (V_{DC} - V_{sp}) V_{ac} \sin (\omega t) + V_{ac}^2 \sin^2 (\omega t) \quad (8)$$

Equation (8) can be written as,

$$V^2 = (V_{DC} - V_{sp})^2 + 2 (V_{DC} - V_{sp}) V_{ac} \sin (\omega t) + V_{ac}^2 (1 - \cos (2\omega t)) \quad (9)$$

From equation (9), it is observed that DC and ωt components contribute to the signal.

Substituting equation (9) in (6) gives us:

$$F = \frac{1}{2} \frac{\partial C}{\partial z} \left\{ [(V_{DC} - V_{sp})^2 + \frac{1}{2} V_{ac}^2] + 2 [(V_{DC} - V_{sp}) V_{ac} \sin (\omega t)] - \frac{1}{2} V_{ac}^2 \cos (2\omega t) \right\} \quad (10)$$

It is observed that even though the 2F component has a significant force, it is not enhanced by the resonance of the cantilever; hence, the cantilever does not respond to that frequency. The term that contributes is the middle one, which shows that the force (amplitude) will be minimized if $V_{DC} = V_{sp}$. It summarizes the working principle of SKPM, where the feedback loop is used to adjust the DC bias on the cantilever to minimize the amplitude.

Important things that need to be kept in mind by the C-AFM/SKPM users are

- The speed of the cantilever should be chosen wisely based on the density and morphology of the NWs. For instance, for a sample with length variations, if low or very high speed is selected, then for the former case, the tip will be dragging and consumes a lot of time for imaging, while for the latter case, the tip might hit a tall NW and break easily.
- Cantilevers/probes should be selected based on the material that needs to be scanned/measured. For example, cantilevers with high spring constant will wear down/break soon. On the other hand, the challenge faced by the cantilever with a

low spring constant is that it will be difficult for the cantilever to overcome the contact resistance between the tip and the sample.

- Apart from finding the resonant frequency to check whether the probe is working, one of the other ways is to do the imaging of a standard sample given by Asylum. If the solid metal tips are used, then the image of the NW tip (for instance) will become larger over a period of time, as the sharp tip will turn blunt. If metal-coated tips are used, One will observe an elongated NW tip image if the metal-coated tip is damaged. It will look as if the NWs are dragged along the tip's scan direction. If the tip has gone bad, then while doing C-AFM imaging, there will be no change in the current with the applied bias voltage (not applicable for insulators).
- Both nano- and micro- gain stages are displayed on the computer. When the head of the AFM scanner is brought down, the current should display zero, as the tip is still not in contact with the sample. If any current is observed during the lowering of the head, it indicates a short circuit. So, it needs to be checked if the cantilever holder is not in contact with anything.
- In the case of SKPM, one has to ensure that the substrate is highly conductive, preferably gold-coated Si substrates. With metallic background reference, it is easier to obtain surface potential data of the NW sample.

2.4 Summary

The surface morphology of NWs was characterized using SEM, whereas Raman spectroscopy was used for finding the structural information of NWs. The RT and 4K μ -PL were used for the determination of optical characteristics of the NWs, which is considered a primary

tool for optimizing the Sb% for the growth of GaAsSb NWs. XPS and UPS, non-destructive surface analytical characterization techniques, were used to find the atomic concentration and work function of Te-doped GaAsSb NWs. C-AFM and SKPM are the other non-destructive tools used for finding the atomic concentration and the doping profile of the Te-doped GaAsSb NWs, respectively. These studies provided a better insight into the doping incorporation in NWs, which aided in the fabrication and realization of high-performance IRPD. The growth of C-S n-i-p GaAsSb NWs was optimized using finite element method simulations of I-V, which was carried out using COMSOL Multiphysics software. SNW and ensemble I-V characteristics, LFN, and C-V measurements were used to determine the junction quality, the figure of merits of the NW device, and charge carrier transport mechanisms of the NW. Rapid feedback from material characterization and the device analysis allowed to accelerate the optimization of the growth, processing, and device design to achieve a high-performance NW PD device.

CHAPTER 3

Study of Dopant Incorporation in Te-Doped GaAsSb and Be-Doped GaAs NWs

3.1 Introduction

In recent years, III-V semiconductor nanowires (NWs) have attracted significant attention due to their one-dimensional architecture, quantum confinement effects, and a higher tolerance for strain mismatch that allow greater freedom in band gap engineering of material systems in a variety of different nanowire architectures to meet the demands of next-generation optoelectronic devices (39, 94). To realize advanced devices in a NW configuration successfully, dopant incorporation with abrupt interfaces in a well-controlled manner is essential and enables one to modulate work functions. Unfortunately, the thin film studies on dopant incorporation and carrier concentration cannot be directly translated to NWs due to the dopant's influence on the growth kinetics and different growth mechanisms along with the axial and radial directions (95). Also, the commonly used measurement techniques in thin films for the determination of carrier concentration, namely Hall effect, field-effect, capacitance-voltage, and thermoelectric measurements, require highly sophisticated lithography steps (129-135). Besides, in the case of nanowire field-effect transistors (FET), the uncertainty of the gate capacitance and contact resistance can further limit the accuracy of carrier mobility and concentration values (136, 137).

In recent years, several characterization methods have evolved for the assessment of dopants in NWs. These are secondary ion mass spectrometry (SIMS) (110, 130), off-axis electron holography (EH) (138-140), and atom probe tomography (APT) (141-144). However, SIMS requires a standard of known dopant concentration and is destructive, as is APT. In the case of the EH technique, sample preparation is complex, and it requires additional information about the NW thickness and homogeneity. Goktas et al. (130) performed a doping assessment of

Beryllium (Be) and Te-doped GaAs NWs using various characterization techniques, namely, the Hall effect, Raman, photoluminescence (PL), and SIMS. For Te-doped NWs, Raman and SIMS indicated carrier concentration on the order of 10^{17} cm^{-3} , which was at least one order of magnitude lower than the expected value. It was also found that the carrier concentration of Te-doped NWs could not be determined from PL and the Hall effect due to the lower Te dopant concentration in the NWs. Suomalainen et al. (131) studied qualitative analysis of Te dopant incorporation in self-assisted GaAs NWs using Raman spectroscopy. Orrù et al. (145) determined a high carrier concentration of 10^{20} cm^{-3} in Te-doped GaAs NWs using a combination of FET transport measurements, KPFM (Kelvin probe force microscopy), and PL. Hakkarainen et al. (140) showed a Te concentration of $4 \times 10^{18} \text{ cm}^{-3}$ in Te-doped GaAs NWs by APT using laser pulses.

Other surface analytical methods, namely X-ray photoelectron spectroscopy/ ultraviolet photoelectron spectroscopy (XPS/UPS), in conjunction with conductive-atomic force microscopy/ scanning Kelvin probe microscopy (C-AFM/SKPM), provide a set of excellent characterization methods for doping assessment, as they do not require any sample preparation. XPS has been more commonly used to identify the elemental compositions of NWs (146-149). Park et al. (150) determined the composition of InAsP NWs, and Timm et al. (151) investigated the interface composition (NW/thin film) of InAs/ Al_2O_3 and InAs/ HfO_2 . UPS has been used in NWs of Cobalt-doped molybdenum carbide to study the effect of doping (152) and Ge-doped ZnO (153) to determine the work function. There has been little work reported on the XPS/UPS evaluation of III-V NWs. In contrast, AFM and SKPM (also known as Kelvin probe force microscopy (KPFM)) are increasingly being used to examine the electrical/ photoelectrical characteristics (60, 154-156) and doping type/profile in III-V NWs (157-164).

In this work, we investigate the effect of different GaTe and Be cell temperatures on Te and Be dopant incorporation and electronic properties of MBE grown Te- doped GaAsSb and Be- doped GaAs NWs, respectively, using several surface analytical characterization techniques tools, namely XPS/UPS and SKPM along with C-AFM. The extensive research interest in GaAsSb NWs stems from its narrow band gap region covering the important optical telecommunication wavelengths of 1.3 μm and 1.55 μm (94). Statistical analyses of these measurement techniques have provided evidence for confirmation of Te incorporation in the GaAsSb NWs and Be incorporation in the GaAs NWs. The values of electron density from UPS concur very well with the values of electron density determined from C-AFM. Hence, these surface analytical tools without contact fabrication are found to be a very powerful tool for direct measurement of the dopant incorporation and doping levels in NWs.

3.2 Experimental Details

The intrinsic and Te-doped NWs were grown in an EPI 930 solid source MBE system with valved As₄ and Sb₂ as the group V constituent cracker sources. The self-catalyzed GaAs stem/GaAsSb core NWs were grown on a chemically cleaned (Piranha/HF) p-type Si (111) substrate at 620 °C/590 °C (43). The intrinsic GaAsSb NWs were grown with a constant group III flux of 6×10^{-7} Torr, and group V flux of 6×10^{-6} Torr and GaTe cell temperatures of 500 °C, 550 °C, and 570 °C were used for doped NWs.

The Self-catalyzed Be-doped GaAs NWs were grown on a heavily doped n-type Si (111) substrate (chemically treated using Piranha/HF) at 620 °C at a constant group-III flux of 6×10^{-7} Torr, and constant group-V flux of 6×10^{-6} Torr and Be cell temperature of 750 °C, 850 °C, and 950 °C, and hereafter, the samples will be referred as Be-750, Be-850, and Be-950, respectively (165).

Morphological characterization of intrinsic and doped NWs was carried out using Carl-Zeiss Auriga-BU FIB FESEM. XPS/UPS measurements were performed with a Thermo ESCALAB 250 Xi using monochromated Al K α X-rays source ($h\nu = 1486.6$ eV) and He-I photon source (21.21 eV), respectively. The base chamber pressure was kept in the 7.5×10^{-10} Torr range at room temperature, and the diameter of the analyzed area was about 300 μm . XPS survey scans of both R and N samples were acquired across binding energy (BE) range from 0 to 1370 eV with a pass energy of 200 eV and an energy step-size of 1 eV, while the core-level high-resolution scans were performed with an energy step-size of 0.1 eV. The XPS energy scale was calibrated with the binding energy of the photoelectron peak of C 1s at 284.8 eV from the gold substrate sample. The elements scanned from R, N-500, N-550, and N-570 samples, are gallium (Ga 3d), arsenic (As 3d), and antimony (Sb 3d) core-levels, whereas for Be-doped GaAs, Ga 3d and As 3d core-levels are scanned. The peak fitting was done by the Advantage analysis software program using a G-L product function with a mix ratio (L/G) of 30% and a smart-type background, which is Shirley BG with the additional constraint that the BG should not be greater than the actual intensity at any point in the selected region. The work function and valence band energy of R and N samples were obtained from UPS. The photoemission spectra were collected at 2 eV pass energy under a stable reverse bias of 4 V to eliminate an instrumental cutoff in the lens system of the analyzer at low kinetic energy.

The electrical characteristics have been investigated with C-AFM MFP-3D Origin (Asylum) in ambient conditions, operating in the contact mode. In conjunction with the topography of the sample, corresponding current mapping under a specific bias of 600 mV and a scan rate of 0.2 Hz is recorded. An I-V measurement was carried out on a SNW by positioning the AFM probe onto the nanowire tip and the other contact at the NW substrate, and varying

voltages between -1.5 V and 1.5 V under dark and laser illumination of 860 nm wavelength. As the probe tip is much smaller than the diameter of NWs (order of 100 nm), SNW I-V characteristics were performed accurately with high spatial resolution (30). Charge mobility of R and N samples were determined using COMSOL Multiphysics fitting of I-V. In addition, Carrier concentration of Te-doped GaAsSb and Be-doped GaAs NWs were calculated from COMSOL Multiphysics fitting of I-V. SKPM scanning of the R and N samples was carried out using lift mode, which uses two separate passes per scan line. The sample topography is measured in the first pass, while the surface potential is measured in the second pass. Ti/Ir conductive tips (Asylum) with a typical radius of curvature of 25 nm at a resonant frequency of 75 kHz were used for both C-AFM and SKPM techniques.

3.3 Results and Discussion

Results and discussion of study of dopant incorporation in Te-doped GaAsSb NWs and Be-doped GaAs NWs are explained in two separate sections 3.3.1 and 3.3.2, respectively.

3.3.1 Study of dopant incorporation in Te-doped GaAsSb NWs. We discuss four MBE grown samples, intrinsic and Te-doped GaAsSb NWs of GaTe cell temperatures of 500 °C, 550 °C, and 570 °C, which will be referred to as R, N-500, N-550, and N-570 samples, hereafter, respectively. The corresponding diameters are 136 ± 6 nm, 140 ± 5 nm, 152 ± 7 nm, and 157 ± 5 nm, respectively, as measured using field emission scanning electron microscopy (FESEM) (59). These are shown in Figures 9(a-d), with the R sample serving as a reference NW sample. In the following sections, evaluation of the electron concentration from the ensemble and single nanowires (SNW) is described consecutively using a combination of contactless/non-destructive techniques (no deposition of contacts), namely, XPS, UPS, C-AFM, and SKPM.

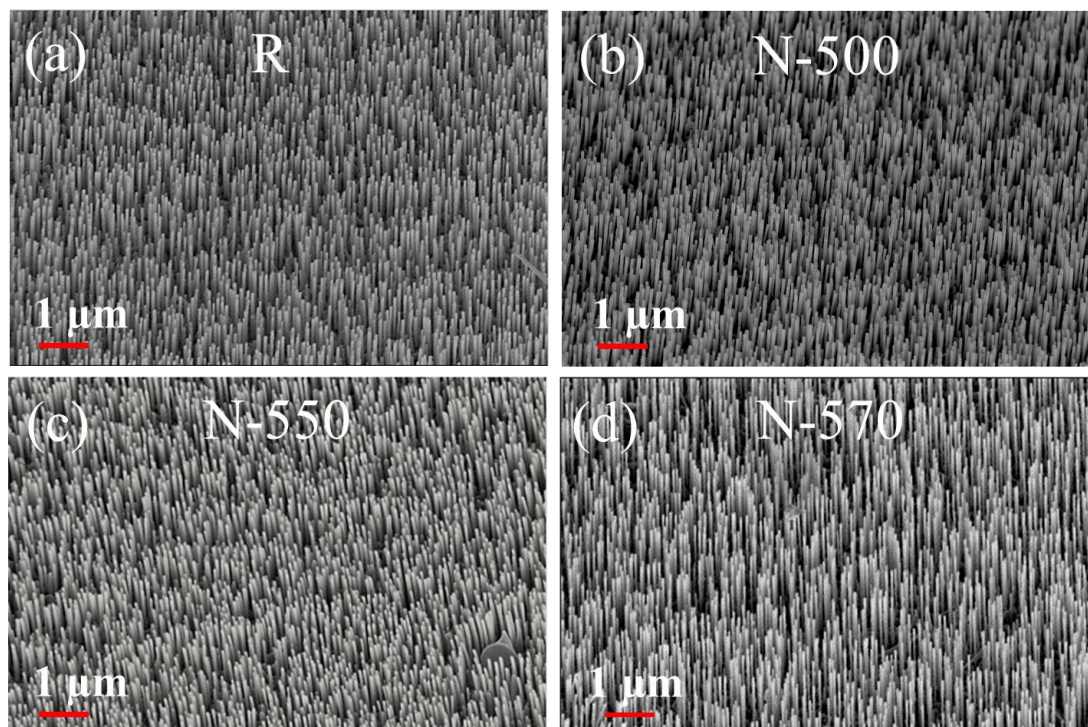


Figure 9. (a - d) SEM images of R, N-500, N-550, and N-570 samples, respectively.

3.3.1.1 XPS. First, we have carried out the compositional analysis of samples R, N-500, N-550, and N-570 using the 3d peaks of Ga, As, and Sb elements in XPS. The XPS survey spectra of the elements present in these four samples are shown in Figure 10. The typical resolution of the instrument is ~ 0.1 eV. The absence of C 1s and O 1s photoelectron spectral peaks in the survey spectra indicated minimal atmospheric contamination.

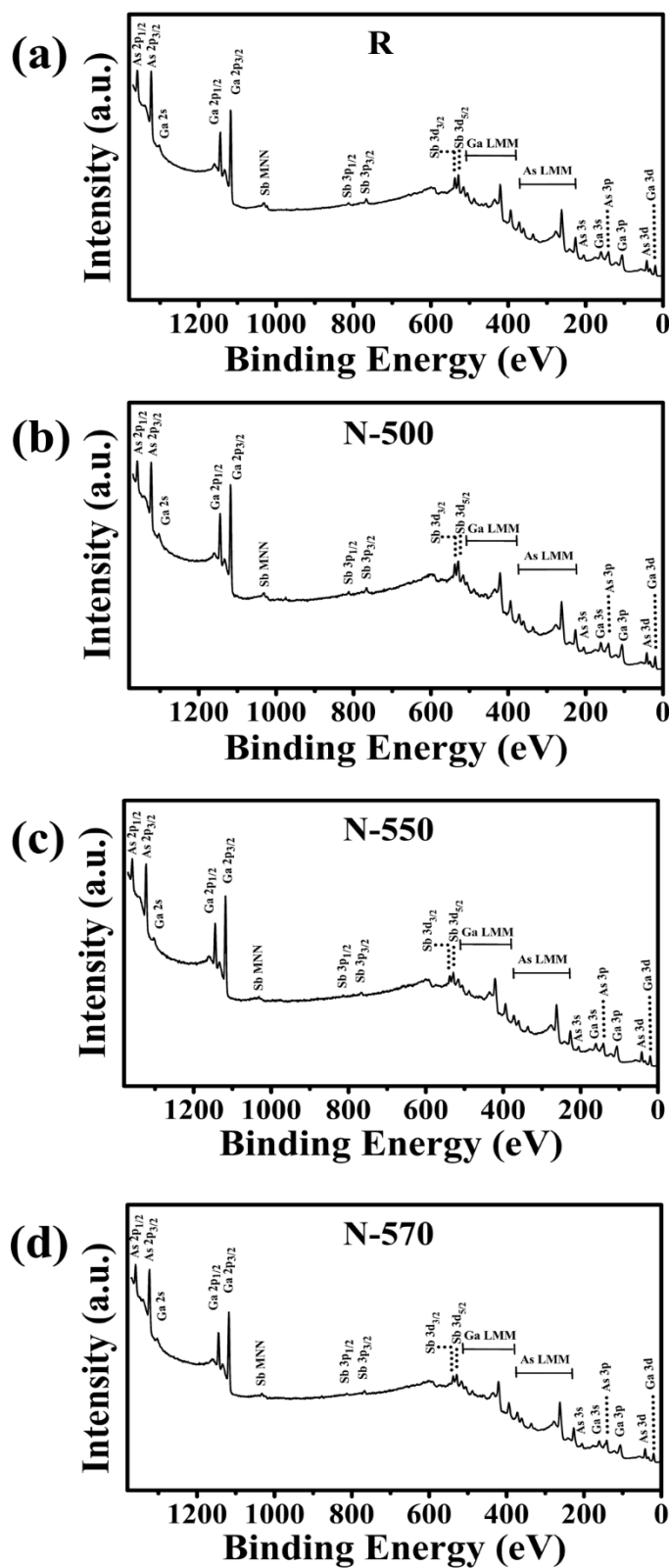


Figure 10. XPS spectra of (a) R, (b) N-500, (c) N-550, and (d) N-570 samples.

Figure 11 shows the core-level XPS spectra, while Figure 12(a) summarizes the extracted value of the Ga, As and Sb atomic concentrations in % for R, N-500, N-550, and N-570 samples, and Figure 12(b) depicts the ratio of Ga/As and Sb/As in those samples. A Gaussian - Lorentzian (G-L) product function is used for peak fitting of the Sb 3d with the constraint on the area ratio of the Sb 3d doublet ($\text{Sb } 3d_{5/2} : \text{Sb } 3d_{3/2}$) to be 3:2 ratio and a doublet peak separation of 9.4 eV according to the degeneracy of the spin state due to the overlap of the binding energy peaks of O 1s and Sb 3d (166, 167). The atomic concentration (%) of each element is then calculated as $(100 \times \text{normalized area of a peak}) / (\text{sum of normalized areas of all the peaks})$.

The atomic ratios (Figure 12(b)) of Ga/As for R, N-500, N-550, and N-570 samples are found to be 1.1, 1.0, 1.1, and 1.0, respectively, while for Sb/As, they are 0.07 for all the four samples. These data represent the surface composition and are in excellent agreement with our earlier reports (17, 59) of concentration determined from the EDS compositional scans of $\text{GaAs}_{0.93}\text{Sb}_{0.07}$ NWs in a transmission electron microscope (TEM).

The peaks observed at 19.5 eV and 41.8 eV in the R sample that are assigned to the Ga 3d and As 3d in GaAs (168-170) (Figures 11(a) and 11(b)), respectively, are shifted towards higher binding energy by 0.2 eV and 0.1 eV, in the N-500 sample (Figures 11(d) and 11(e)), 0.9 eV and 0.4 eV, in the N-550 sample (Figures 11(g) and 11(h)), and 0.4 eV and 0.2 eV, in the N-570 sample (Figures 11(j) and 11(k)). It is noted that though the values of binding energy shifts of the N-500 sample are comparable to the resolution of the instrument of 0.1 eV, the observed shifts were obtained at six different spots and the shifts were consistent and reproducible. Also, the NW diameter exhibited a slight increase with respect to the R sample. All of these observations suggest the onset of Te incorporation in the NWs. The peaks observed in R and N samples at 528.6 eV and 538 eV (Figures 11(c), 11(f), 11(i), and 11(l)) are associated with the

doublet Sb 3d_{5/2} and Sb 3d_{3/2}, respectively (171), attributed to Sb - Sb bond and 531.8 eV corresponds to O 1s (166). From the XPS core-level spectra, the concentration of O 1s is found to be <1 % in the intrinsic and doped GaAsSb samples. The large FWHM broadening of all the peaks observed in all the samples is attributed to the one-dimensional configuration of NWs, leading to enhanced contribution from surface roughness, electron shadowing effect, and shadowing effect of NWs (172) in comparison to the thin film counterpart. Further, the absence of Te 3d peak (173, 174) in the N samples suggests that the concentration of Te is less than 10¹⁹ cm⁻³. The XPS lower detection limit of Te is in the mid-10¹⁹ cm⁻³, it is further difficult to detect the dopant concentration in the range of detection limit in a ternary alloy. Hence, XPS surface analysis only provides a qualitative comparison of the dopant level. The shifts of Ga and As associated 3d peaks toward higher binding energies indicate increased free-electron density-induced shifts of the core elements, whereas the Sb 3d peak did not exhibit any shift. In GaAsSb, Ga can form bonds with As, Sb, as well as with Te in Te-doped GaAsSb. These peak shifts reflect corresponding shifts in the Fermi level higher in the band diagram, as the binding energies are measured relative to the Fermi level. Therefore, the N-550 sample is found to be heavily doped as compared to other samples N-500 and N-570.

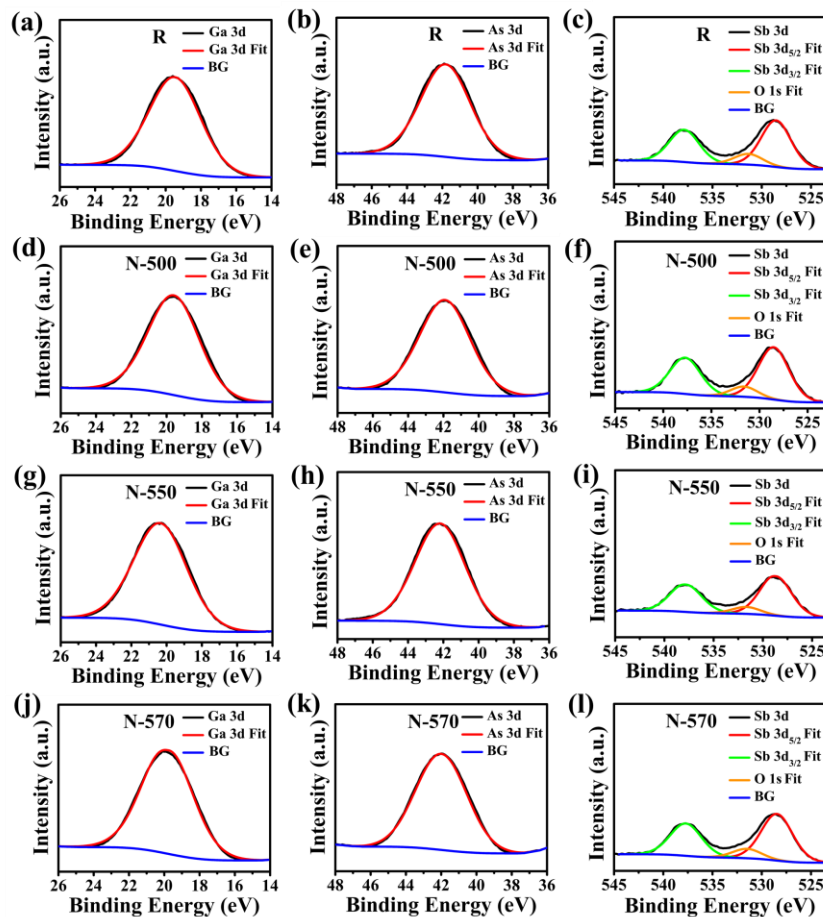


Figure 11. XPS spectra for (a, d, g, j) Ga 3d, (b, e, h, k) As 3d, (c, f, i, l) Sb 3d core levels of (1st row) R, (2nd row) N-500, (3rd row) N-550, and (4th row) N-570 samples, respectively.

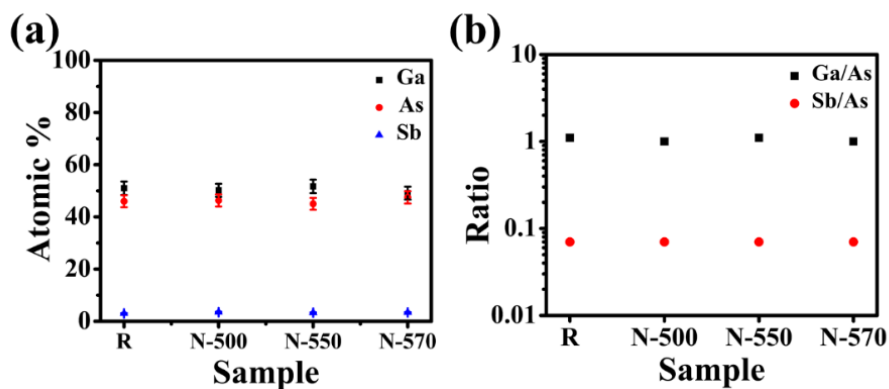


Figure 12. (a) Atomic % of Ga, As, and Sb in R, N-500, N-550, and N-570 samples and (b) ratio of Ga/As and Sb/As in R, N-500, N-550, and N-570 samples.

3.3.1.2 UPS. Next, electron concentration in the N samples was evaluated using UPS, which can provide a direct measurement of the work function and valence band energy. The work function is extracted from the difference between the energy of the UV photons and the secondary electron cutoff (high-binding energy (BE) cutoff). Figures 13(a) - 13(h) show low and high BE slopes of He I spectra of R, N-500, N-550, and N-570 samples, and also entire UPS spectra of the corresponding samples are shown and summarized in Figure 14. The intersection of the slope of the high BE with the extrapolated slope of the background electron intensity yielded work function values of 5.1 eV, 4 eV, 3.6 eV, and 3.9 eV for R, N-500, N-550, and N-570 samples, respectively, while similar intersection point at lower BE enabled the determination of the corresponding values of the valence band maximum (VBM) location to be at 0.3 eV, 1.3 eV, 1.7 eV, and 1.4 eV below the Fermi level (175). The significant difference between the work function of R and N-550 is evident, with N-550 being heavily doped. Using the Fermi-Dirac integral ($F_{1/2}(\eta_F)$) (96, 176) values of 2.2, 64.0, 13.0 derived from the UPS spectra, an electron concentration of $9.7 \times 10^{17} \text{ cm}^{-3}$, $2.8 \times 10^{19} \text{ cm}^{-3}$ and $5.7 \times 10^{18} \text{ cm}^{-3}$ for N-500, N-550, and N-570, respectively, was calculated using equation (11).

$$n_0 = \frac{2}{\sqrt{\pi}} N_C F_{1/2}(\eta_F) \quad (11)$$

Where n_0 is the electron concentration, N_C is the effective density of states in the conduction band, and ($F_{1/2}(\eta_F)$) is the Fermi-Dirac integral. From the comparison of the valence band line shape in all materials (Figures 14(a-d)), it seems that at least the filled density of states does not change. Assuming similar invariance in conduction band's empty density of states in these NWs, the following equations (12) and (13) are used in the calculation of carrier concentration from UPS using equation (11). This value is in excellent agreement with the value

obtained from COMSOL and Padovani-Stratton fit (177), which will be discussed in the following section (Figure 17(e)).

$$\eta_F = \frac{E_F - E_C}{kT} \quad (12)$$

$$F_{1/2}(\eta_F) = \int_0^\infty \frac{\eta^{1/2} d\eta}{1 + \exp(\eta - \eta_F)} \quad (13)$$

Where E_F and E_C represent the Fermi energy and conduction band energy, respectively. kT is the product of Boltzmann's constant and temperature, and $(F_{1/2}(\eta_F))$ is the Fermi-Dirac integral.

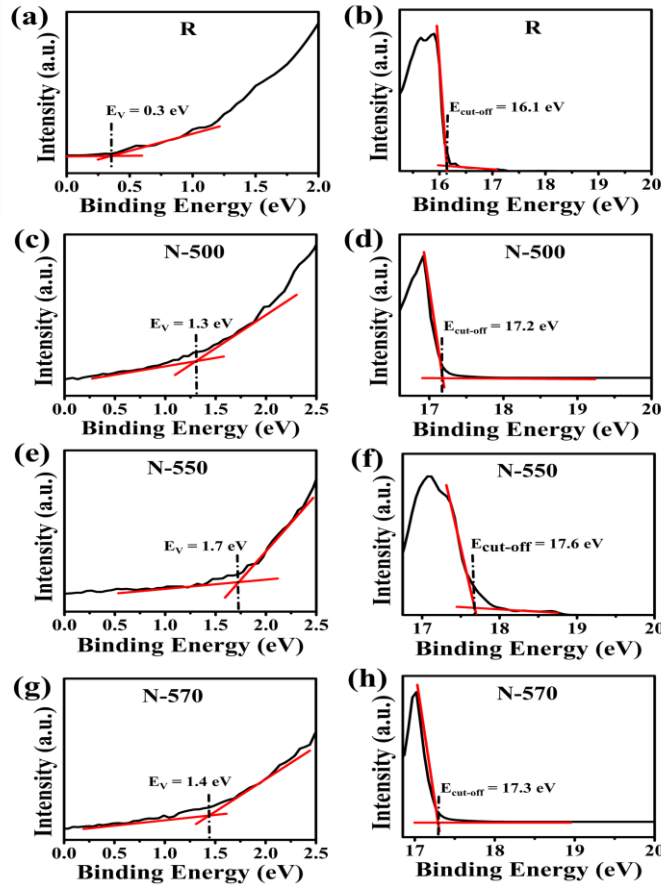


Figure 13. (a, c, e, g) Low-BE slope and (b, d, f, h) high-BE slope of the UPS spectra of R, N-500, N-550, and N-570 samples, respectively.

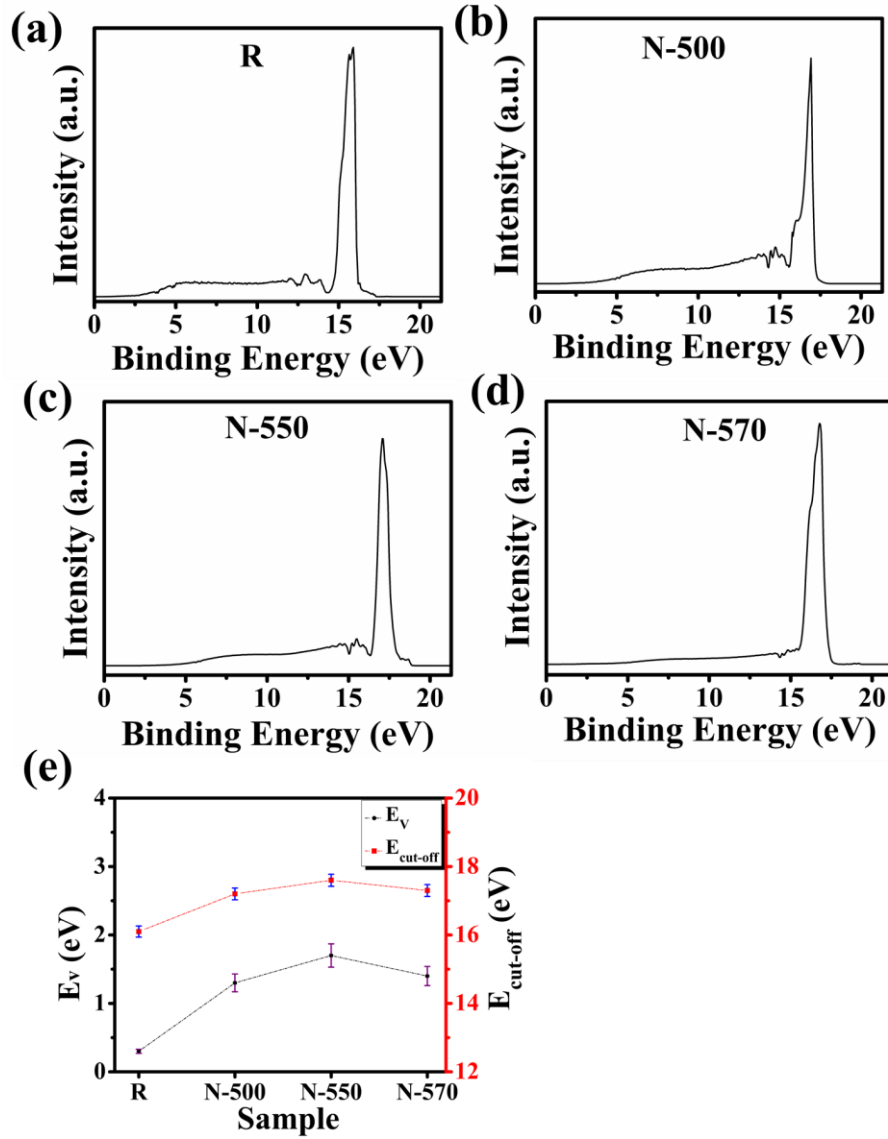


Figure 14. UPS spectra of (a) R, (b) N-500, (c) N-550, and (d) N-570 samples and (e) E_v and $E_{\text{cut-off}}$ of R, N-500, N-550, and N-570 samples using UPS.

3.3.1.3 C-AFM. Next, the carrier concentration of the N samples was also determined from the I-V characteristics using C-AFM. Figures 15(a) and 15(b) represent the topography and the corresponding current map of an array of vertically aligned R NWs, while Figures 15(c, e, and g) and 15(d, f, and h) represent those of N NWs. Figure 16(a) shows the current map histogram (number of pixels vs current) of R, N-500, N-550, and N-570 samples, plotted with

points. It is found that the background of the four samples is the same; hence, the increase in current is from the nanowires themselves. The histogram indicates both the dramatic increase in current ‘hot spots’ and the significant increase in the average value of the current at those ‘hot spots’ in N samples compared to the R sample, thereby confirming the incorporation of Te in the NWs. From the current mapping, it is evident that the N-550 sample is more conductive. This is also corroborated from the higher photoresponse of 5 nA observed in SNW of N-550 sample (Figure 16(d)) compared to 248 pA in SNW of R sample (Figure 16(b)).

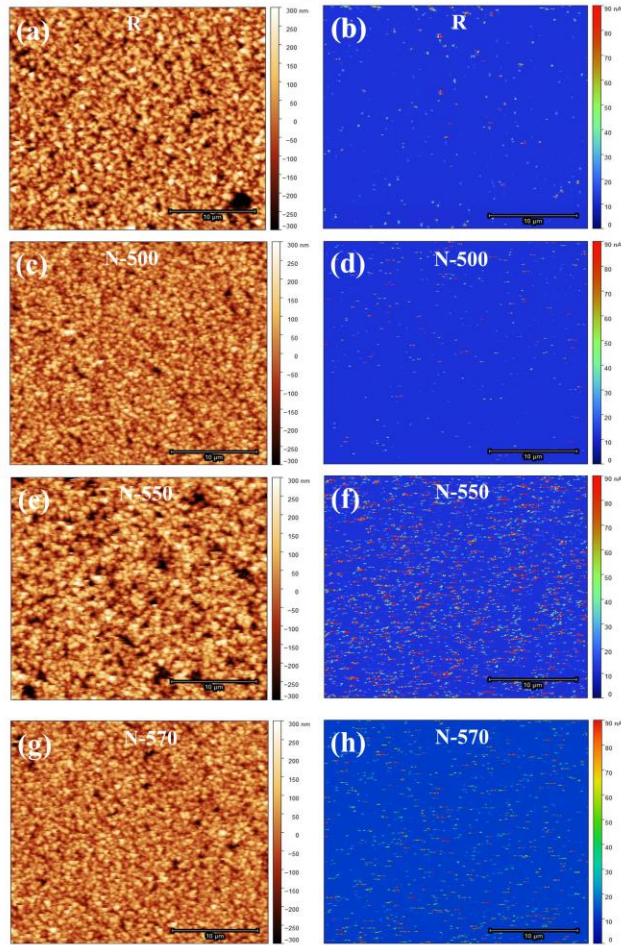


Figure 15. (a, c, e, g) Topography and (b, d, f, h) corresponding current map of R, N-500, N-550, and N-570 sample, respectively, using C-AFM.

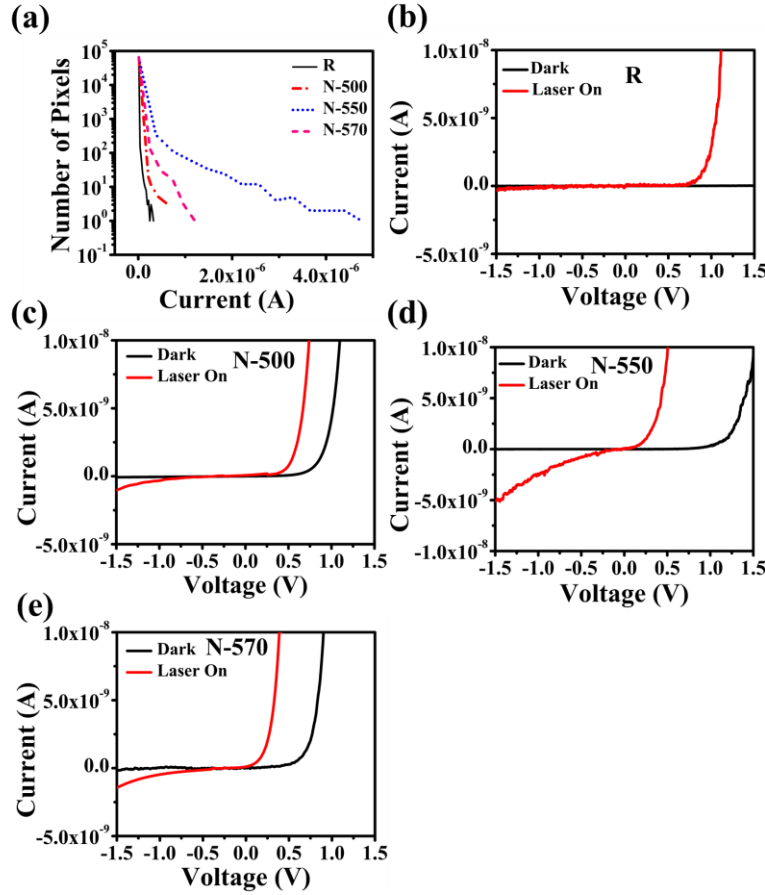


Figure 16. (a) Histogram of the current map of samples R, N-500, N-550, and N-570 samples, I-V characteristic of (b) R, (c) N-500, (d) N-550, and (e) N-570 samples using C-AFM.

Figure 17a shows that the I-V curve under forward bias follows a power-law relationship $I \propto V^m$, with $m = 4$, thereby confirming the trap-associated space charge limited current mechanism (SCLC) exhibited by the R sample (178). The finite element method (FEM) numerical solving technique was used to model nanowires with Schottky contact on one side and rectifying contact on the other side, using COMSOL Multiphysics simulation software for N sample. Figure 17(b-d) show the best fit of the simulated I-V characteristics of the nanowires to the experimental data yielding electron mobility values of $1400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $1235 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and $1200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the N-500, N-550, and N-570 samples, respectively, hole mobility of 70

$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, with an estimated carrier concentration of $7.1 \times 10^{17} \text{ cm}^{-3}$, $3.0 \times 10^{19} \text{ cm}^{-3}$, and $3.0 \times 10^{18} \text{ cm}^{-3}$, respectively, with an estimated error bar of 5%. It is to be noted that the highest carrier concentration was achieved for GaTe cell temperature of 550 °C. The decrease in carrier concentration at 570 °C is consistent with reduced conductivity observed in the current map of C-AFM and higher dark current along with the decline in photoresponse in the corresponding I-V characteristics (see Figure 16(b-e)).

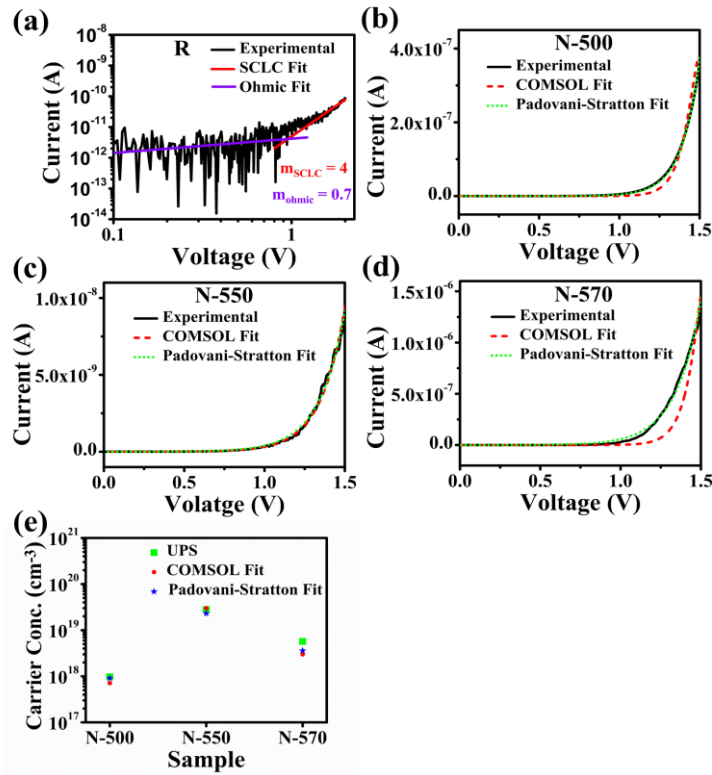


Figure 17. (a) Log-log I-V characteristic of R sample exhibiting linear and power dependence, (b-d) experimental I-V dark, simulated COMSOL fit, and Schottky diode fitting of dark I-V characteristics of (b) N-500, (c) N-550, and (d) N-570 samples, and (e) carrier concentration of N-500, N-550, and N-570 samples extracted from UPS, COMSOL fit, Padovani-Stratton fit.

Also, the carrier concentration of $\sim 9.1 \times 10^{17} \text{ cm}^{-3}$, $2.3 \times 10^{19} \text{ cm}^{-3}$, and $3.6 \times 10^{18} \text{ cm}^{-3}$, for the N-500, N-550, and N-570 samples, respectively, was determined from the best fit of the

experimental dark I-V data (Figure 17(b-d)) using the following exponential fitting equations (14) and (15) of the tunneling mechanism in the forward bias (Padovani-Stratton fit) (177),

$$I = A \exp \left\{ \frac{V}{E_{00} \coth \left(\frac{E_{00}}{KT} \right)} \right\} \quad (14)$$

$$E_{00} = \frac{qh}{4\pi} \sqrt{\frac{N_d}{m^* \epsilon}} \quad (15)$$

Where A is the reverse saturation current, the exponential term in equation (14) is known as the tunneling parameter, E_{00} is the Padovani-Stratton parameter, q is the electronic charge, h is the Planck's constant, m^* is the electron effective mass, and ϵ is the semiconductor permittivity. The Padovani-Stratton parameter (E_{00}) for N-500, N-550, and N-570 was found to be 20 meV, 100 meV, and 40 meV, respectively. The value of the carrier concentration is closer to the values extracted from UPS spectra and COMSOL (Figure 17(e)). A decrease in carrier concentration with an increase in GaTe cell temperature is consistent with the variation of the carrier concentration with Te flux reported (179, 180) in GaAs thin films, where carrier concentration peaks at $2-3 \times 10^{19} \text{ cm}^{-3}$ and reduces with further increase in dopant incorporation.

In NWs, Te dopant incorporation occurs predominantly through the Ga catalyst at the liquid-solid growth front interface via the VLS mechanism (59, 140). Devkota et al. (59) carried out a detailed morphological study on our samples reported in this work. A decrease in the aspect ratio of the NWs was observed with an increase in GaTe cell temperature from 500 °C to 570 °C. With Te being a surfactant, the accumulated Te on the surface of the NW enhances the adatom adsorption rate, thereby decreasing the adatom diffusion length, resulting in increased diameter and decreased length of the NWs (181, 182). It is to be noted that different BE shifts observed in As and Ga core level XPS spectra (disregarding Sb due to its low atomic percentage) and also,

the difference in core level and valence band BE shifts show a complex dopant distribution in Te-doped NWs. Also, Bennett et al. (183) observed surface segregation of Te in the MBE grown Te-doped GaAs thin films using a GaTe captive doping source at a high growth temperature of 600 °C by SIMS technique. At a higher GaTe cell temperature of 570 °C used in our work, a decrease in carrier concentration is observed. The Te induced defects have often been cited (179) to be the cause for the reduction in carrier concentration at higher doping incorporation in thin films. However, the high surface to volume ratio in the one-dimensional NWs, the observed decrease in NW aspect ratio, the combination of both the high growth temperature of 590 °C along with high Te flux at a higher GaTe cell temperature of 570 °C, strongly suggests Te segregation is more likely the cause for the carrier concentration decrease. The doping inhomogeneity arising from segregation cannot be ruled out. It is to be pointed out that the inhomogeneity can potentially be suppressed (140) using a higher V/III ratio for the NW growth.

3.3.1.4 SKPM. Finally, the SKPM technique has been used to obtain direct evidence of Te incorporation in N-500, N-550, and N-570 samples. For analyzing the change in contact potential difference (CPD) between the NW and Au deposited substrate, surface potential mapping using SKPM was carried out. Figure 18 shows the topography (Figures 18(a, c, e, and g)) and corresponding surface potential map (Figures 18(b, d, f, and h)) of R, N-500, N-550, and N-570 sample, respectively. Topography maps of R and N SNW samples (Figures 18(a) and 18(c, e, and g)) reveal the average surface roughness of ~ 2.2 nm and ~ 4.9 nm, respectively. An increase in surface roughness in the N samples is due to the surfactant nature of Te (181) and can be reckoned to be indicative of Te incorporation. The following equation (16) shows the CPD between the NW and Au surface ($CPD_{(NW-Au)}$) (184, 185).

$$CPD_{(NW-Au)} = W_{Au} - W_{NW} \quad (16)$$

Where W_{Au} and W_{NW} are the work functions of Au and NW samples, respectively. An increased CPD between the NW and Au surface can be observed in the N samples (Figure 19), reflecting reduced work function and hence is direct evidence of Te incorporation (186). Figure 19 reveals the highest CPD of ~ 140 mV between the N-550 sample and the Au surface. This result confirms high Te incorporation in the N-550 sample, which is consistent with the UPS measurements, where the reduction in work function is observed in the N-550 sample. However, as the measurement is carried out at room temperature, the biased voltage, probe tips, and also the presence of absorbent and surface states in the nanoscale regime have a significant effect on the surface potential measurement. Hence, quantitative analysis was not performed.

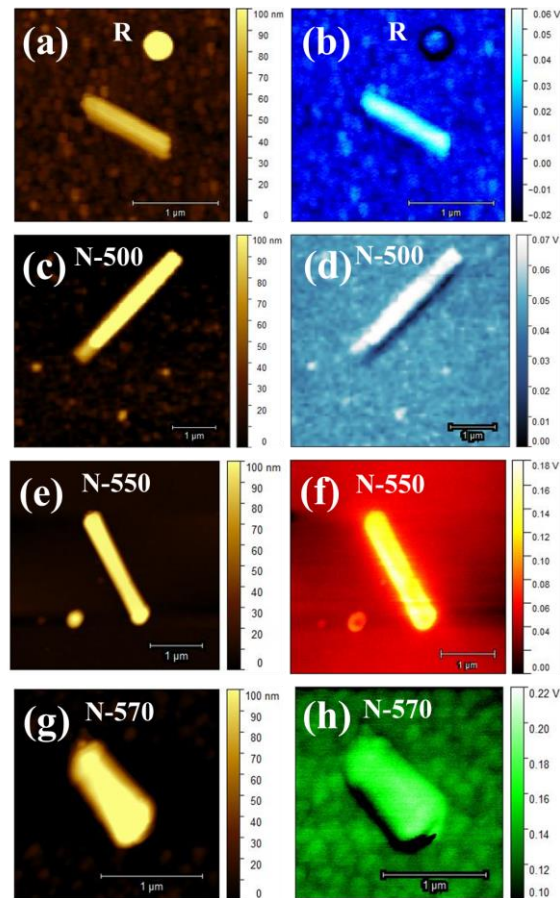


Figure 18. (a, c, e, g) Topography and (b, d, f, h) corresponding surface potential map of R, N-500, N-550, and N-570 sample, respectively, using SKPM.

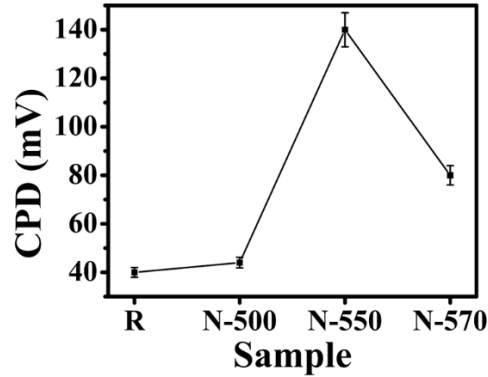


Figure 19. CPD between the NW sample and Au surface.

From the above measurements, it can be observed that the N-550 sample is representative of a heavily doped n-type sample with Te. Also, the increase in conductivity and CPD from C-AFM/SKPM measurements attest to the Te incorporation in the N samples. From XPS, incorporation of Te dopant was confirmed, while the carrier concentration of the N-550 sample obtained from UPS and C-AFM (Padovani - Stratton fit) was $2.8 \times 10^{19} \text{ cm}^{-3}$ and $2.3 \times 10^{19} \text{ cm}^{-3}$, respectively. A carrier concentration of $4 \times 10^{19} \text{ cm}^{-3}$ was extracted from an independent simulation of the curve fitting of the I-V characteristics of ensemble doped NWs using two probe I-V reported elsewhere (43). Though there is some variation in the carrier concentration, these values can be viewed as excellent agreement as these data are from the single nanowire, ensemble NWs and also probing depth for the data collection are also quite different. Thus, the remarkable agreement between the surface composition, energy bands, carrier, and dopant concentration using the surface analytical techniques with the corresponding values extracted from the electrical measurements shows that the dopant incorporation is homogeneous throughout the NW along with good uniformity amongst the NWs. In such a case, the surface analysis technique can provide reliable data that is representative of the entire NW. Thus, the combination of XPS/UPS and C-AFM/SKPM tools have been demonstrated to be a simple,

direct, promising method for evaluating the dopant concentration in a homogeneously doped NW.

3.3.2 Study of dopant incorporation in Be-doped GaAs NWs. The current mapping (Figure 20(a-c)) and current-voltage measurements of the vertical SNW using C-AFM (Figure 20(d) and 20(e)) exhibited a significant enhancement in current with high photoresponse of 300 nA at -3 V for GaAs sample doped with Be cell temperature at 950 °C. A statistical increase in the carrier concentration of Be-doped GaAs at Be cell temperature of 750 °C, 850 °C, and 950 °C is found to be $9 \times 10^{15} \text{ cm}^{-3}$, $7 \times 10^{17} \text{ cm}^{-3}$, and $5 \times 10^{18} \text{ cm}^{-3}$, respectively from COMSOL, thereby confirming an increase in doping of NWs with increasing Be cell temperature. Also, the elemental composition, work function, and carrier concentration of Be-doped GaAs NWs are further determined using XPS and UPS as shown in Figure 21(a-d). With increasing Be cell temperature for GaAs NWs, a shift in Fermi level towards the valence band provided evidence towards higher Be incorporation with Be cell temperature of 950 °C doped NWs having work function and carrier concentration of $\sim 5.6 \text{ eV}$ and $6.0 \times 10^{18} \text{ cm}^{-3}$, respectively, whereas the work function and carrier concentration was found to be $\sim 5.4 \text{ eV}$ and $4.0 \times 10^{16} \text{ cm}^{-3}$, respectively, for Be-750 sample. The values of electron density from UPS concur very well with the values of electron density determined from C-AFM (Figure 20(f)).

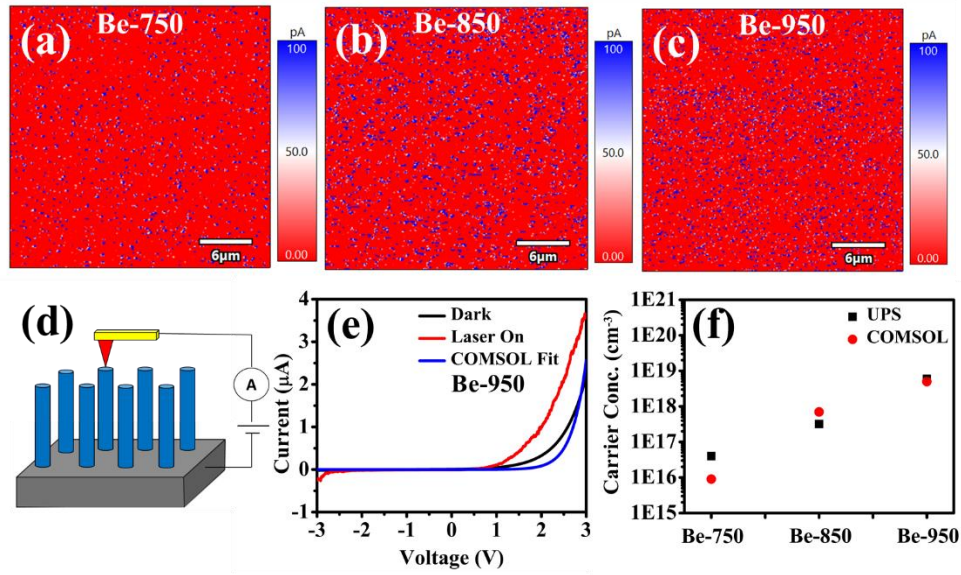


Figure 20. (a-c) Current mapping of Be-doped NWs, (d) schematic of C-AFM, (e) I-V characteristics and simulated COMSOL fit of Be-950, and (f) carrier concentration extracted UPS and COMSOL.

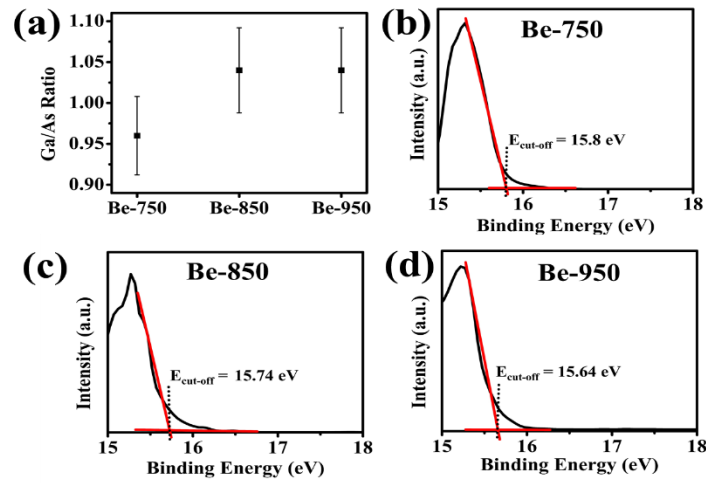


Figure 21. (a) Ga/As ratio from XPS spectra, (b-d) high-BE slope of the UPS spectra of Be-750, Be-850, and Be-950, respectively.

3.4 Conclusion

XPS/UPS and C-AFM/SKPM were successfully used to ascertain the Te and Be incorporation, electron concentration in Te-doped GaAsSb and Be-doped GaAsSb NWs samples

grown by varying GaTe and Be cell temperatures. Te-dopant incorporation in GaAsSb NWs was determined from the XPS spectroscopic shift of the binding energies of the core constituent elements towards higher energy. The lowering of the work function manifested by a positive shift in the binding energy of the UPS spectra of Te-doped GaAsSb NWs grown at the GaTe cell temperature of 550 °C revealed the sample to be a heavily n-doped sample with a carrier concentration of $2.8 \times 10^{19} \text{ cm}^{-3}$. This value is in excellent agreement with the carrier concentration of $2.3 \times 10^{19} \text{ cm}^{-3}$ obtained from dark I-V measurements on SNW by C-AFM. C-AFM showed enhanced photoresponse in doped SNW samples compared to intrinsic SNW corroborating Te incorporation and an increase in carrier concentration results from XPS/UPS. The increase in surface potential observed in doped NWs in SKPM characterization also provided strong evidence of Te incorporation. The different binding energy shifts in As and Ga core levels and between core levels and valence band suggest a complex dopant distribution in the NWs. Finally, the decrease of carrier concentration at higher GaTe cell temperature of 570 °C along with high growth temperature attributed to the Te segregation in the NWs. In the case of Be-doped GaAs NWs, a statistical increase in the carrier concentration of Be-doped GaAs with Be cell temperature is observed from COMSOL, thereby confirming an increase in doping of NWs with increasing Be cell temperature. Furthermore, a shift in Fermi level towards the valence band with increasing Be cell temperature for GaAs NWs, provided evidence towards higher Be incorporation with Be cell temperature of 950 °C doped NWs having work function and carrier concentration of $\sim 5.6 \text{ eV}$ and $6.0 \times 10^{18} \text{ cm}^{-3}$, respectively.

This work is the first report on the Te and Be dopant incorporation using a combination of non-destructive techniques, namely XPS, UPS, C-AFM, and SKPM, and published in Scientific Reports 2021 and OSA Technical Digest, 2021. (Priyanka

Ramaswamy et al., A study of dopant incorporation in Te-doped GaAsSb nanowires using a combination of XPS/UPS and C-AFM/SKPM. Scientific Reports 11, 8329 (2021) and Priyanka Ramaswamy, et al., Be-doping assessment in Self-Catalyzed MBE Grown GaAs Nanowires, Conference on Lasers and Electro-Optics, OSA Technical Digest, SW2F.7 (2021)).

CHAPTER 4

Study of Al₂O₃ Dielectric on Ga-Assisted MBE Grown GaAs_{1-x}Sb_x NWs

4.1 Introduction

To realize optoelectronic NW-based devices, passivation of NWs is important, as the surface states arising due to large surface-to-volume ratio and formation of defect states near surfaces can hamper the efficiency of the optoelectronic devices (187). The high density of surface states in NWs emanates from un-passivated dangling bonds of surface atoms. In general, these surface states can act as surface charge traps, non-radiative recombination centers, and also cause Fermi level pinning by forming an additional density of electronic states within the bandgap (188-190). A surface pinned Fermi level can form an undesirable depletion layer that hinders the movement of free carriers, thereby affecting the transport of carriers and making it entirely non-conducting (191). Fermi level pinning is reported to be common among III-V semiconductor materials, as they do not have stable oxide surfaces free from ionized defects, and it is also dependent on the diameter of the NWs (192-195). In order to reduce surface states, various large bandgap surface passivation layers that are chemically inactive to prevent further formation of surface states, namely sulfur (196), hydrazine-sulfide (197), AlGaAs (178, 198), InGaP (199), GaN (200, 201), InP (202), AlN (203), (Ga₂O₃)_{1-x}(Gd₂O₃)_x (204), phosphorous (205, 206), were investigated. It is observed that the growth of in-situ passivation shells such as AlGaAs, InGaP, GaN, InP, AlN are quite challenging due to the high aspect ratio, shadowing effect of NWs, and the high process temperature over 400 °C may also affect many applications (207, 208).

In the past decade, advances have been made on this front by utilizing atomic layer deposition (ALD) of high-k dielectrics, namely, Al₂O₃, AlN, and HfO₂, as potential candidates

for passivation of III-V semiconductor materials due to the self-cleaning effect (208-211). In addition, a certain thermal oxide stoichiometry has been reported to improve the interface quality (212, 213). ALD enables the deposition of uniform and continuous films of a wide range of materials conformally on topographically complex high aspect ratio structures with excellent control over the thickness of the layer (191). Since in-situ deposition requires high process temperature, which degrades the surface quality of III-V NWs, ALD is found to be an excellent low cost-scalable technique in which passivation shells can be deposited at low temperatures and vacuum. Bosund et al. (208) demonstrated capacitive plasma ALD grown AlN passivation layers at 200 °C using Trimethylaluminum (TMA) and ammonia (NH₃) enhanced by nitrogen plasma as precursors.

Among these high-k dielectrics, Al₂O₃ is the most desirable because of its large bandgap, high thermal stability (> 1,000°C), easily wet-etched, and robustness against interfacial reactions and non-hygroscopic. It is to be noted that thermal ALD deposited Al₂O₃ is exploited as a passivation shell for GaAs systems as the TMA precursor used for Al₂O₃ deposition is well known to clean up the native oxide of GaAs by reducing and replacing the native oxide with Al₂O₃ within a few cycles of deposition (214). Also, a decrease in interfacial density ($D_{it} < 10^{12}$ eV⁻¹ cm⁻²) with the deposition of ALD grown Al₂O₃ on GaAs was reported by Ye et al. (215) and Xuan et al. (216). Frank et al. (217) studied the interfacial layer thickness and composition in ALD grown HfO₂ /GaAs and Al₂O₃/GaAs heterostructures. It was observed that the native oxide of GaAs remained intact underneath the HfO₂ deposition but decreased after Al₂O₃ growth. It was also reported that HF acid etching treatment before ALD deposition had minimized the interlayer thickness. In addition, thermal treatments at 600 °C are critical for the decomposition of arsenic oxides and the removal of interfacial oxygen.

It was observed that surface treatment prior to the ALD high-k dielectric deposition is necessary to improve the quality of the interfaces between the passivation layer and III-V semiconductors, as native oxides and interfacial trap defects are detrimental to the optical and electrical properties of the III-V semiconductor devices (218). Several other methods like sulfur passivation (H_2S , $(\text{NH}_4)_2\text{S}$, $\text{CH}_3[\text{CH}_2]_{17}\text{SH}$, $(\text{C}_n\text{H}_{2n+1}\text{-SH where } n = 3, 6, 12, 18, 20)$) (219-227), cleaning (acids, NH_4OH) (209, 217, 219), and thermal treatment (217), have been investigated on surface treatments to have precise control over interfacial oxides between the dielectric and III-V materials, thereby reducing the interface traps density. Various sulfur passivation schemes have been frequently used to enhance the III-V semiconductor device performance, GaAs in particular, as they reduce the interface trap density and defect density, suppress the oxidation states related to the diffusion of substrate atoms, and provide better stability (221, 228, 229). Jeng et al. (230) reported an amelioration in electrical properties of GaAs using a combination of sulfur and fluorine passivants ($\text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S}_x$ and HF solution). Chen et al. (221) demonstrated a significant reduction in the dark current of GaAs single NW photodetector with sulfur passivation. However, Dhaka et al. (191) reported the absence of PL emission in Al_2O_3 passivated GaAs NWs due to Fermi level pinning of thin NWs. In contrast, Ren et al. (231) observed significant room temperature PL emission and suppression of surface recombination velocity (SRV) of $\sim 10^3$ cm/s in InAsSb NWs using the ex-situ $(\text{NH}_4)_2\text{S}/\text{Al}_2\text{O}_3$ passivation technique.

The interface characteristics of various ALD deposited high-k dielectrics on GaAs (227, 232), InAs (210, 233, 234), InP (235), InGaAs (219, 236, 237) have been studied using X-ray photoelectron spectroscopy (XPS). However, there is a limited passivation study on ternary GaAsSb semiconductors; hence there is a need to exploit various passivation techniques to yield

stable, uniform, and improved surface properties. In this work, a systematic study on the effect of ex-situ passivation of thermal ALD deposited Al_2O_3 dielectric on MBE-grown GaAsSb NWs is carried out. With the utilization of surface and optical techniques, XPS and Raman spectroscopy, the stoichiometry of Al_2O_3 , characteristic of the interface between Al_2O_3 and GaAsSb NW are investigated. XPS analysis indicated that the precleaning with sulfur treatment before the deposition of the Al_2O_3 shell layer effectively removed III-V native oxides formed on the NW surface, thereby eliminating their role in optical degradation of the Al_2O_3 passivated NW samples. From Raman analysis, increased background scattering, spectral broadening of LO and TO Raman modes, and enhanced redshift compared to the as-grown NWs suggest increased density of point defects due to complex NW/dielectric interface reconstruction. These act as non-radiative recombination centers and can be the main contributors to the optical degradation of ALD deposited Al_2O_3 passivation layer on GaAsSb NWs.

In addition, the effect of in-situ and ex-situ annealing on ALD deposited Al_2O_3 passivated NW is studied using conductive-atomic force microscopy (C-AFM), as the thermal treatment plays an effective role in the annihilation of the defect traps, thereby reducing the trap density and its distribution, which leads to enhanced electrical property (178). There have been several investigations on the impact of annealing on thin films, NWs, quantum dots, and so on. Many researchers have reported that annealing has boosted the optical and electrical performance of thin films and NWs, attributing to the suppression of the surface-related interstitial defect states and homogeneity across the NW surface, leading to an improved surface order. For example, Sharma et al. (58) demonstrated suppression of band tail states and non-radiative channels by in-situ annealing, which enhanced GaAsSb/AlGaAs Schottky barrier-based photodetector device

performance. In addition, Parakh et al. (178) showed an improved conductivity in in-situ annealed GaAsSb NWs.

4.2 Results and Discussion

We discuss three MBE grown samples, as-grown GaAsSb NWs, as-grown with ex-situ Al_2O_3 passivation layer, and as-grown with sulfur treatment followed by ex-situ Al_2O_3 passivation layer, which will be referred to as R, AO, and SAO samples, respectively (238). It is to be noted that the process of Al_2O_3 ALD on GaAsSb NWs and photoluminescence spectra (PL) are explained in detail in Mehul Parakh's dissertation (239).

Also, two other MBE-grown GaAsSb NW samples, as-grown with ex-situ Al_2O_3 passivation layer followed by in-situ annealing for 10 mins in N_2 ambient under vacuum of 1 Torr, have been examined. The second NW sample was ex-situ annealed at 250°C for 10 mins post Al_2O_3 deposition in an external annealing furnace in N_2 ambient under vacuum, which will be referred to as in-situ and ex-situ NW samples, respectively.

4.2.1 Effect of ex-situ passivation of thermal ALD deposited Al_2O_3 on GaAsSb NWs.

4.2.1.1 XPS. XPS spectra of binding energy between 0 and 150 eV of self-catalyzed GaAsSb NW samples R, AO, and SAO are shown in Figure 22. The peaks of O 2s, Al 2p, and Al 2s at 23.3 eV, 74.6 eV, and 118.9 eV, respectively, present only in AO and SAO NW samples, attest to the formation of the Al_2O_3 passivation layer on the surface (240).

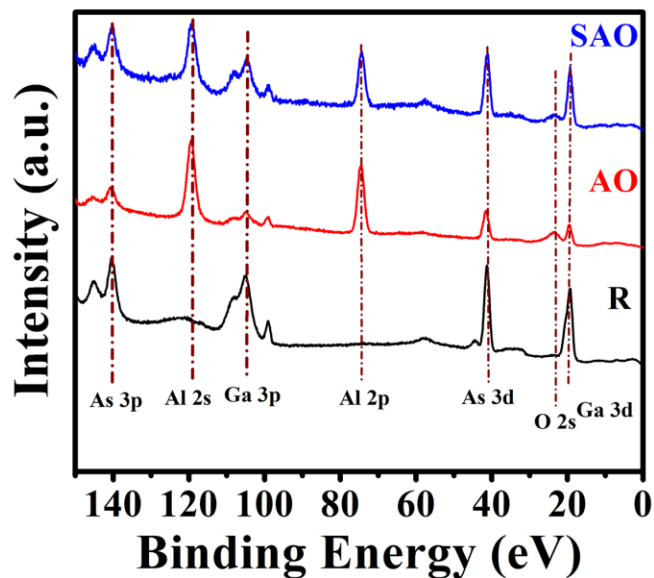


Figure 22. XPS spectra of R, AO, and SAO samples.

The core-level spectra of Ga 3d and As 3d of as-grown R sample are depicted in Figure 23, whereas Figure 24 represents Al 2s, O 1s, Ga 3d, and As 3d spectra of AO and SAO samples. The peaks observed at 21 eV and 44.5 eV (Figures 23(a) and 23(b)) are assigned to Ga and As complex native oxide-related peaks, respectively (241). The atomic ratio of O/Al is 1.7 and 1.3 for AO (Figures 24(a) and 24(b)) and SAO (Figures 24(c) and 24(d)) samples, respectively.

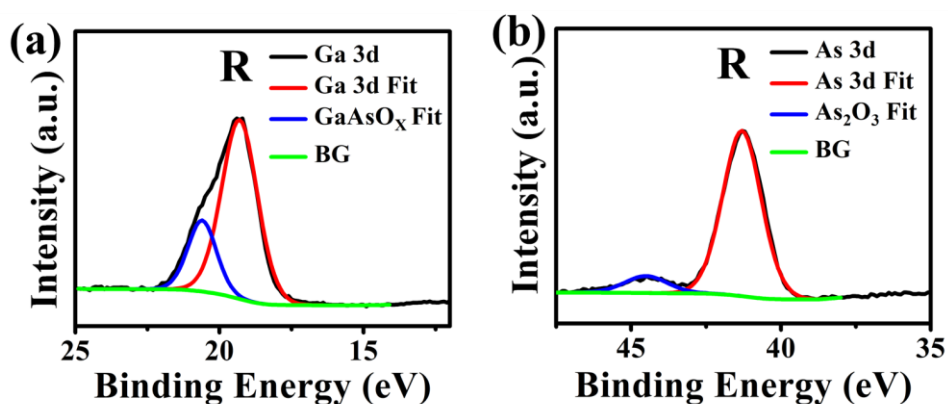


Figure 23. XPS spectra of Ga 3d and As 3d of R sample.

The appearance of Ga-O (Figure 24(e)) only in the AO sample corroborates the observed increase in O: Al stoichiometry in this sample. It is speculated that the interdiffusion of oxygen during ALD deposition from native oxides to the Al_2O_3 passivation layer has contributed to the higher O/Al ratio in the AO sample. The absence of satellite peaks (Figure 24(a)-24(d)) rules out the formation of any other sub-oxide species of Al during the ALD deposition of the Al_2O_3 passivation layer on NWs (240). A lack of As-O peak (Figure 24(f) and 24(h)) on Al_2O_3 deposited NWs in both non-sulfur and sulfur treated samples can be viewed as evidence of the self-cleaning process of TMA (219). Therefore, sulfur treatment before the deposition of 3 nm of the Al_2O_3 passivation layer effectively removes the native oxides of Ga in NW samples (Figure 24(g)). Further, Sb 3d signal was not registered in any of the GaAsSb NWs due to the overlapping binding energies of O 1s and Sb 3d peaks, which we attribute to a strong O 1s signal (121). The other contributing factors could also arise from radial variation in Sb composition due to the As-Sb exchange mechanism at the NW surface (242), manifesting in Sb composition reduction at the surface as the XPS probing is confined only to shallow depths.

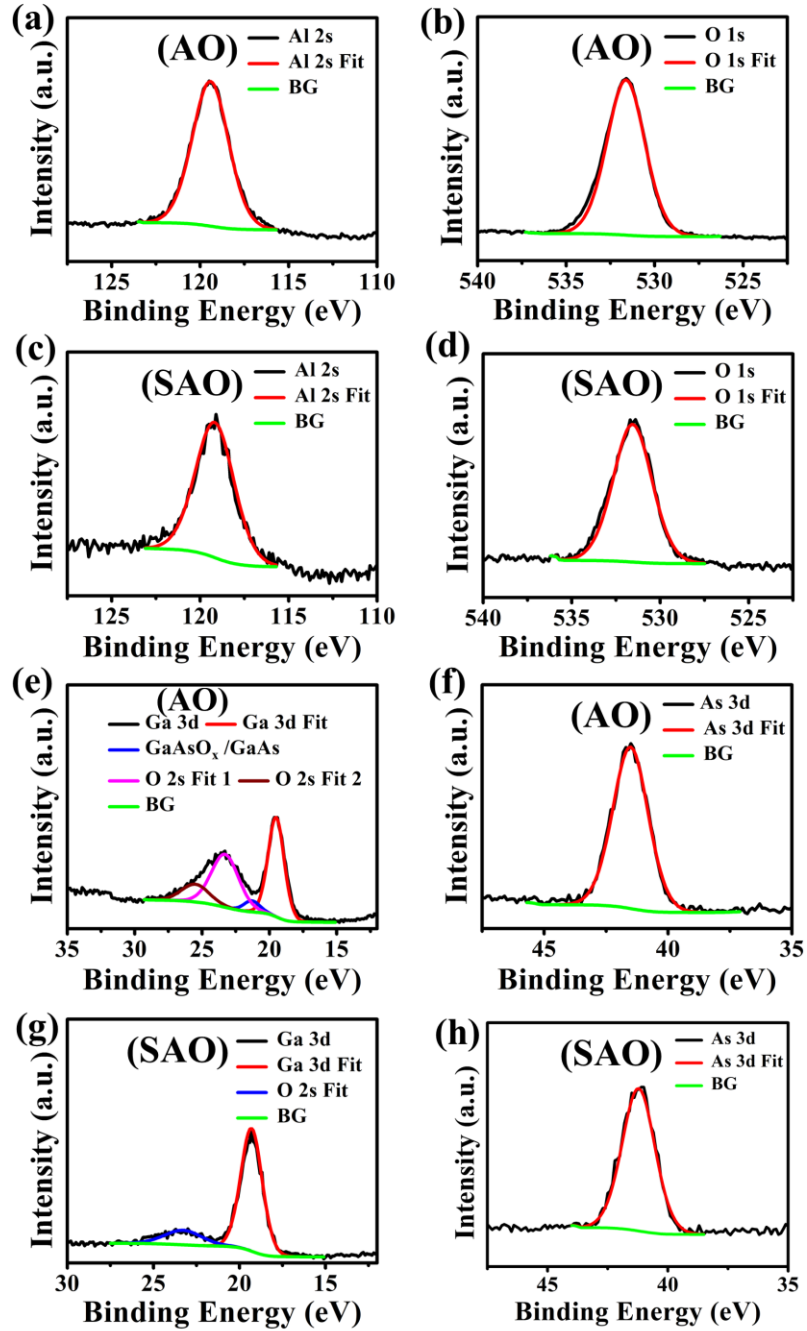


Figure 24. XPS spectra for (a,c) Al 2s and (b,d) O 1s of (1st row) AO and (2nd row) SAO NW samples, respectively. XPS spectra for (e,g) Ga 3d and (f,h) As 3d of (3rd row) AO and (4th row) SAO NW samples, respectively.

4.2.1.2 Raman characterization. Raman spectra were carried out as the shape of the Raman peak, and spectral shift direction can reveal further insight into the nature of the defects. It has been reported that point defects induce spectral shift but do not give rise to asymmetry and vice versa for planar defects (60, 108, 243, 244). Figure 25 shows the RT Raman spectra comparison of R, AO, and SAO samples. GaAs TO and LO vibrational mode peaks at 265 cm^{-1} and 285 cm^{-1} , respectively, were observed in the R sample (60). The AO sample demonstrates a significant redshift of 3.5 cm^{-1} and a broad LO and TO mode spectra relative to the R sample, attributed to the induced strain on the NW surface during oxide deposition and phonon localization at the defects.

Further, the broad asymmetry is consistent with our conjecture of defect enhancement arising from complex NW/dielectric interface reconstruction, as explained in detail in the dissertation of Mehul Parakh. Similar features are observed in the SAO sample with reduced peak broadness, suppressed background scattering intensity, and a comparatively smaller redshift of 2.5 cm^{-1} . These are possibly related to the more effective removal of III-V native oxides formed on the NW surface by sulfur treatment in SAO samples compared to AO, as observed from XPS measurements, aiding in reducing defects (58). In addition, nearly symmetric LO and TO peaks and smaller redshifts in the SAO sample indicate the nature of defects being predominantly point defects. Hence, Raman characterization further strengthens the conjecture of defect creation at NW/dielectric interface on Al_2O_3 deposition and ascertains the positive effect of pre-sulfur treatment on NWs before oxide deposition.

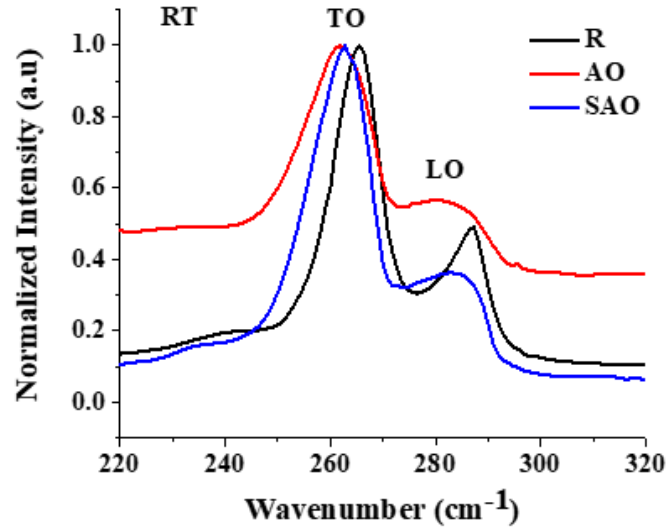


Figure 25. Normalized RT Raman spectra comparison of R, AO, and SAO samples.

Mehul Parakh (239) showed a significant decrease in PL intensity of ~ 10 -fold in thermal ALD deposited Al_2O_3 passivation on GaAsSb NWs (irrespective of prior surface treatment with sulfur) compared to as-grown NW samples. This result is in good agreement with Raman spectra, which suggests optical degradation due to increased density of point defects arising from the NW/dielectric interface reconstruction contributing to non-radiative recombination centers.

4.2.2 Effect of in-situ and ex-situ annealing of thermal ALD deposited Al_2O_3 on GaAsSb NWs.

4.2.2.1 Conductive-atomic force microscopy (C-AFM). Current mapping using C-AFM was performed on in-situ and ex-situ NW samples, as shown in Figures 26(a) and 26(b). An increased density of conducting NWs was observed for in-situ NW compared to ex-situ annealed NW samples. Figure 26(c) depicts a histogram plot of current vs. number of pixels between in-situ and ex-situ NW samples, plotted with points. The graph shows a significant increase in the current ‘hot spots’ and the average value of current contributed by those ‘hot spots’ in the in-situ

NW sample, confirming a decrease in trap density in the in-situ annealed NWs, leading to enhanced photogenerated current.

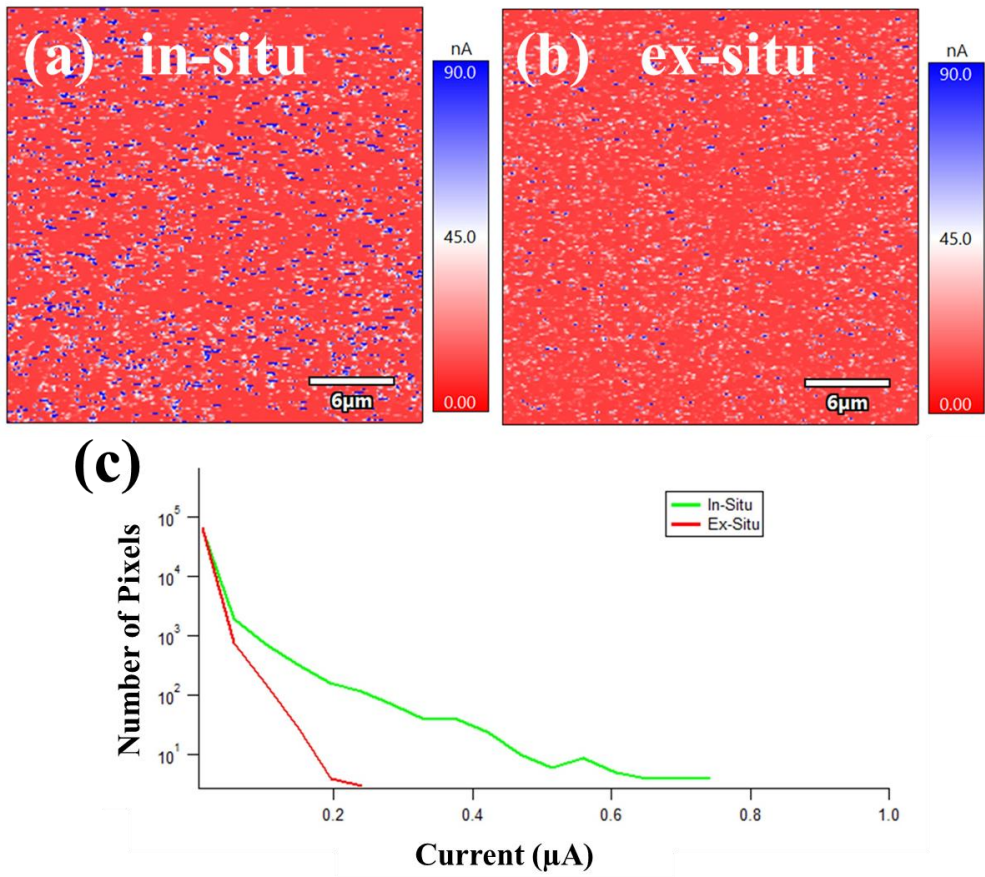


Figure 26. Current map of (a) in-situ and (b) ex-situ NW samples, (c) histogram of the corresponding current map of in-situ and ex-situ NW samples using C-AFM.

4.3 Conclusion

The effect of sulfur treatment and thermal ALD ex-situ deposition of Al₂O₃ passivation on Ga-catalyzed GaAsSb NWs using XPS and Raman were successfully studied. The XPS spectral analysis indicated that precleaning with sulfur treatment before Al₂O₃ ALD deposition effectively removed III-V native oxides formed on the NW surface, thus ruling out the effect of native oxides on optical degradation. Further, the Raman characterization observed significant redshifts, peak broadening, and asymmetry for Al₂O₃ passivated NWs when compared to as-

grown NWs, suggesting the presence of point defects on Al_2O_3 ALD deposition. The dramatic increase in current conduction in Al_2O_3 passivated in-situ annealed GaAsSb NW sample provided strong evidence of annihilation of surface trap states due to thermal treatment. Therefore, ALD deposited Al_2O_3 layer is not an effective passivation layer for GaAsSb NWs.

CHAPTER 5

C-S n-i-p GaAsSb NWs for the Application of NIRPD up to 1.5 μm .

5.1 Introduction

Various nanostructures, namely, axial and C-S NWs (28, 245), QW (246), QD (247), nanopillars (248), nanorods (249, 250), and nanotubes (251), have evolved in the pursuit of high-performance NIRPD. In recent years, very few studies have been demonstrated on the III-V core-shell IR photodetectors, and most of the study focuses on the axial p-n junction PD due to ease of growth and contact fabrication. Pal et al. (252) demonstrated C-S p-Si/n-InP with a peak responsivity and detectivity of 2.74 A/W and 5.52×10^{11} Jones, respectively, at 920 nm at -2V. Christesen et al. (100) evaluated the axial and radial p-i-n NW structures using finite element simulations and showed that the latter is insensitive to surface recombination. Surface recombination velocities (SRVs) to be as low as 10^3 - 10^4 cm/s is required for the axial device to achieve internal quantum efficiency of 95%, as the depletion region is exposed to the surface. Whereas in the case of radial device, a high SRV of 10^5 cm/s is found to generate a similar level of performance as axial. C-S p-n GaAs_{1-x}Sb_x/InAs NW photodetector with a responsivity of 0.12 A/W at $V_{\text{ds}} = -0.3$ V at 1310 nm and a high response up to 1800 nm with an on/off ratio of 2.5 has been reported by Wang et al. (106). It is to be noted that to the best of our knowledge, no study on III-V core-shell n-i-p GaAsSb NW IRPD has been reported.

In this work, we demonstrate the fabrication and characterization of MBE-grown conventional and a new design structure, hybrid axial C-S GaAsSb n-i-p NW devices for the application of near-IR photodetectors at wavelengths approaching 1.1 μm and 1.5 μm . The reason for the choice of n-i-p on n-substrate instead of p-i-n on p-substrate is the surfactant nature of Te and Be dopants. As i-GaAsSb exhibits p-type nature and in the case of a p-i-n

structure with p- as core, the Be dopants being a surfactant, will tend to diffuse into the i-segment, thereby converting the i-segment from p⁻ to p-type, which leads to the formation of a p⁺-p-n junction instead of a p-i-n junction (109, 111, 253). In addition, several reports on Be incorporation show that the preferential site for the incorporation of Be is through the NW sidewall. In contrast, to Be incorporation, Dubrovskii et al. (133) reported that Te incorporation occurs predominantly through the droplet via the VLS mechanism. It is to be noted that the diffusion of Te into the i-region favors the n-i-p junction formation, as the Te dopants compensate for the p-type nature of GaAsSb. Therefore, an n-i-p junction is preferred over a p-i-n junction for the abrupt formation of high-quality junctions. The effect of Te and Be dopant incorporation, and thickness variation are studied using various characterization techniques, including simulation using COMSOL for electric field distribution, I-V characterization of SNW using C-AFM, and ensemble NW using two-probe Keithley system, and LFN and C-V measurements. The significant findings of these studies are (1) Te compensation of i-region enhances the performance of IRPD, (2) increase in p-doped shell thickness, Be and GaTe cell temperature improve the series resistance, rectification ratio, hence, the quality of the junction and it promotes the formation of ohmic contact, (3) RT C-S n-i-p GaAsSb with a high responsivity of 190 A/W and detectivity of 1.1×10^{14} Jones at -1 V under 1.1 μm wavelength illumination was successfully demonstrated using conventional design approach, which led to the novel design of hybrid axial C-S n-i-p structure, and, (4) the new design exhibited high room temperature responsivity of 18 A/W and detectivity in the range of 10^{13} Jones up to 1.5 μm wavelength. The successful demonstration of novel design hybrid axial C-S n-i-p GaAsSb NWs has paved the way to realize high-performance RT-NIRPD beyond 1.5 μm . Furthermore, the

novel design structure can expand to other designs that have not been explored for the application of next-generation optoelectronic devices.

5.2 Results and Discussion

The orientation, diameter, and density of NWs should be optimized to unleash the full potential of core-shell (C-S) GaAsSb NWs as IRPD. The tuning of diameter, segment lengths, density, parasitic growth, dopant concentration, and the structure design of NWs allows us to optimize the light absorption and efficiently generate photocarriers in the intrinsic region of the n-i-p junction C-S NWs. In addition, the vertical orientation of the NWs is one of the most important criteria to have a uniform junction and avoid short circuits/leakages.

5.2.1 Effect of oxidation time. The oxidation time, the growth temperature of the Si substrate, Ga opening time, and V/III ratio are the parameters that can be tuned to reduce the 2-D growth and enhance the growth of vertical NWs. Typical problem researchers face when growing III-V NWs on Si is the non-vertical growth of NWs in four possible non-polar low energy directions on Si. In this section, we determined the critical oxidation time for vertical uniform growth of NWs. The unique property of vertical NWs is that they can act as a light concentrator; that is, the absorption cross-section of the NW enormously exceeds their geometrical cross-section. This property makes them superior to their thin-film counterparts, as the material usage and the cost are also reduced. Also, if a part of the mesa structure PD is short-circuited, then the whole PD stops working. However, short-circuited NWs will act as a fuse and break, making the NW PD still operatable. It is to be noted that the property mentioned above is applicable only for the NWs grown perpendicular to the Si substrate. Uccelli et al. (254) investigated multiple growth directions of GaAs on Si substrates and derived the geometrical rules leading to multiple-order 3D twinning. Krogstrup et al. (255)

and Russo-Averchi et al. (256) demonstrated the effect of the V/III ratio on NW orientations. It is to be noted that no study has been done on the growth of GaAsSb NWs on n-type Si substrate. Matteini et al. (257) reported a systematic study of GaAs NW growth on Si substrate for several types of SiO₂. They showed that the roughness related to the critical thickness of the oxide layer is an essential parameter for the formation of pinholes, which is necessary for the successful growth of NWs.

As the first step, the oxidation time has been varied from 50 mins to 220 mins to improve the quality of the nanowire device. Figure 27 shows the effect of variation in oxidation time on NW growth. Sb being a surfactant enhances surface diffusion and promotes a flat surface, which favors 2-D growth as the supersaturation decreases; hence Figure 27(a) shows more parasitic growth due to the hydrophilic nature of droplet and opening of Ga for a longer time of 11 sec. Following are the reasons for the formation of tilted NWs and low yield (Figure 27(d)). i) Thick oxide layers of silicon dioxide have been shown to increase the contact angle of the Ga droplet much greater than 90 degrees which results in tilted NWs, and ii) larger contact angles along with continued pre-deposition of Ga may lead to over-filling of the oxide holes, which will eventually start crawling onto the oxide surface, thereby reducing the nucleation, thus the yield of the crystallite's formation (258). Figures 27(b) and 27(c) show that the oxidation duration of 90 (sample# I-90) and 120 mins (sample# I-120) promote more vertical, uniform, dense NWs with less 2-D growth than other samples. Low-frequency noise (LFN) measurements were carried out to determine the quality of the I-25 and I-120 NWs (Figure 28). It was found that a higher oxidation time of 120 mins had better noise in the order of 10^{-7} V²/Hz at -1V, while for the lower oxidation time of 90 mins, 10^{-5} V²/Hz at -1V. In addition, I-120 depicted a lower cut-off frequency of 5 Hz than the 10 Hz of I-25, which indicated low noise and better device

performance; hence these results have outpaced the others. This comparison of different oxidation times has led us to select the oxidation time of 120 mins to be a desirable choice for the vertical growth of GaAsSb C-S NWs.

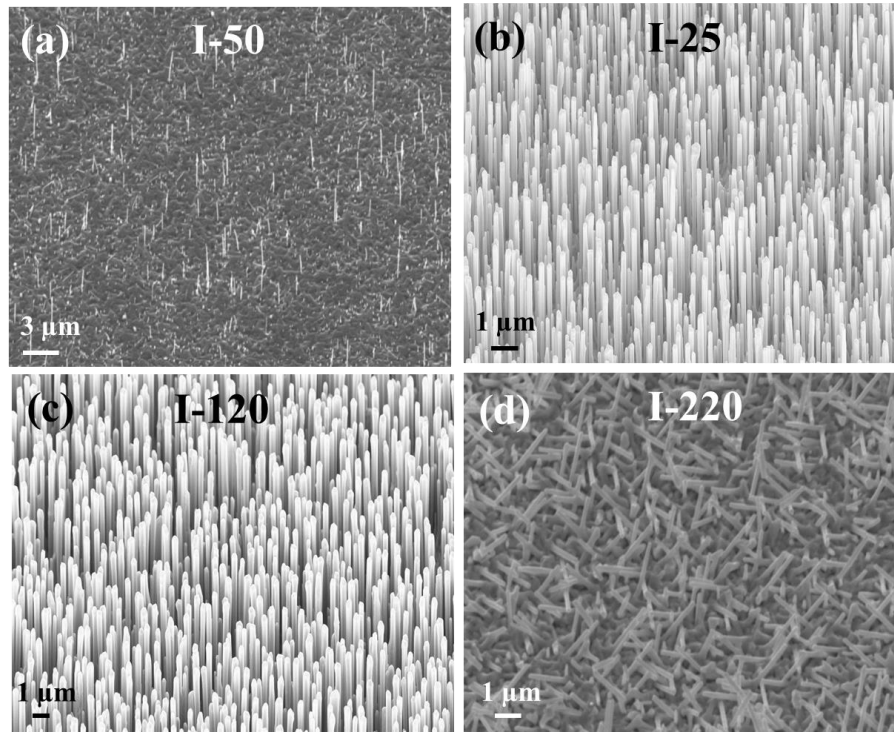


Figure 27. SEM images of (a-d) I-50, I-25, I-120, and I-220, respectively.

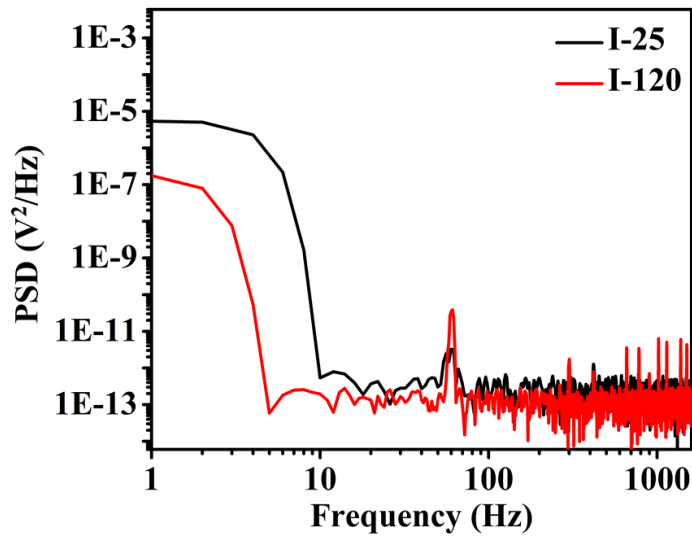


Figure 28. LFN measurements of I-25 and I-120 samples.

5.2.2 Effect of substrate temperature. The formation of vertical NWs in the self-assisted growth mode with desired density and diameter of NW remains a challenge. In the Ga-assisted NW nucleation, the nanometer-sized pinhole formation in the SiO₂ layer, droplet nucleation, and NW growth are considered competing processes. Therefore, making it challenging to control the diameter and density of NWs. Selective area growth by patterning using the e-beam lithography (EBL) technique is possible. However, EBL is found to be time-consuming, expensive, and unable to fabricate large-area patterning, and also, the nanoimprint lithography (NIL) is found to be complex (259). Hence, the substrate temperature plays a vital role in tuning the density of the nanowires without involving any sophisticated instruments. From Figure 29(a), it is understood that large Ga droplets are formed in the I-620 sample at a higher substrate temperature of 620 °C due to the increase in Ga adatom diffusion length and high mobility, tends to get incorporated in the already existing cluster that is nucleating (260). The existence of many Ga droplets shows that the high substrate temperature is not favorable for the growth of GaAsSb NW as the growth temperature had either approached or exceeded the decomposition temperature of GaSb (261). Hence, the substrate temperature is reduced to 615 °C so that the diffusion length of impinging Ga adatom is reduced; consequently, more Ga droplets are nucleated, increasing the density of NWs in the I-615 sample (Figure 29(b)). In addition, GaAs stem for 8 mins is grown prior to the GaAsSb core growth to increase the nucleation of Ga droplets, the density of NWs, and reduce the lattice mismatch with the Si (258).

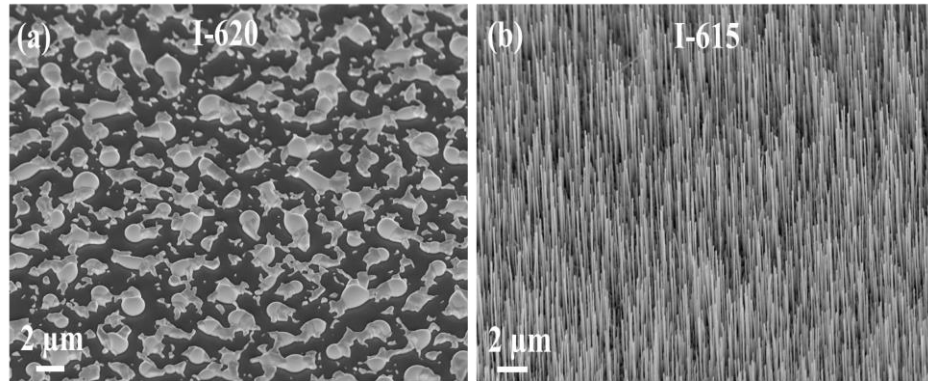


Figure 29. SEM images of (a) I-620 and (b) I-615 samples.

5.2.3 Effect of V/III ratio. Different V/III ratios of shells were investigated to improve the incorporation of Be dopants in the outer p-GaAsSb shell. Figure 30(a) depicts the SEM image of n-i-p GaAsSb with a V/III shell ratio of 10. The inset of Figure 30(a) shows a beak-like NW tip attributed to Be's effect on Ga. The average length of the I-10 sample is $2.7\ \mu\text{m}$, and the beak length is around $800\ \text{nm}$, which shows the formation of a beak-like NW tip can be due to the surface energy. The stacking faults at the NW tip tend to form higher surface energy facets than the facets at the surface. Therefore, these facets with higher surface energy are energetically favorable for nucleation. In the case of shell growth with high Be dopant concentration, the surfactant nature of the Be enhances the Ga adatom's mobility. Thus, the Ga adatoms with improved mobility can move to the stacking faults and promote nucleation and growth of lumps/beak-like NW tips (262). In addition, the Ga-rich surface provided by a low V/III ratio supports the accumulation of Be, hence the change of surface energy. Be dopants are said to be substituting Ga sites due to the thermodynamic equilibrium maintained by the Ga droplet. When NWs are saturated, excess Be atoms, being a surfactant, accumulate inside the Ga droplets leading to the change in dynamics of the droplet (263). Hence, the reasons mentioned earlier are the possibility of forming a beak-like NW tip. Hence, to reduce the accumulation of Be on the p-

shell, the V/III ratio is increased to 11 in the I-25 NW sample, thereby making it an As-rich condition. Figure 30(b) shows uniform n-i-p GaAsSb NWs and the absence of a peak with a proper NW terminated tip for this sample.

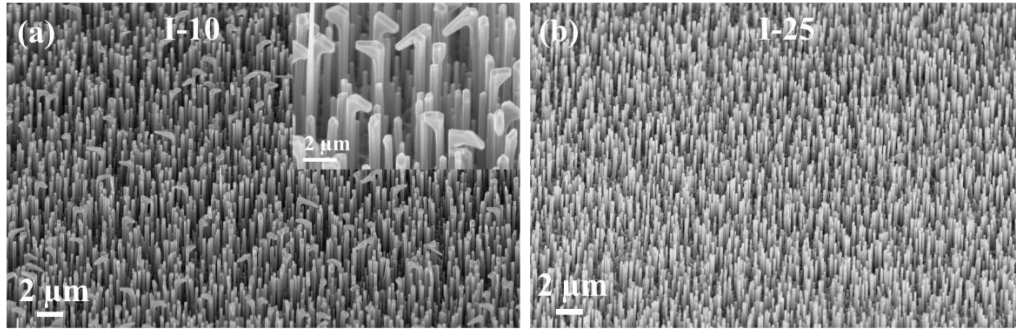


Figure 30. SEM images of (a) I-10 and (b) I-25 samples.

5.2.4 Effect of Te compensated intrinsic shell. As intrinsic GaAsSb is slightly p-type, therefore, to have a complete depletion region, the intrinsic GaAsSb is compensated by pulsing Te, an n-type dopant, during the growth. A nominal concentration of undoped GaAsSb is in the range of 10^{16} cm^{-3} , shows p-type behavior, and exhibits non-excitonic residual acceptor impurity such as Ga vacancy-related defects and Ga antisite defects ($V_{\text{Ga}}\text{GaSb}$) (111). Hence, in order to compensate for the p-type nature of the intrinsic region, Te- pulsing was introduced during the growth of the i-GaAsSb shell. Figure 31(a) shows the I-V characteristics of uncompensated ensemble I-R and Te-compensated I-120 samples. From table 1, the I-120 sample showed an improved device performance whose responsivity and detectivity were found to be 10.6 A/W and $2.7 \times 10^{12} \text{ Jones}$, while for the I-R sample, responsivity and detectivity were calculated to be $3.7 \times 10^{-4} \text{ A/W}$ and $6.1 \times 10^7 \text{ Jones}$, respectively. As a result, the carrier concentration is reduced to $1.4 \times 10^5 \text{ cm}^{-3}$ from the slope of the $1/C^2$ vs. V graph (Figure 31(b)) with built-in voltage of 0.2 V, which shows that the Fermi level is shifted away from the valance band, thereby suppressing the p-type behavior. The effect of Te compensation is further confirmed by the enhanced

rectification ratio and on-off ratio (Table 1) and reduced noise in the I-120 sample compared to the I-R sample. Figure 31(c) shows the LFN of uncompensated I-R and Te compensated I-120 NW samples. It is observed that the cut-off frequency of I-R is 10 Hz. At the same time, for compensated I-120 sample, it is found to be 5 Hz, which suggests the suppression of generation-recombination (G-R) noise components arising from the G-R centers. In addition, the I-R sample shows frequency dependence beyond 10 Hz; however, Te compensated I-120 sample exhibits frequency-independent noise beyond 5 Hz. Hence, Te- compensation is found to be an effective approach to neutralizing the p-type behavior from I-V, C-V, and LFN noise measurements.

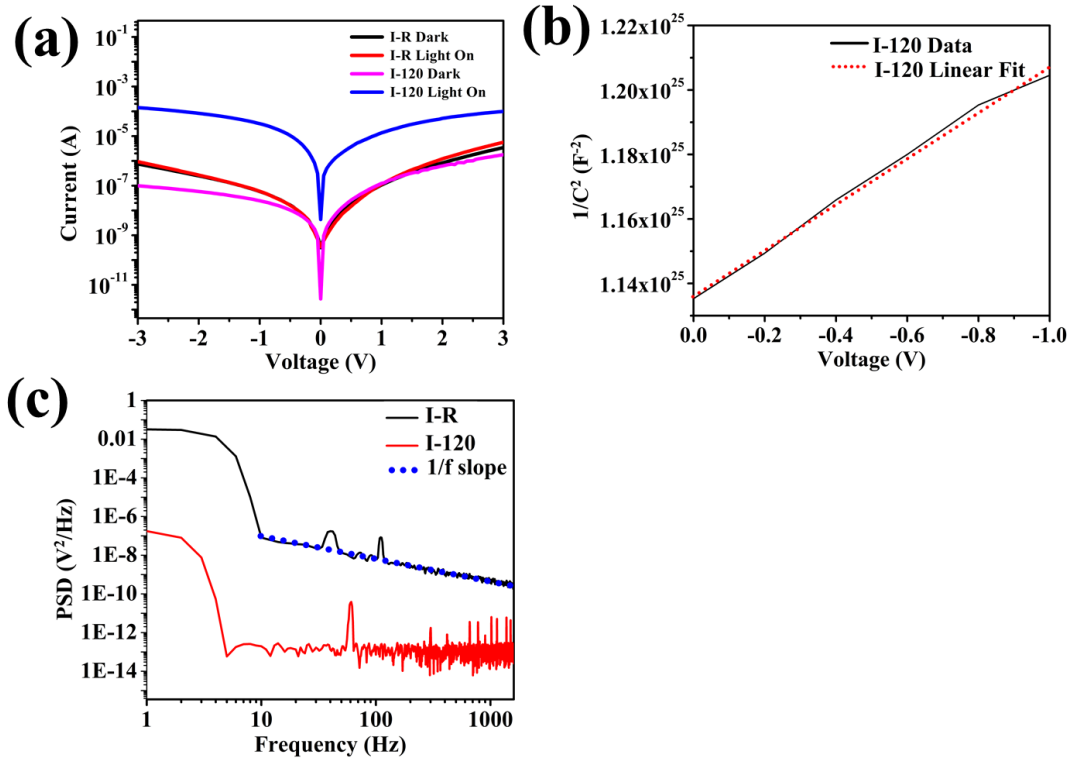


Figure 31. (a) I-V characteristics of ensemble I-R and I-120 samples, (b) C-V characteristic of I-120 sample, and (c) LFN measurements of I-R and I-120 samples.

Table 1. Figure of merits of I-R and I-120 samples.

Sample Name	I-R	I-120
Dark Current @-1V (A)	5.8×10^{-8}	2.4×10^{-8}
Photocurrent (A)	6.0×10^{-8}	3.1×10^{-5}
Responsivity (A/W)	3.7×10^{-4}	10.6
Detectivity (Jones)	6.1×10^7	2.7×10^{12}
Rectification Ratio	1.8	18
On-Off Ratio	1.02	1300

5.2.5 Electrostatic mapping from COMSOL simulation. Electrostatics of the C-S n-i-p GaAsSb NW has been studied using COMSOL Multiphysics Modeling Software by varying thickness and doping concentration of n-, i- and p- layer as shown in Figure 32 and Figure 33. Kendall Dawkins of our group carried out the COMSOL simulation. As the electric field is a function of built-in potential and applied bias voltage, the distribution of the electric field at a constant voltage bias of -1V for various parameters such as carrier concentration, length, and thickness of nanowires are studied. Intrinsic region of n-i-p acts as a space charge region, where electrons and holes are swept away by the electric field. thereby causing the current to flow. Also, the e-h pairs that are generated in the p- and n- regions within the Deby length,will diffuse into the depletion regioncontributing to the current.

One of the advantages of n-i-p junction over p-n junction is that the former makes it possible to widen the strong electric field region. The maximum electric field depends on the doping concentrations, applied voltage, and NW radius. For the n-i-p junction, it was observed that the thickness of n- core does not affect the peak electric field; therefore, an optimum radius

of 35 nm is chosen for n- core. Figure 32 shows that the peak electric field increases with an increase in doping concentration and decreases with intrinsic thickness and also, as the i- region moves away from the core, for the corresponding n- and p- carrier concentration of $5 \times 10^{17} \text{ cm}^{-3}$ (Figure 32(a)), $5 \times 10^{18} \text{ cm}^{-3}$ (Figure 32(b)), and $5 \times 10^{19} \text{ cm}^{-3}$ (Figure 32(c)), respectively. As the peak electric field increases with the doping concentration, it was observed that the electric field is more defined at the n-i and i-p junction of the highly doped n and p region of C-S n-i-p NW. From the simulation, the doping concentration in the order of 10^{19} cm^{-3} is optimum for the n-i-p C-S NW photodetector as the heavy doping favors ohmic contact. It is to be noted that the electric field is in the range of kV/cm with the variation in intrinsic thickness, which shows that intrinsic thickness can be varied from 10 nm to 60 nm for the optimization of high-performance devices. Figure 33 depicts the change in electric field with p- thickness of 30 nm and 40 nm at constant n- radius = 35 nm, i- thickness = 60 nm with carrier concentration of n-and p- segment: $5 \times 10^{19} \text{ cm}^{-3}$. It is observed that the electric field is not affected by the thickness of the p-shell. From the COMSOL simulations (Figure 32 and Figure 33), it is clear that the electric field is still in the range of 100s of kV/cm for the variation in the n-i-p segment thickness and carrier concentration. This analysis suggests that the electric field is not affected drastically for the given variation in thickness and concentration. However, the effect of thickness and dopant concentration can significantly affect the optical absorption and ohmic contact formation of the NWs. Hence, the effect of doping, variation in p- and i- segment thickness on the series resistance and device performance are investigated in the following section.

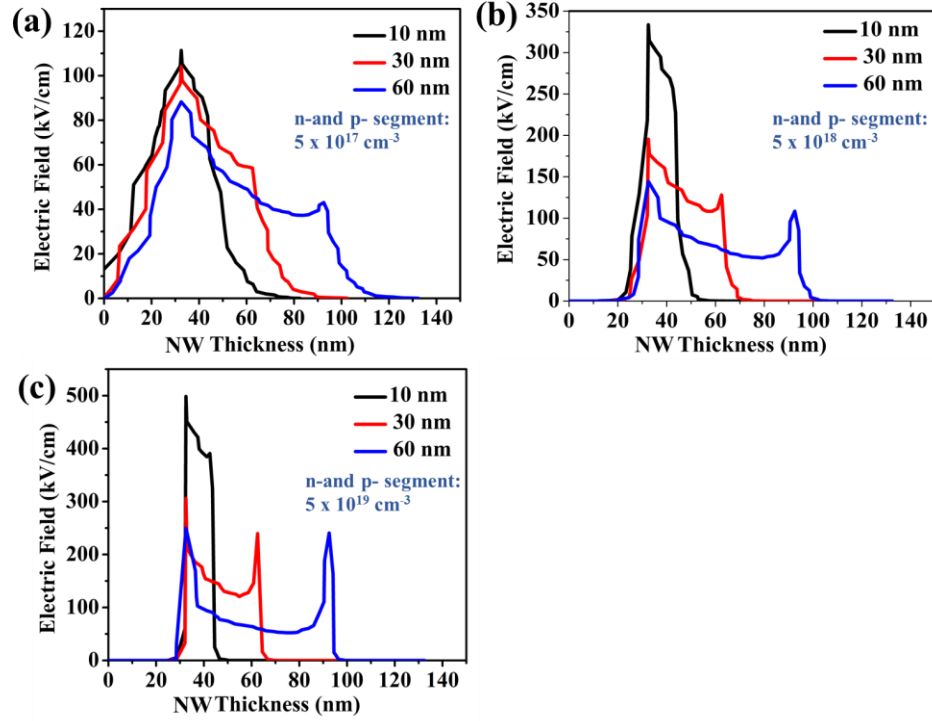


Figure 32. Electric field vs. NW thickness for different i- thickness at constant n- radius = 35 nm, p- thickness = 40 nm with carrier concentration of (a) n-and p- segment: $5 \times 10^{17} \text{ cm}^{-3}$, (b) n-and p- segment: $5 \times 10^{18} \text{ cm}^{-3}$, and (c) n-and p- segment: $5 \times 10^{19} \text{ cm}^{-3}$, respectively.

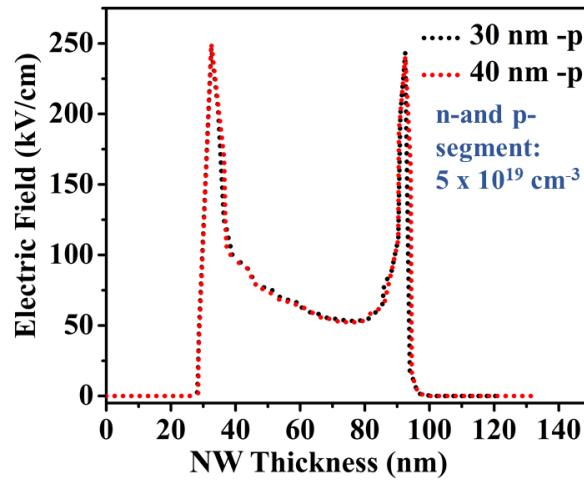


Figure 33. Electric field vs. NW thickness for different p- thickness at constant n- radius = 35 nm, i- thickness = 60 nm with carrier concentration of n-and p- segment: $5 \times 10^{19} \text{ cm}^{-3}$.

5.2.6 Effect of Te and Be cell temperatures and Be segment thickness. Amongst the n-type dopants, Te is the better choice due to its high solubility nature in Ga droplet, high incorporation efficiency, and low diffusion coefficient. Furthermore, high concentrations of Te doping can be achieved at a lower temperature than other dopants via the VLS mechanism (264-266). The other significant advantage of using GaTe as a captive dopant source in MBE is negligible crosstalk and memory issues (183, 267). Devkota et al. (59) and Ramaswamy et al. (121) investigated the incorporation of Te doping in GaAsSb as an n-type dopant by varying GaTe cell temperature from 500 to 570 °C and found that the high carrier concentration in the order of 10^{19} cm^{-3} is achieved with GaTe cell temperature of 550 °C.

Be is the commonly used p-type dopant in III-V semiconductor NWs due to its small diffusion coefficient and high solubility (268). There have been several reports on Be dopant incorporation in GaAs NWs in the literature (109, 121, 182, 253, 269, 270). For example, Casadei et al. (253) reported that the Be atoms are preferentially incorporated via the side facets of the NW and also found that the path of incorporation through the Ga droplet is negligible. Furthermore, Ojha et al. (109) demonstrated that in a C-S NW, Be incorporation through the side facets of the shell by the VS mechanism is efficient as opposed to the Ga droplet via the VLS mechanism.

From the properties mentioned above, Te-doped GaAsSb and Be-doped GaAsSb as the core and outer shell, respectively, in the n-i-p configuration is more effective than the C-S p-i-n junction. In order to evaluate the effect of Te and Be dopant incorporation on the n-i-p junction, GaTe and Be cell temperatures were varied as follows, 520 °C and 750 °C (sample# I-750), 520 °C and 850 °C (sample# I-850), and 540 °C and 925 °C (sample# I-25). Figure 34(a) shows the dark I-V characteristic using C-AFM (saturated current in the I-25 sample is due to the

instrument limitation) and series resistance (Figure 34(b)) of I-Be750, I-Be850, and I-25 SNW samples. An increase in the dark current is observed with a decrease in the series resistance in the I-25 sample, attributed to the increase in the incorporation of Be and Te dopants. The low series resistance of $1 \times 10^5 \Omega$ of the I-25 NW sample shows the improved quality of the n-i-p junction. The low doped n-i-p GaAsSb NW samples (I-750 and I-850) depict Schottky contact with high resistance. However, with the increase in Be and GaTe cell temperatures, highly doped n-core and p-shell are formed, thus giving rise to a good ohmic contact (14). Ohmic contact plays a crucial role in realizing the full potential of PD. It is to be noted that Nie et al. (271) demonstrated an improvement in the performance of organic PD with detectivity up to 10^{13} Jones and a response speed of $0.8 \mu\text{s}$ due to the ohmic contact formation. Therefore, GaTe cell temperature of 540°C and Be cell temperature of 925°C are optimum temperatures for the formation of ohmic contact and a good quality n-i-p junction.

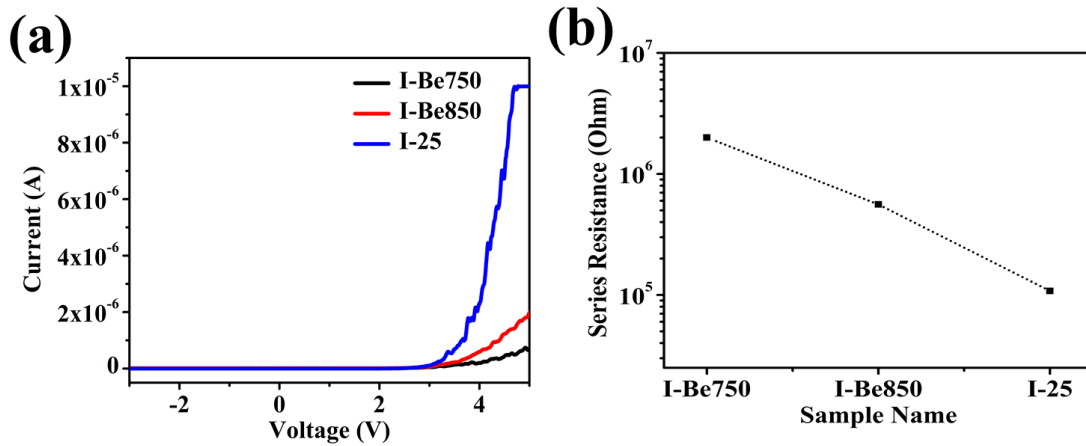


Figure 34. (a) Dark I-V characteristic using C-AFM and (b) series resistance of I-Be750, I-Be850, and I-25 SNW samples.

Figure 35 shows the dark I-V characteristics of Ensemble I-15 and I-30 NW samples. The duration of the p-shell growth of I-15 and I-30 are 15 and 20 mins, respectively. The highest rectification ratio of I-15 and I-30 NW samples at -3V is 11 and 106, respectively. Furthermore,

the higher dark current of 1.3×10^{-7} A, along with the low rectification ratio of sample I-15, show that the smaller thickness of the p-shell deteriorates the performance of PD, as the metal-semiconductor p-shell interface is in the proximity of the intrinsic region. It is speculated that the high density of states at the p-shell surface could pin the Fermi level, thereby forming a Schottky barrier instead of ohmic contact, and/or the over-etching of thin p-shell could lead to the exposure of the intrinsic region, thereby reducing the rectification ratio and enhancing the dark current (14). From these observations, a p-shell growth duration of 20 mins is found to be the optimum time to mitigate the contact issue.

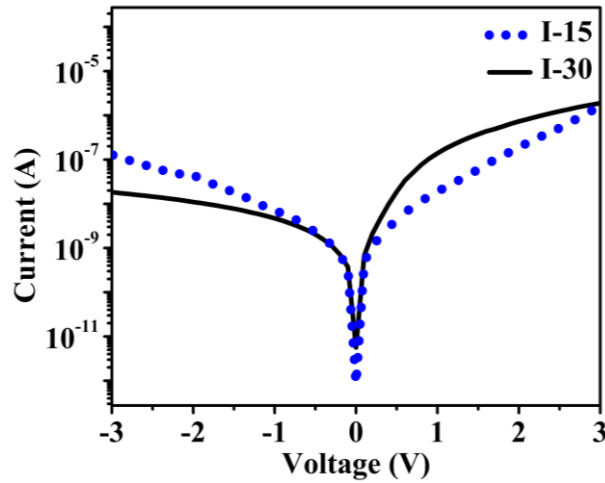


Figure 35. Dark I-V characteristics of Ensemble I-15 and I-30 NW samples.

5.2.7 Effect of variation with intrinsic thickness. The intrinsic region plays the most crucial role in an n-i-p junction PD, as the thickness of the intrinsic (depletion) region determines the response speed and quantum efficiency of the PD. A thin depletion region reduces the carrier's transit time, thereby improving the response speed. On the contrary, a thicker depletion region increases the quantum efficiency as a large area is available for the light to be absorbed and generate carriers. Hence, optimization of the intrinsic region based on the application is mandatory. In this section, the variation in the intrinsic region width is studied. The intrinsic

region of two samples, I-25 and I-30, are grown for 25 mins and 30 mins, respectively, keeping all other parameters constant.

The SEM images of the core-shell n-i-p GaAsSb NWs are shown in Figures 36(a) and 6(b). A comparison of RT and 4K PL (Figure 36(c) and 36(d)) reveals a 66-fold increase in intensity and reduction in full width at half maxima (FWHM) at 4K PL. From Figure 36(c), peaks at ~ 1.16 eV and ~ 1.22 eV with an FWHM of 90 meV and 142 meV, respectively, have been observed in RT PL spectra. While in 4K PL (Figure 36(d)), a peak at ~ 1.24 eV with an FWHM of 71 meV is observed, along with a distinct shoulder peak at ~ 1.31 eV with an FWHM of 72 meV have been observed in 4K PL. The lower energy peak is attributed to the PL emission from the intrinsic region $\text{GaAs}_{0.75}\text{Sb}_{0.25}$.

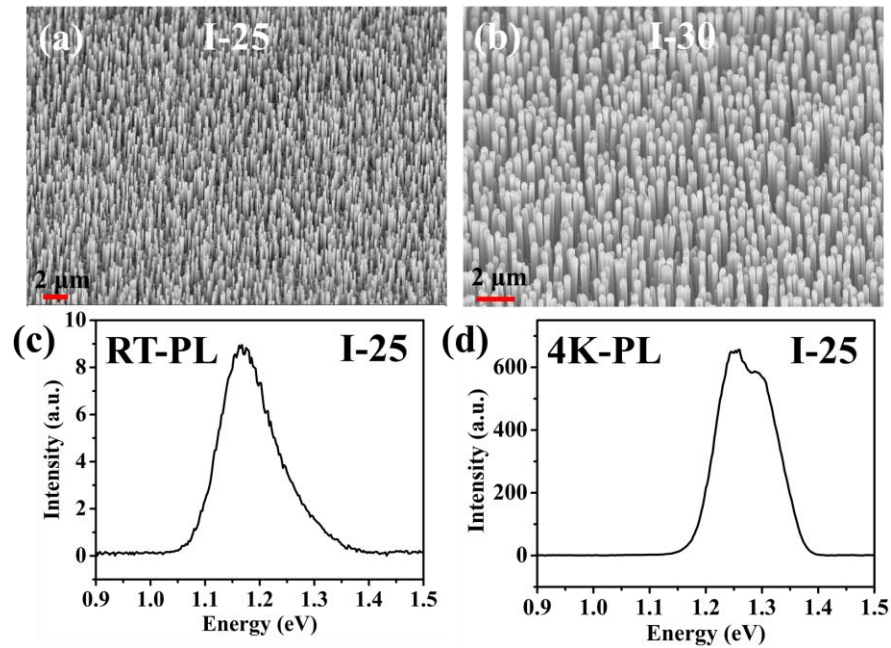


Figure 36. (a, b) SEM images of I-25 and I-30, (c) RT PL spectra, and (d) 4K PL spectra of the I-25 sample.

5.2.7.1 I-V characterization and LFN measurements of ensemble PD. The wavelength-dependent current-voltage measurements at room temperature are carried out to assess the spectral sensitivity of I-25 and I-30 samples (Figures 37(a) and 37(b)). It was observed that the photogenerated current was in the range of 6 μA and 600 μA for the illumination of 633-1100 nm incident light at -1 V for I-25 and I-30, respectively. The reverse current increases by three orders of magnitude in the I-25 and five orders of magnitude in I-30 under illumination. Figures 37(c, d) and 37(e, f) depict the spectral responsivity and detectivity of I-25 and I-30 NW samples. The responsivity of I-25 and I-30 at -1V for the wavelength of 1100 nm is found to be 1.82 A/W and 190 A/W, respectively, due to the increase in intrinsic region thickness using equation (17). The external quantum efficiency (EQE) of the NW samples is calculated using equation (18) and was found to be $2.2 \times 10^3 \%$ and $2.2 \times 10^4 \%$ for I-25 and I-30, respectively.

$$R = I_{\text{ph}}/(P \cdot S) \quad (17)$$

$$\text{EQE} = R \cdot \{hc/e\lambda\} \quad (18)$$

Where R is the responsivity, I_{ph} is the photocurrent, P is the laser power density, S is the effective device area, h is the Planck's constant, c is the speed of light, and λ is the wavelength of incident light. Relatively high responsivity and EQE are ascribed to increased intrinsic region thickness. The beam spot area of optical illumination (0.25 cm^2) is considered the effective device area. The specific detectivity of the p-i-n photodetectors as a function of reverse bias voltage and wavelength was calculated from equation (19) for the NW samples that are limited by shot noise and equation (20) that are limited by 1/f noise (272).

$$D^* = R(S/2eI_{\text{dark}})^{1/2} \quad (19)$$

$$D^* = R(S \cdot \Delta f)^{1/2}/I_{\text{noise}} \quad (20)$$

where D^* is the specific detectivity, Δf is the measurement bandwidth, and I_{noise} is the noise current. Amongst these two samples, I-30 shows a high detectivity over a broad spectral range from 800 to 1,100 nm at -1 V and -2V and was found to be in the order of 10^{14} Jones. It can be observed that as the reverse bias voltage increases, the detectivity also increases. I-30 shows the highest on-off ratio of 1.2×10^5 for the wavelength of 1100 nm. The responsivity, detectivity, and on-off ratio of I-30 are higher than those reported in the core-shell NW configuration (106). The rectification ratio, series resistance, and shunt resistance of I-25 is found to be 2.8×10^6 ohms, and 5×10^9 ohms while for I-30, the rectification ratio, series resistance, and shunt resistance are 111, 7×10^5 ohms, and 2×10^8 ohms, respectively. High rectification ratio and lower series resistance are the critical parameters for a good quality junction formed in the I-30 NW sample (273). From Figures 37(g) and 37(h), the obtained result suggests that sample I-25 is dominated by $1/f$ noise with the slope of one, while sample I-30 is dominated by white noise beyond 10 Hz, as frequency-independent noise is observed.

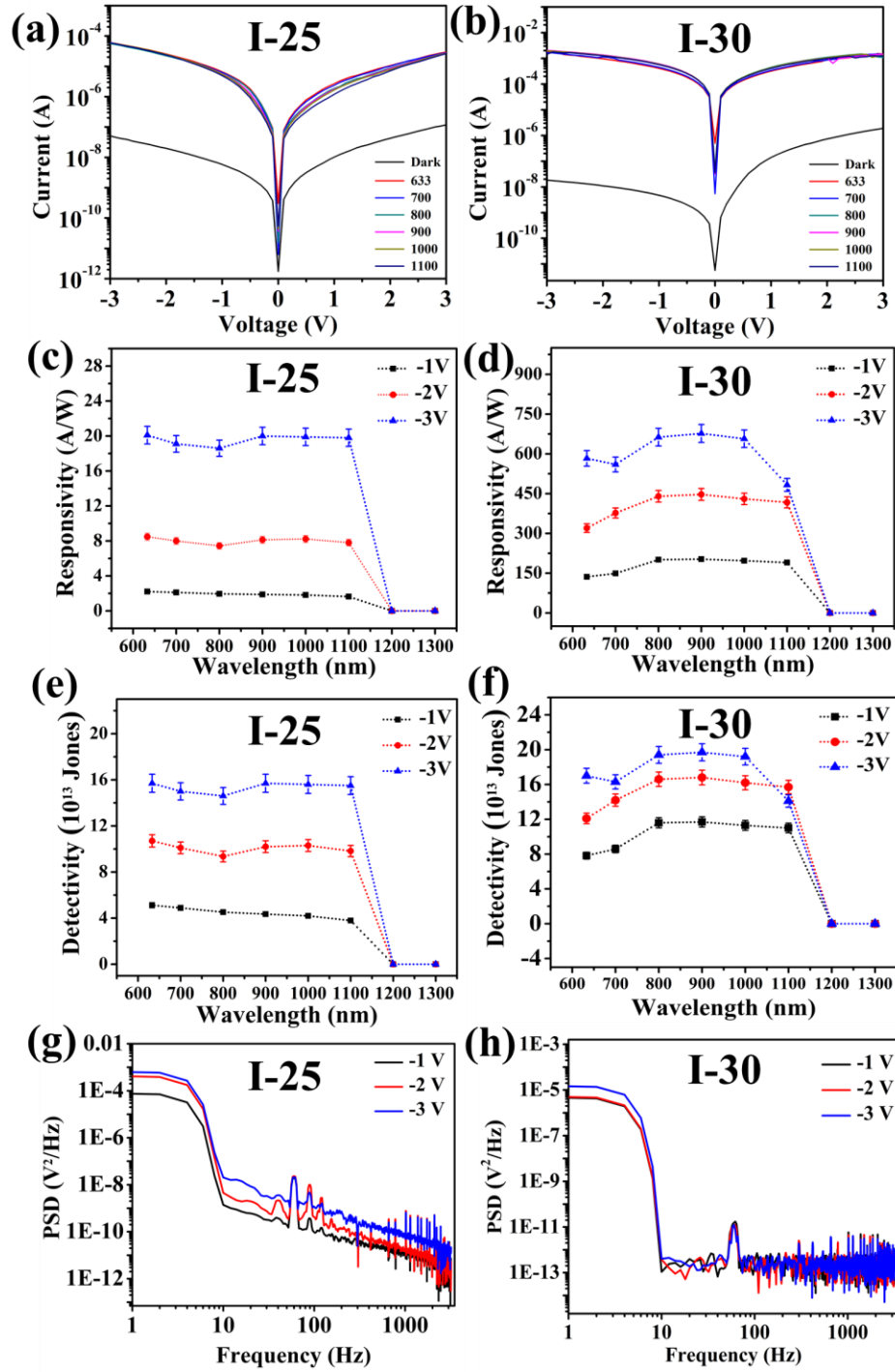


Figure 37. (a, b) Wavelength dependent I-V characteristics of I-25 and I-30, (c, d) responsivity versus wavelength of I-25 and I-30, (e, f) detectivity versus wavelength of I-25 and I-30, and (g, h) noise spectrum of I-25 and I-30, respectively.

5.2.7.2 C-V measurements of ensemble PD. In the case of core-shell NW, as the junction is axially long, covering a length of around 2 μm , it is technically challenging to form a defect-free junction, especially with both the n-type and p-type dopants being a surfactant. In addition, the intrinsic region is closer to the top metal contact, which is considered a disadvantage due to band bending or extension of the depletion region into the p-region. The effect of interface defects on the device characteristic is reflected in the C-V graph (Figure 38). The C-V measurements are performed for fixed frequencies ranging between 1 kHz and 1 MHz under dark conditions on the I-25 (Figure 38(a)) and I-30 (Figure 38(b)) NW samples. The inset of Figures 38(a) and 38(b) depict the semi-logarithmic plot of C-V. The inset of Figure 38(a) shows a distinct frequency dispersion of the C-V plot, which is speculated to be caused by the interface defects. This result is in excellent agreement with the trend observed in the noise spectrum of the I-25 sample. C-V measurements give us the value of capacitance which is calculated by the ratio of change in total charge (ΔQ) to the change in the applied voltage (ΔV). It is to be noted that the ΔQ constitutes the charges removed from the undepleted region and the trap states. The negative capacitance at the low frequency of I-25 samples shows the existence of interface trap states and deep level traps (defect states). It is known that the carrier releasing process from the defect states is comparatively slower than the carrier trapping process. Therefore, the defect states can trap and release the carriers in response to the low-frequency perturbation only. In the case of higher frequency, the rate at which the carrier trapping and releasing occurs at the defect states cannot follow the AC signal; hence the defect states do not contribute/affect the capacitance (274, 275). In the case of I-30 NW, positive capacitance is observed with a maximum frequency in the range of pf at 1 kHz. However, a small change in frequency from 1 kHz to 1 MHz is

speculated to be arising from G-R centers, which is in good agreement with the frequency-independent noise as shown in Figure 37(h).

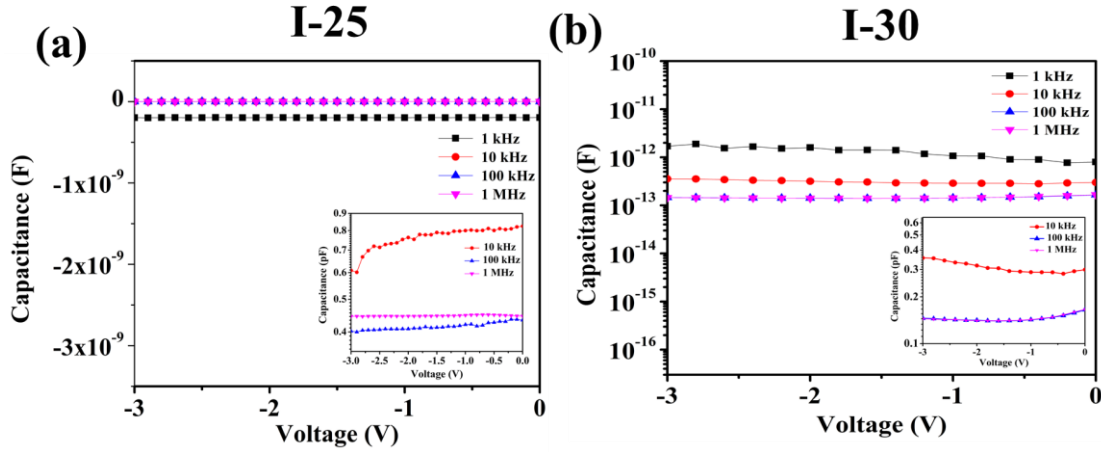


Figure 38. C-V measurements of (a) I-25 NW sample and (inset) C-V plot in semi-logarithmic scale, (b) I-30 NW sample and (inset) C-V plot in semi-logarithmic scale.

5.2.7.3 I-V characterization using C-AFM. Figures 39(a-f) show the topography, corresponding current map, and I-V characteristic of the core-shell n-i-p GaAsSb NWs of I-25 and I-30 NW samples. From SNW I-V of the I-25 sample (Figure 39(e)), it was found that the sample exhibited a low dark current of 3.7 pA and photoresponse of 1.8×10^{-10} A at -1V, hence the responsivity of 10 mA/W. The rectification ratio and detectivity of the I-25 SNW sample (Figure 39(e) and 39(g)) were found to be 5.7 and 6.3×10^{12} Jones, respectively. It was observed that the dark current was in the range of pA for sample I-30 (Figure 39(f)). The rectification ratio and detectivity of SNW (Figure 39(h)) were found to be 2.3×10^3 and 1.4×10^{13} Jones, respectively. It is observed that the trend in device performance of I-25 and I-30 SNW samples concur very well with the ensemble devices.

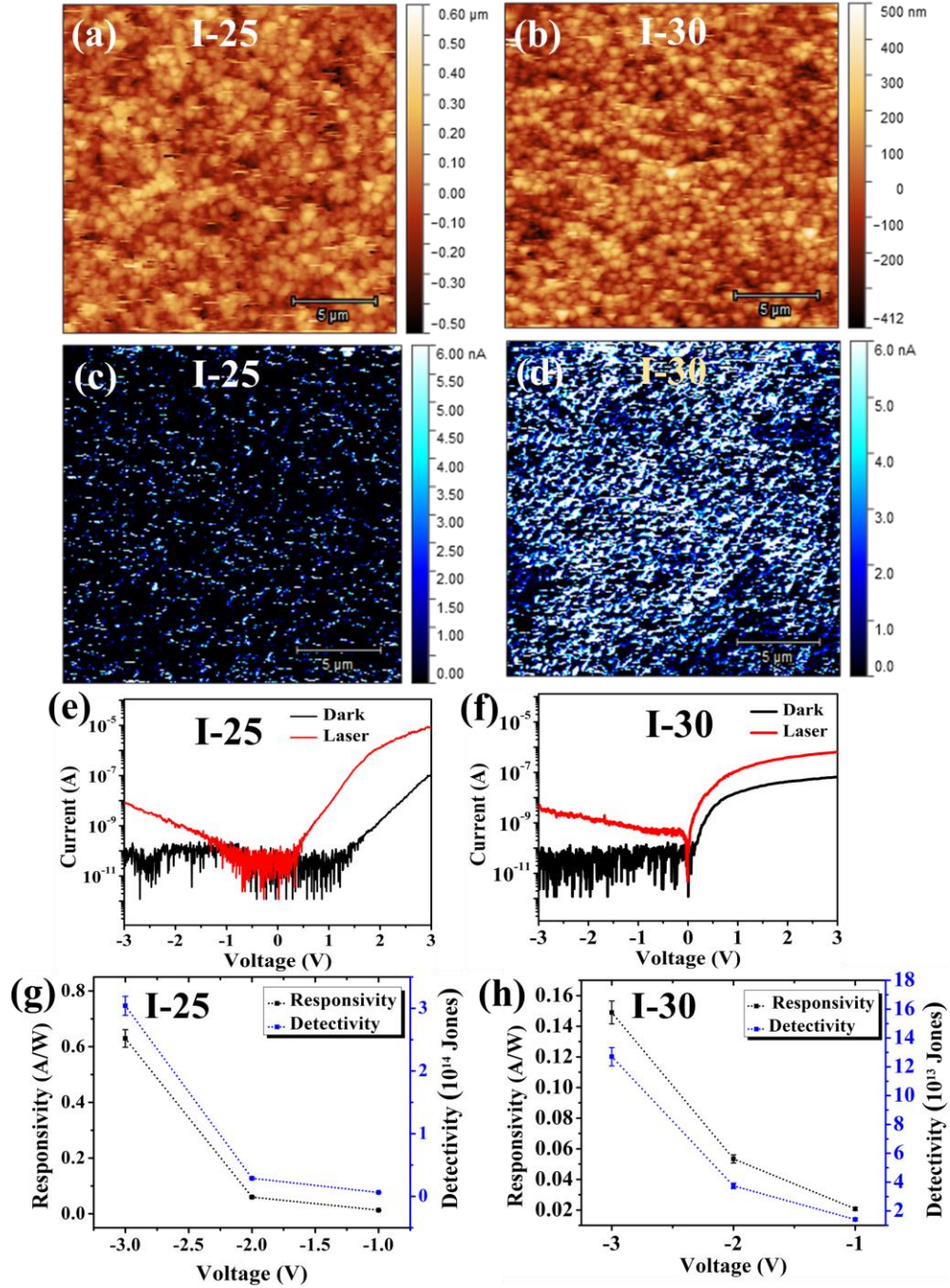


Figure 39. (a, b) Topography, (c, d) corresponding current map, (e, f) I-V characteristic, and (g, h) responsivity and detectivity of single NW I-25 and I-30 samples, respectively.

5.2.8 C-S n-i-p GaAsSb NIRPD at the wavelength of 1.5 μm . In this section, we demonstrated the modified architecture of C-S n-i-p NWs to tailor the photoresponse, quantum

efficiency, and improve the junction quality for the application of the NIRPD at a wavelength approaching 1.5 μm . Besides several advantages of C-S NW devices, most research focuses on axial fabrication, as the fabrication of contacts is comparatively easy (262). Hence, in order to overcome the disadvantage of conventional C-S NW, hybrid C-S axial n-i-p GaAsSb NW is designed to increase the absorption volume of the intrinsic region, thereby improving the EQE of the IRPD. In the case of conventional C-S NW structure, over-etching of p- and i- segment will lead to the formation of core n- GaAsSb Schottky diode, which is detrimental to the whole ensemble NW IRPD device. However, the impact of over-etching on device performance is reduced in hybrid C-S axial n-i-p GaAsSb NW structure, as the core i-n junction NW is still intact, thereby limiting the formation of the Schottky diode. Therefore, a hybrid axial C-S n-i-p structure is demonstrated to mitigate this issue, which showed an enhanced EQE, optical absorption, high rectification ratio, low series resistance, low dark current, and high detectivity (Figure 1(b)). Figure 1 from chapter 1 is again reproduced below. The limitation of the traditional C-S n-i-p structure (Figure 1(a)) is the restricted variation of intrinsic thickness due to the diameter constraint. Hence, a hybrid form of axial and C-S structure has been designed for more absorption of incident photons, which further enhances the responsivity, EQE, and detectivity of the NIRPD. Also, even if the NWs are over etched, the PD will still operate.

Further, in this novel configuration, the NW growth is initiated with GaAs stem followed by the Te-GaAs stem (276), which minimizes the shunt path at the NW base. In-situ vacuum annealing was carried out after each n-, i-, p- segment's growth to form a uniform junction. Figure 40 (a) shows the electric field vs. thickness distribution with variation in i- thickness at a constant n- radius and p- thickness of 35 nm and 40 nm, respectively, and carrier concentration of n-and p- segment as $1 \times 10^{19} \text{ cm}^{-3}$ and schematic of electric field distribution at the core n-i

and C-S n-i-p junction (Figure 40 (b)). It is to be noted that the peak electric field of C-S n-i-p segment is around 1570 kV/cm for the i-thickness of 10 nm and drops to 670 kV/cm for the i-thickness of 60 nm, which shows that the intrinsic region can be varied between 10 nm and 60 nm. In the case of C-S i-i-p segment, the peak electric field is around 134 kV/cm.

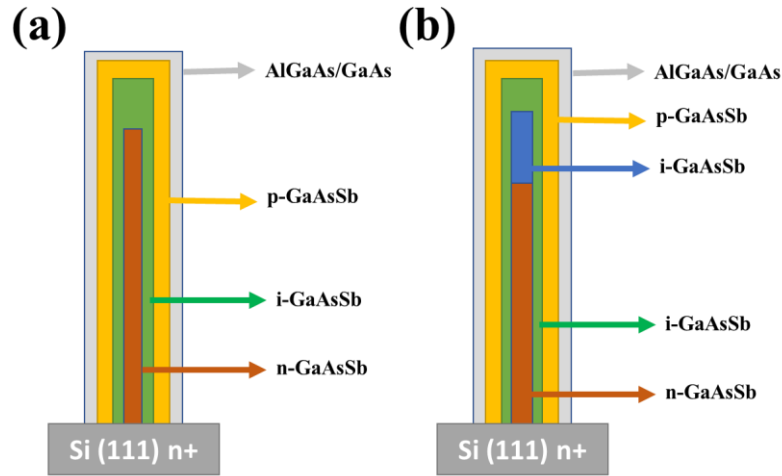


Figure 1. Schematic of (a) conventional and (b) hybrid axial - C-S n-i-p GaAsSb NW structure, with lower Sb composition of 25% and higher Sb composition of 30 %.

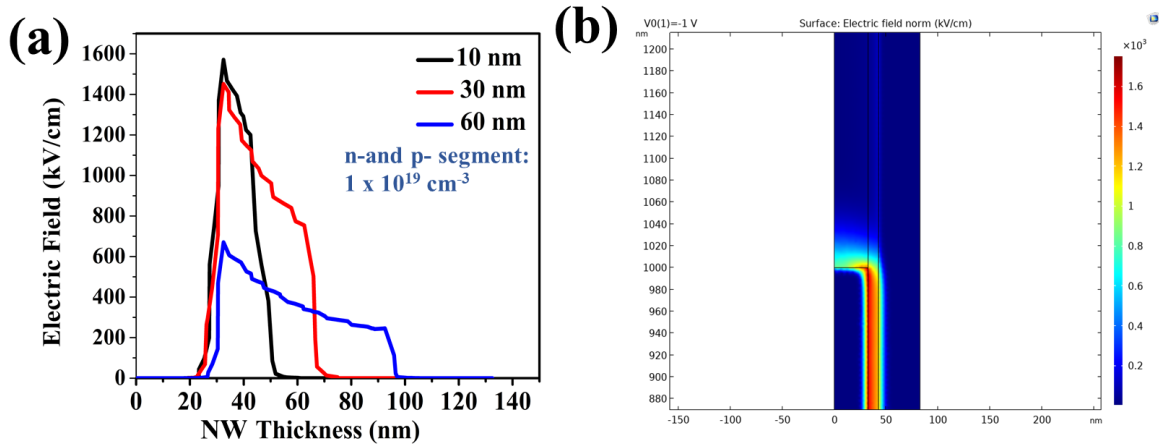


Figure 40. (a) Electric field vs. NW thickness for different i- thickness at constant n- radius = 35 nm, p- thickness = 40 nm with carrier concentration of n-and p- segment: $1 \times 10^{19} \text{ cm}^{-3}$ and (b) schematic of electric field distribution at the core n-i and C-S n-i-p junction.

The SEM image of the MI sample is shown in Figure 41(a). The 4K-PL spectra of the MI NW sample are depicted in Figure 41(b), and the inset shows the RT-PL spectra. From 4K-PL spectra (Figure 41(b)), peaks at ~ 0.98 eV and ~ 1.13 eV with an FWHM of 73 meV and 117 meV, respectively, have been observed. While RT-PL spectra (Figure 41(b) inset) exhibit a peak at ~ 0.83 eV with an FWHM of 64 meV and a distinct peak at ~ 1.07 eV with an FWHM of 126 meV have been observed in RT-PL. The lower energy peak of ~ 0.83 eV is attributed to the PL emission from the intrinsic region $\text{GaAs}_{0.70}\text{Sb}_{0.30}$.

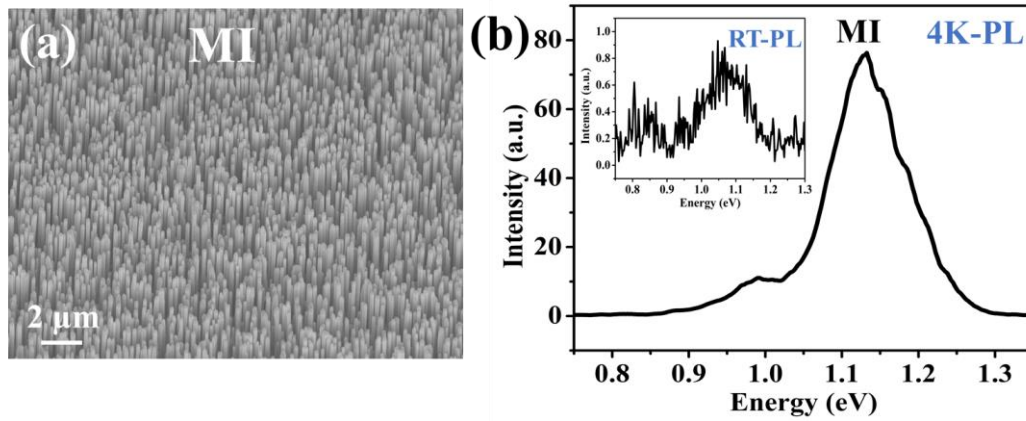


Figure 41. (a) SEM image and (b) 4K-PL spectra, and (inset) RT-PL spectra of MI sample.

5.2.8.1 I-V characterization and LFN measurements of ensemble PD. I-V characteristic of ensemble MI NW PD is demonstrated in Figure 42(a). A low dark current of 4 nA and an improvement in the rectification ratio of 122 were observed, attributed to the high-quality junction and C-S NW structure formation. A maximum responsivity of 18 A/W at -1 V, 88 A/W at -2V, and 225 A/W at -3V, and corresponding detectivity of 1.1×10^{13} Jones, 2.4×10^{13} Jones, and 2.5×10^{13} Jones, respectively, for the illumination wavelength of 1500 nm is observed (Figure 42(b) and 42(c)). Figure 42(d) shows the noise spectrum obtained from the LFN measurement. It is observed that the cut-off frequency of the MI sample is around 2.5 Hz at -1V, and beyond the cut-off frequency, frequency-independent noise or white noise. From the 4K-PL

spectra and the LFN measurement, the G-R noise below the cut-off frequency is attributed to the presence of shallow traps generated from the band tail states (59). The C-V characteristic of the MI NW sample has been carried out for frequency range from 1 kHz to 1 MHz, and the results are shown in Figure 42(e). In comparison with the C-V measurement of I-25 and I-30 NW samples, the positive capacitance of the MI NW sample depicts better junction formation, which is corroborated by a high rectification ratio, low series resistance, and high shunt resistance of 122 , 3×10^4 ohms, and 4×10^9 ohms, respectively. The inset of Figure 42(e) shows the bias dependence for the 10 kHz, 100 kHz, and 1 MHz frequency, which decreases from 0 V to -3 V due to deep level traps and/or high resistivity of the intrinsic region (277). Similar frequency dependence is observed in other p-i-n junction-based materials, namely, 4H-SiC (277), a-Si: H (278), Si (279), GaN (280), and AlGaN (281).

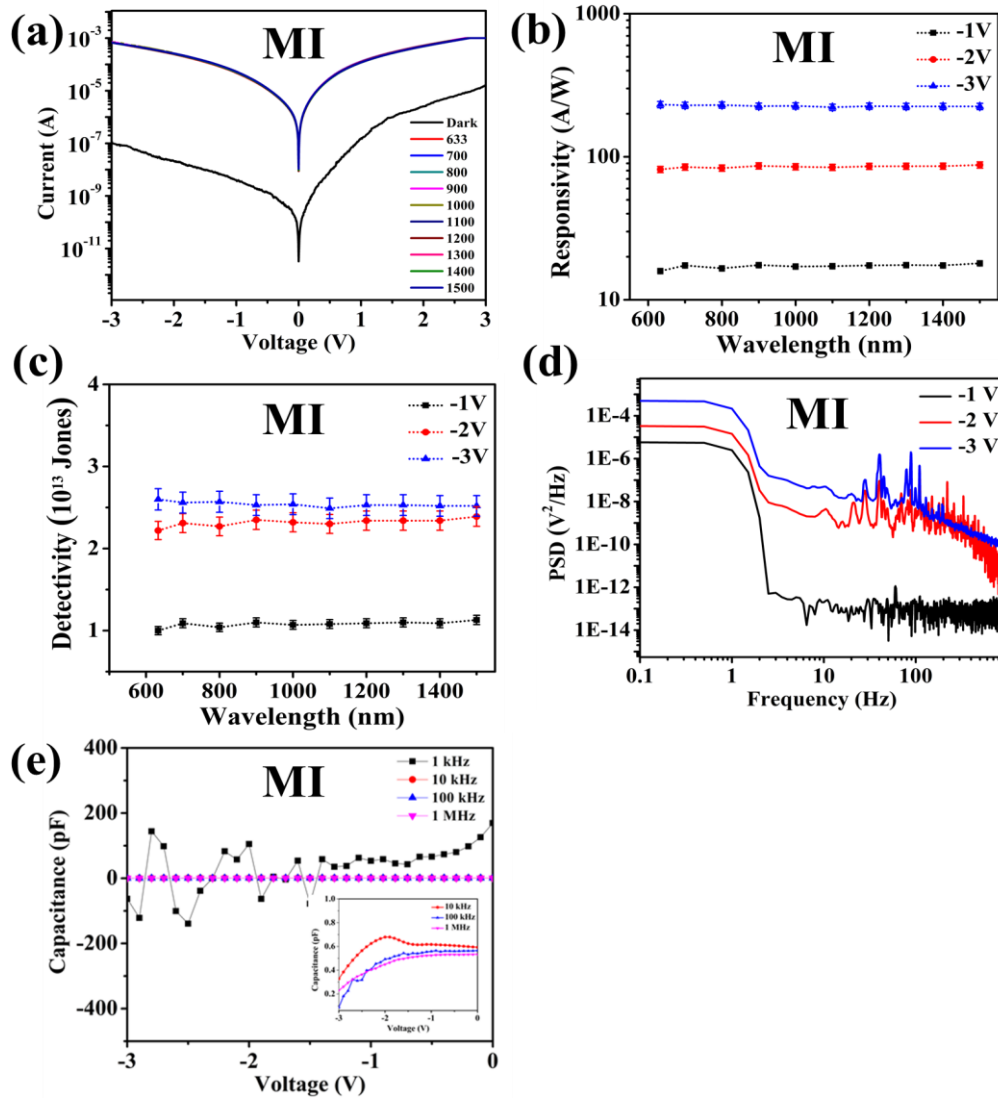


Figure 42. (a) Wavelength dependent I-V characteristic, (b) responsivity versus wavelength, (c) detectivity versus wavelength, (d) noise spectrum, and (e) C-V measurement of MI NW sample.

5.2.8.2 Device performance at 77K and temperature-dependent measurements. Figure 43(a) shows the responsivity and detectivity for the wavelength range between 633 nm and 1500 nm at 77 K. An enhanced device performance is observed at a low temperature of 77 K with a detectivity of 4.9×10^{13} Jones at 1500 nm illumination, which is attributed to the low dark current in the range of pA. From Figure 43(b), the temperature-dependent noise shows a small

yet linear increase in noise with temperature spanning from 77 K to 300 K. The cut-off frequency of 3 Hz is observed, after which frequency-independent noise is observed.

Temperature-dependent capacitance measured at 1 MHz under the reverse bias from 0 V and 3 V is shown in Figure 43(c). It can be observed that the capacitance increases with the increase in temperature from 77 K to 300 K, which is due to the increase in thermally activated carriers at the elevated temperature, thereby increasing the effective space charge density, hence the capacitance. In Figure 43(d), it can be seen that the minimum ideality factor (n) of 4 is achieved for the temperature beyond 250 K. It is to be noted that the ideality factor decreases with the increase in temperature and is found to be $n \gg 2$ indicate deep level assisted tunneling conduction mechanism (282) contributing to the quantum tunneling electrons through the energy barrier between the deep defect level, and conduction band is the primary transport mechanism at low temperatures. Ideality factor far greater than one is speculated to be caused by the interfacial layer between the silver metal contact and the NW (283). The small activation energy of 7 meV observed for the temperature below 250 K from the Arrhenius plot (Figure 43(e)) is due to the reduced barrier for the carrier injection in C-S, further showing that the shell provides the low barrier contact to the core (284). The high activation energy of 214 meV is ascribed to the lattice defects of GaAsSb NWs.

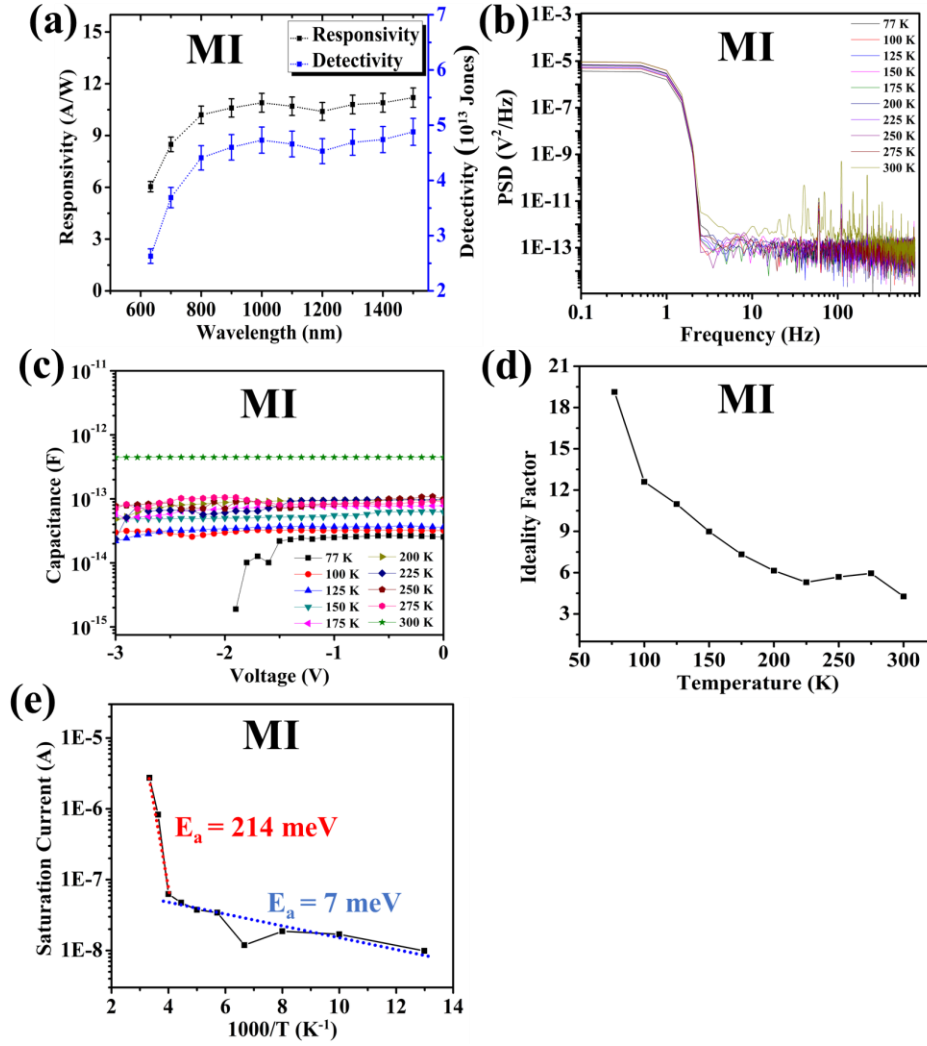


Figure 43. Responsivity and detectivity versus wavelength at -1V, (b) temperature-dependent noise measurement at -1V, (c) temperature-dependent C-V measurement at 1 MHz, (d) temperature dependence of the ideality factor, and (e) Arrhenius plot of the saturation current of MI NW sample.

5.2.8.3 I-V characterization using C-AFM. The topography and corresponding current map of the core-shell n-i-p GaAsSb NWs of the MI NW sample are shown in Figures 44(a) and 44(b). From the SNW I-V characteristic of the MI sample (Figure 44(c)), it was found that the sample exhibited a maximum photoresponse of 6 nA at -3V. The responsivity and detectivity of

SNW (Figure 44(d)) were 16 mA/W and 1.12×10^{13} Jones, respectively, at -1V for the 860 nm wavelength illumination.

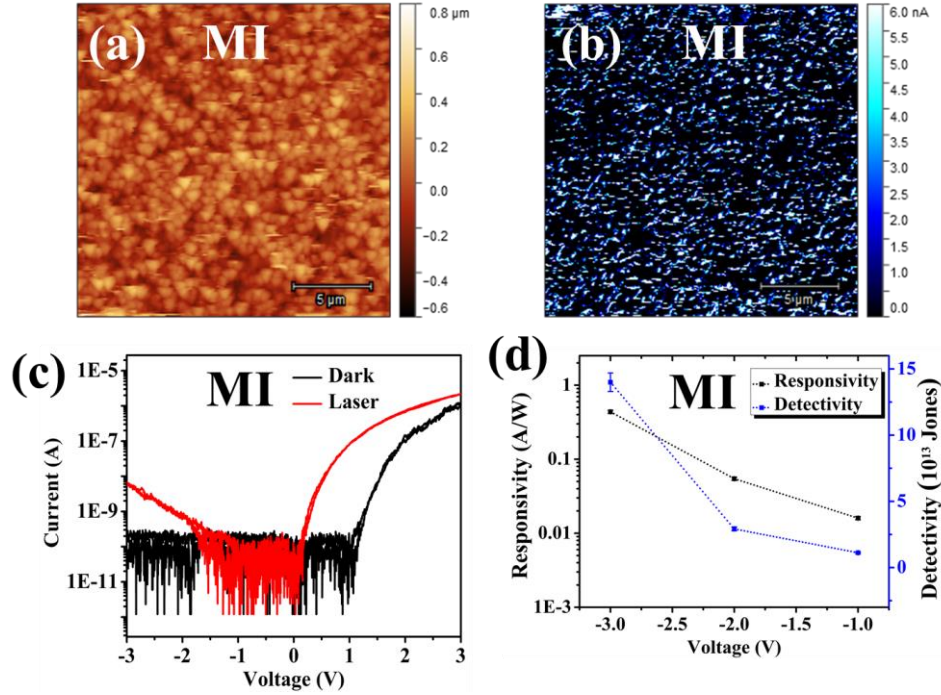


Figure 44. (a) Topography, (b) corresponding current map, (c) I-V characteristic, and (d) responsivity and detectivity of single NW MI sample using C-AFM.

5.3 Conclusion

In this work, we successfully demonstrated RT C-S n-i-p GaAsSb NW based on a novel hybrid axial C-S design structure for NIRPD application up to 1.5 μm wavelength. The conventional C-S n-i-p configuration resulted in the high device performance C-S n-i-p GaAsSb NWs with responsivity, detectivity, and series resistance of 190 A/W, 1.1×10^{14} Jones, and 7×10^5 ohms, respectively, for the 1.1 μm illumination wavelength. In contrast, the hybrid axial C-S n-i-p structure showed responsivity, detectivity, and series resistance of 18 A/W, 1.1×10^{13} Jones, and 3×10^4 ohms, respectively, for the 1.5 μm illumination wavelength. As the electric field, which is responsible for carrier extraction, has not drastically changed with variation in segment

thickness and carrier concentration. Hence, it was found that the low series resistance and ohmic contact formation play crucial role in enhancing the C-S n-i-p GaAsSb (conventional and hybrid) IRPD performance,

CHAPTER 6

Summary and Scope of Future Work

In this dissertation, we have successfully demonstrated C-S n-i-p GaAsSb heterojunction IRPD in the ensemble NW configuration using novel axial and C-S heterojunction combination with detectivity of 1.1×10^{13} Jones and responsivity of 18 A/W at 1.5 μm wavelength. Furthermore, the determination of carrier concentration in the different segments forming the heterojunction in the NWs, which is crucial to the success of this work, were ascertained from the ensemble and SNW using a unique combination of non-destructive techniques (no deposition of contacts), namely, XPS, UPS, C-AFM, and SKPM. Further, the study of the efficacy of the ALD deposited Al_2O_3 passivation layer on self-catalyzed GaAsSb NWs was carried out in the quest of finding a better alternative to the AlGaAs/GaAs passivation shell. These studies, along with other detailed and systematic studies on the material and device using various characterization techniques, led to the successful realization of NIRPD up to 1.5 μm wavelength in GaAsSb based C-S n-i-p junction in ensemble NW configuration. A new hybrid axial C-S-based n-i-p GaAsSb design was implemented in order to achieve high-performance NIRPD. In this new design, the i- GaAsSb segment was grown on an n-doped core GaAsSb, to improve the absorption volume of the intrinsic region and enhance the device performance. A detailed summary of the work is provided below.

6.1 Summary

6.1.1 Study of dopant incorporation in Te-doped GaAsSb and Be-doped GaAs NWs.

This work described the methodology developed to assess the Te dopant incorporation in GaAsSb NWs and Be dopant incorporation in GaAs NWs using Ga-assisted MBE with Te (T_{GaTe}) and (T_{Be}) cell temperatures, respectively. Be and GaTe temperatures varying from 500 $^{\circ}\text{C}$

to 570 °C and 750 °C to 950 °C were investigated. From XPS and UPS spectra, the atomic percent, work function, and carrier concentration of Te-doped GaAsSb and Be-doped GaAs NWs are determined. These were complemented using C-AFM, where the carrier concentrations were computed from the best fit of the I-V experimental data with those determined from COMSOL Multiphysics fitting. In addition, SKPM provided strong evidence of Be and Te incorporation by surface potential change observed in doped NWs. It was observed that the values of carrier concentration from UPS and C-AFM concurred very well. **This work is the first report on the Te and Be dopant incorporation using a combination of non-destructive techniques, namely XPS, UPS, C-AFM, and SKPM, and published in Scientific Reports 2021 and OSA Technical Digest, 2021.** (*Priyanka Ramaswamy et al., A study of dopant incorporation in Te-doped GaAsSb nanowires using a combination of XPS/UPS and C-AFM/SKPM. Scientific Reports 11, 8329 (2021) and Priyanka Ramaswamy, et al., Be-doping assessment in Self-Catalyzed MBE Grown GaAs Nanowires, Conference on Lasers and Electro-Optics, OSA Technical Digest, SW2F.7 (2021)*).

6.1.2 Study of Al₂O₃ dielectric on Ga-assisted MBE grown GaAs_{1-x}Sb_x NWs. In this work, we studied the efficacy of the ex-situ passivation of thermal ALD deposited Al₂O₃ passivation layer on self-catalyzed GaAsSb NWs using XPS and Raman spectroscopy. In addition, the effect of in-situ and ex-situ annealing on ALD deposited Al₂O₃ passivated NW using C-AFM was carried out. The stoichiometry of Al₂O₃ was found to be 1.3, and the characteristic of the interface between Al₂O₃ and GaAsSb NW were investigated using XPS and Raman spectroscopy. The XPS spectral analysis indicated that precleaning with sulfur treatment before Al₂O₃ ALD deposition successfully removed III-V native oxides formed on the NW surface. However, the Raman characterization confirmed the presence of point defects on Al₂O₃

ALD deposition. Even though the increase in current conduction was observed in Al_2O_3 passivated in-situ annealed GaAsSb NW sample. It was found that the Al_2O_3 passivation is not as efficient as AlGaAs/GaAs passivation shell. Thereby concluding that ALD deposited Al_2O_3 layer is not an effective passivation layer for GaAsSb NWs. **This work is currently under review in IOP Nanotechnology, 2022.**

6.1.3 Demonstration of C-S n-i-p GaAsSb NWs with 1.5 μm emission. In this work, we successfully demonstrated a novel n-i-p design for NIRPD applications. The conventional C-S n-i-p GaAsSb NWs exhibited PL emission at ~ 1.16 eV and ~ 1.22 eV at RT, while a modified configuration with higher Sb% showed a peak at ~ 0.83 eV and a distinct peak of ~ 1.07 eV at RT. The conventional C-S n-i-p configuration resulted in the high device performance C-S n-i-p GaAsSb NWs with responsivity and detectivity of 190 A/W and 1.1×10^{14} Jones for the 1.1 μm illumination wavelength. In contrast, the new design, hybrid axial C-S n-i-p structure, showed responsivity and detectivity of 18 A/W and 1.1×10^{13} Jones, respectively, for the 1.5 μm illumination wavelength. Following are the steps are taken to fabricate high-performance NIRPD.

- Electrostatic mapping from COMSOL simulation - The electrostatics mapping of the C-S n-i-p junction NW using COMSOL Multiphysics Modeling Software by varying thickness and dopant concentration of n-, i- and p- layer were performed. It was found that the electric field was still in the range of 100s of kV/cm for the variation in thickness and carrier concentration, thereby suggesting that the electric field does not significantly affects IRPD device performance.
- Firstly, the oxidation time was optimized for the vertical uniform growth of Te-doped GaAsSb on an n-type Si substrate. Then, a low-frequency noise (LFN)

measurement was carried out to determine the noise spectra of the device as well as the quality of the grown NWs.

- The substrate temperature for the initial growth of GaAs stem/GaAsSb was optimized for the dense vertical growth of NWs without using any sophisticated instruments like e-beam lithography (EBL) and nanoimprint lithography (NIL).
- The effect of the V/III ratio on the p- shell was examined to suppress the accumulation of Be and the enhancement of Be incorporation. The V/III ratio of 10 and high shell growth temperature were attributed to the beak-like NW tip formation. The V/III ratio was increased to 11 to suppress the mobility of Ga adatom, which plays a detrimental role in the formation of beak-like NW tip, resulting in a uniform NW tip.
- The pulsing of Te, an n-type dopant during the growth of the intrinsic shell, is employed to compensate for the p-type nature of GaAsSb. The success of this technique was demonstrated by enhanced detectivity, rectification ratio, and on-off ratio from the I-V characteristic of the ensemble PD device. The carrier concentration is found to be $1.4 \times 10^5 \text{ cm}^{-3}$ from the C-V measurement, which confirms the neutralization of p-type behavior. In addition, LFN measurement was carried out to provide better insight into the generation-recombination (G-R) noise components arising from the G-R centers. The decreased cut-off frequency and reduced noise observed in the Te compensated NW sample shows the suppression of G-R noise, which further demonstrated the effect of Te compensation on the suppression of the p-type nature of the intrinsic region.

- Sb% composition in the n-i-p layer was optimized to form a heterojunction, which creates an energy barrier. The energy barrier confines the injected charge carriers, thereby reducing the series resistance in the intrinsic region, the insertion loss compared to the homojunction, and suppressing the dark current (113, 114). A wide-bandgap p⁺ shell (Be-doped GaAs_{0.90}Sb_{0.10}) acts as a window for the light to enter the intrinsic region ((i- GaAs_{0.75}Sb_{0.25}). The wide-bandgap material of the n-i-p window determines the short-wavelength cut-off, while the small-bandgap of the intrinsic region decides the long-wavelength cut-off of the photoresponse (115). The heterojunction C-S n-i-p GaAsSb NW resulted in an RT-PL spectrum with emission peaks at ~1.16 eV and ~1.22 eV corresponding to the i- GaAs_{0.75}Sb_{0.25} and p- GaAs_{0.90}Sb_{0.10}, respectively.
- The effect of dopant concentration on n- core and p-shell was studied. The heavily doped n- and p- region provides a better n-i-p junction with comparatively low series resistance.
- The effect of Be- thickness was reported, and an increase in the rectification ratio was observed in thicker Be shells. The higher dark current and the lower rectification ratio in thin p-shell could be due to the pinning of high surface density at the p-shell to the Fermi level, as the metal-semiconductor p-shell interface is in the proximity of the intrinsic region.
- The variation in the intrinsic region width was investigated to realize the high-performance C-S n-i-p GaAsSb NW IRPD. An increase in the volume of the intrinsic region showed an enhanced responsivity and detectivity of 190 A/W and 1.1×10^{14} Jones, respectively, at -1V for the wavelength illumination of 1100 nm

for the ensemble PD, while for SNW, the responsivity and detectivity were found to be 21 mA/W and 1.4×10^{13} Jones, respectively, at -1 V for the wavelength irradiation of 860 nm. The improved device performance in SNW and ensemble PDs is attributed to the large volume available for the light to be absorbed and generate more photogenerated carriers in the intrinsic region. It was also found that the optical absorption and ohmic contact formation depends on the p- and i-segment thickness and dopant concentration of p- and n- segment. This work provided a better insight into the device performance of conventional C-S n-i-p junction configuration (Figure 1(a)), and their feedback was used to design a novel hybrid axial C-S structure to fabricate a high-quality C-S n-i-p junction (Figure 1(b)).

- The structure of the C-S n-i-p GaAsSb was redesigned in which a small segment of i-GaAsSb is grown on the core Te-doped GaAsSb, thereby improving the light absorption area for enhanced device performance, without compromising the series resistance.
- The NW growth was initiated with GaAs stem for 3 mins followed by Te-doped GaAs for 2 mins to eliminate the shunt current path.
- In this work, intrinsic shell Sb% is optimized for the emission at wavelength 1.5 μm and was determined to be of GaAs_{0.70}Sb_{0.30} composition, while a wide-bandgap GaAs_{0.90}Sb_{0.10} is grown as n-core and p-shell. In the case of ensemble PD, responsivity is calculated to be 18 A/W and detectivity of 1.1×10^{13} Jones at -1 V for the illumination of 1.5 μm wavelength.

- In-situ vacuum annealing after the growth of each n-, i-, p- segment is found to be an effective way for the formation of a uniform junction. From the C-V measurement, the positive capacitance of the NW sample was observed, depicting better junction formation. It is corroborated by a high rectification ratio of 122 and a low series resistance of 6.9×10^4 ohms.

This work is the first to report on the novel design, hybrid axial C-S n-i-p GaAsSb configuration with high room temperature detectivity in the range of 10^{13} Jones up to 1.5 μm wavelength and 1.1×10^{14} Jones at 1.1 μm in par with the current photodetectors present in the market. This work is in preparation to be submitted to a suitable journal for publication.

6.2 Future Work

As dopants play an important role in realizing advanced optoelectronic devices, a study on dopants using SKPM at low temperature and inert atmosphere will be helpful to understand the dopant distribution along the NWs. The successful demonstration of a novel design based on hybrid axial C-S n-i-p GaAsSb NWs as RT-NIRPD up to 1.5 μm wavelength emission paved the way to realize high-performance PD beyond 1.5 μm , and the novel design structure can expand to other designs that have not been conceived. The study of the intrinsic shell with variation in Sb%, V/III ratio, and dilute nitride GaAsSb NW as intrinsic can be explored to improve the PL emission beyond 1.5 μm . The patterned growth of C-S NWs would reduce parasitic growth and enable better PD performance. C-S configuration has more room to modify the structure, for instance, insertion of QW of AlGaAs to improve the figure of merits. A detailed study on the time response will be helpful to unleash the full potential of the C-S configuration.

References

1. Angizi S, Alem SAA, Azar MH, Shayeganfar F, Manning MI, Hatamie A, et al. A comprehensive review on planar boron nitride nanomaterials: From 2D nanosheets towards 0D quantum dots. *Progress in Materials Science*. 2022;124:100884.
2. García de Arquer, F Pelayo, Talapin DV, Klimov VI, Arakawa Y, Bayer M, Sargent EH. Semiconductor quantum dots: Technological progress and future challenges. *Science*. 2021;373(6555):eaaz8541.
3. Agarwal A, Misra G, Agarwal K. Semiconductor III–V Nanowires: Synthesis, Fabrication and Characterization of Nanodevices. *Journal of The Institution of Engineers (India): Series B*. 2021:1-11.
4. Fukata N, Rurali R. *Fundamental Properties of Semiconductor Nanowires*. Springer; 2021.
5. Kim H, Bae H, Chang T, Huffaker DL. III–V nanowires on silicon (100) as plasmonic-photonic hybrid meta-absorber. *Scientific Reports*. 2021;11(1):1-8.
6. Reznik RR, Kotlyar KP, Gridchin VO, Ilkiv IV, Khrebtov AI, Samsonenko YB, et al. III-V nanowires with quantum dots: MBE growth and properties. *Journal of Physics: Conference Series*; IOP Publishing; 2021.
7. Vaitiekėnas S, Liu Y, Krogstrup P, Marcus CM. Zero-bias peaks at zero magnetic field in ferromagnetic hybrid nanowires. *Nature Physics*. 2021;17(1):43-7.
8. Zhang L, Song T, Shi L, Wen N, Wu Z, Sun C, et al. Recent progress for silver nanowires conducting film for flexible electronics. *Journal of Nanostructure in Chemistry*. 2021;11(3):323-41.
9. Hu H, Qin M, Fong PW, Ren Z, Wan X, Singh M, et al. Perovskite Quantum Wells Formation Mechanism for Stable Efficient Perovskite Photovoltaics—A Real-Time Phase-Transition Study. *Adv Mater*. 2021;33(7):2006238.
10. Maserati L, Refaely-Abramson S, Kastl C, Chen CT, Borys NJ, Eisler CN, et al. Anisotropic 2D excitons unveiled in organic–inorganic quantum wells. *Materials Horizons*. 2021;8(1):197-208.
11. Meng Z, Mahler B, Houel J, Kulzer F, Ledoux G, Vasil'Ev A, et al. Perspectives for CdSe/CdS spherical quantum wells as rapid-response nano-scintillators. *Nanoscale*. 2021;13(46):19578-86.
12. Yu J, Dang C. Colloidal Metal Chalcogenide Quantum Wells for Laser Applications. *Cell Reports Physical Science*. 2021;2(1):100308.

13. Steiner MA, France RM, Buencuerpo J, Geisz JF, Nielsen MP, Pusch A, et al. High Efficiency Inverted GaAs and GaInP/GaAs Solar Cells With Strain-Balanced GaInAs/GaAsP Quantum Wells. *Advanced Energy Materials*. 2021;11(4):2002874.
14. Zhang Y, Sanchez AM, Aagesen M, Huo S, Fonseka HA, Gott JA, et al. Growth and Fabrication of High-Quality Single Nanowire Devices with Radial p-i-n Junctions. *Small*. 2019;15(3):1803684.
15. Kawaguchi K, Takahashi T, Okamoto N, Sato M. Demonstration of GaAsSb/InAs nanowire backward diodes grown using position-controlled vapor–liquid–solid method. *Applied Physics Express*. 2018;11(2):025001.
16. Butanovs E, Kuzmin A, Piskunov S, Smits K, Kalinko A, Polyakov B. Synthesis and characterization of GaN/ReS₂, ZnS/ReS₂ and ZnO/ReS₂ core/shell nanowire heterostructures. *Appl Surf Sci*. 2021;536:147841.
17. Ahmad E, Kasanaboina PK, Karim MR, Sharma M, Reynolds CL, Liu Y, et al. Te incorporation in GaAs_{1-x}Sb_x nanowires and pin axial structure. *Semiconductor Science and Technology*. 2016;31(12):125001.
18. Arif O, Zannier V, Rossi F, Ercolani D, Beltram F, Sorba L. Self-Catalyzed InSb/InAs Quantum Dot Nanowires. *Nanomaterials*. 2021;11(1):179.
19. Zhang F, Zhang X, Li Z, Yi R, Li Z, Wang N, et al. A new strategy for selective area growth of highly uniform InGaAs/InP multiple quantum well nanowire arrays for optoelectronic device applications. *Advanced Functional Materials*. 2021:2103057.
20. Cao L, White JS, Park J, Schuller JA, Clemens BM, Brongersma ML. Engineering light absorption in semiconductor nanowire devices. *Nature materials*. 2009;8(8):643-7.
21. Mokkaapati S, Jagadish C. Review on photonic properties of nanowires for photovoltaics. *Optics express*. 2016;24(15):17345-58.
22. Krogstrup P, Jørgensen HI, Heiss M, Demichel O, Holm JV, Aagesen M, et al. Single-nanowire solar cells beyond the Shockley–Queisser limit. *Nature photonics*. 2013;7(4):306-10.
23. Borg BM, Dick KA, Eymery J, Wernersson L. Enhanced Sb incorporation in InAsSb nanowires grown by metalorganic vapor phase epitaxy. *Appl Phys Lett*. 2011;98(11):113104.
24. Ghasemi M, Leshchenko ED, Johansson J. Assembling your nanowire: An overview of composition tuning in ternary III-V nanowires. *Nanotechnology*. 2020.
25. Chen C, Braidy N, Couteau C, Fradin C, Weihs G, LaPierre R. Multiple quantum well AlGaAs nanowires. *Nano letters*. 2008;8(2):495-9.

26. Mukherjee A, Ren D, Vullum P, Huh J, Fimland B, Weman H. GaAs/AlGaAs Nanowire Array Solar Cell Grown on Si with Ultrahigh Power-per-Weight Ratio. *ACS Photonics*. 2021;8(8):2355-66.
27. Ilkiv IV, Kotlyar KP, Kirilenko DA, Osipov AV, Soshnikov IP, Mikushev SV, et al. Formation of Hexagonal Ge Stripes on the Side Facets of AlGaAs Nanowires: Implications for Near-Infrared Detectors. *ACS Applied Nano Materials*. 2021;4(7):7289-94.
28. Anabestani H, Shazzad R, Al Fattah MF, Therrien J, Ban D. Review on GaAsSb Nanowire Potentials for Future 1D Heterostructures: Properties and Applications. *Materials Today Communications*. 2021:102542.
29. Li Z, Tan HH, Jagadish C, Fu L. III–V Compound Semiconductor Nanowire Solar Cells. *Atomic and Nano Scale Materials for Advanced Energy Conversion*. 2022;2:531-58.
30. Yuan X, Pan D, Zhou Y, Zhang X, Peng K, Zhao B, et al. Selective area epitaxy of III–V nanostructure arrays and networks: Growth, applications, and future directions. *Applied Physics Reviews*. 2021;8(2):021302.
31. LaPierre RR, Robson M, Azizur-Rahman KM, Kuyanov P. A review of III–V nanowire infrared photodetectors and sensors. *J Phys D*. 2017;50(12):123001.
32. Tan CL, Mohseni H. Emerging technologies for high performance infrared detectors. *Nanophotonics*. 2018;7(1):169-97.
33. Rouvié A, Reverchon J, Huet O, Djedidi A, Robo J, Truffer J, et al. InGaAs focal plane array developments at III-V Lab. *Infrared Technology and Applications XXXVIII*; International Society for Optics and Photonics; 2012.
34. Rogalski A, Chrzanowski K. Infrared devices and techniques (revision). *Metrology and Measurement Systems*. 2014;21(4).
35. Guan X, Yu X, Periyangounder D, Benzigar MR, Huang J, Lin C, et al. Recent progress in short-to long-wave infrared photodetection using 2D materials and heterostructures. *Advanced Optical Materials*. 2021;9(4):2001708.
36. Rogalski A. HgCdTe infrared detector material: history, status and outlook. *Reports on Progress in Physics*. 2005;68(10):2267.
37. Karimi M. Infrared Photodetectors based on Nanowire Arrays with Embedded Quantum Heterostructures [dissertation]. Lund University; 2020.
38. Gallo EM, Chen G, Currie M, McGuckin T, Prete P, Lovergine N, et al. Picosecond response times in GaAs/AlGaAs core/shell nanowire-based photodetectors. *Appl Phys Lett*. 2011;98(24):241113.

39. Deshmukh P, Li J, Nalamati S, Sharma M, Iyer S. Molecular beam epitaxial growth of GaAsSb/GaAsSbN/GaAlAs core-multishell nanowires for near-infrared applications. *Nanotechnology*. 2019;30(27):275203.
40. Soci C, Zhang A, Bao X, Kim H, Lo Y, Wang D. Nanowire photodetectors. *Journal of nanoscience and nanotechnology*. 2010;10(3):1430-49.
41. Shen L, Pun EY, Ho JC. Recent developments in III–V semiconducting nanowires for high-performance photodetectors. *Materials Chemistry Frontiers*. 2017;1(4):630-45.
42. Rogalski A. Infrared and terahertz detectors. CRC Press; 2019.
43. Chen H, Lai KWC, Sun X, Xi N, Meyyappan M. Indium Antimonide (InSb) Nanowire-Based Photodetectors. In: *Nano Optoelectronic Sensors and Devices*. Elsevier; 2012. p. 209-24.
44. Rogalski A, Adamiec K, Rutkowski J. Narrow-gap semiconductor photodiodes. SPIE Press; 2000.
45. Hou JJ, Han N, Wang F, Xiu F, Yip S, Hui AT, et al. Synthesis and characterizations of ternary InGaAs nanowires by a two-step growth method for high-performance electronic devices. *ACS nano*. 2012;6(4):3624-30.
46. Miao J, Hu W, Guo N, Lu Z, Zou X, Liao L, et al. Single InAs nanowire room-temperature near-infrared photodetectors. *ACS nano*. 2014;8(4):3628-35.
47. Miao J, Hu W, Guo N, Lu Z, Liu X, Liao L, et al. High-responsivity graphene/InAs nanowire heterojunction near-infrared photodetectors with distinct photocurrent on/off ratios. *small*. 2015;11(8):936-42.
48. Joyce HJ, Docherty CJ, Gao Q, Tan HH, Jagadish C, Lloyd-Hughes J, et al. Electronic properties of GaAs, InAs and InP nanowires studied by terahertz spectroscopy. *Nanotechnology*. 2013;24(21):214006.
49. Zhou C, Zhang X, Zheng K, Chen P, Lu W, Zou J. Self-assembly growth of In-rich InGaAs core-shell structured nanowires with remarkable near-infrared photoresponsivity. *Nano letters*. 2017;17(12):7824-30.
50. Tan H, Fan C, Ma L, Zhang X, Fan P, Yang Y, et al. Single-crystalline InGaAs nanowires for room-temperature high-performance near-infrared photodetectors. *Nano-micro letters*. 2016;8(1):29-35.
51. Zhang H, Wang W, Yip S, Li D, Li F, Lan C, et al. Enhanced performance of near-infrared photodetectors based on InGaAs nanowires enabled by a two-step growth method. *Journal of Materials Chemistry C*. 2020;8(47):17025-33.

52. Chiba K, Yoshida A, Tomioka K, Motohisa J. Vertical InGaAs nanowire array photodiodes on Si. *ACS Photonics*. 2019;6(2):260-4.
53. Ren P, Hu W, Zhang Q, Zhu X, Zhuang X, Ma L, et al. Band-selective infrared photodetectors with complete-composition-range InAs_xP_{1-x} alloy nanowires. *Adv Mater*. 2014;26(44):7444-9.
54. Li D, Yip S, Li F, Zhang H, Meng Y, Bu X, et al. Flexible Near-Infrared InGaSb Nanowire Array Detectors with Ultrafast Photoconductive Response Below 20 μ s. *Advanced Optical Materials*. 2020;8(22):2001201.
55. Ma L, Hu W, Zhang Q, Ren P, Zhuang X, Zhou H, et al. Room-temperature near-infrared photodetectors based on single heterojunction nanowires. *Nano letters*. 2014;14(2):694-8.
56. Li Z, Yuan X, Fu L, Peng K, Wang F, Fu X, et al. Room temperature GaAsSb single nanowire infrared photodetectors. *Nanotechnology*. 2015;26(44):445202.
57. Li Z, Yuan X, Gao Q, Yang I, Li L, Caroff P, et al. In situ passivation of GaAsSb nanowires for enhanced infrared photoresponse. *Nanotechnology*. 2020;31(24):244002.
58. Sharma M, Ahmad E, Dev D, Li J, Reynolds CL, Liu Y, et al. Improved performance of GaAsSb/AlGaAs nanowire ensemble Schottky barrier based photodetector via in situ annealing. *Nanotechnology*. 2018;30(3):034005.
59. Devkota S, Parakh M, Johnson S, Ramaswamy P, Lowe M, Penn A, et al. A study of n-doping in self-catalyzed GaAsSb nanowires using GaTe dopant source and ensemble nanowire near-infrared photodetector. *Nanotechnology*. 2020;31(50):505203.
60. Pokharel R, Ramaswamy P, Devkota S, Parakh M, Dawkins K, Penn A, et al. Epitaxial high-yield intrinsic and Te-doped dilute nitride GaAsSbN nanowire heterostructure and ensemble photodetector application. *ACS Applied Electronic Materials*. 2020;2(9):2730-8.
61. Schmidt V, Wittemann JV, Senz S, Gösele U. Silicon nanowires: a review on aspects of their growth and their electrical properties. *Adv Mater*. 2009;21(25-26):2681-702.
62. Das S, Dhyani V, Georgiev YM, Williams DA. High sensitivity silicon single nanowire junctionless phototransistor. *Appl Phys Lett*. 2016;108(6):063113.
63. Liang F, Wang J, Li Z, Luo L. Near-infrared-light photodetectors based on one-dimensional inorganic semiconductor nanostructures. *Advanced Optical Materials*. 2017;5(14):1700081.
64. Zeng L, Wang M, Hu H, Nie B, Yu Y, Wu C, et al. Monolayer graphene/germanium Schottky junction as high-performance self-driven infrared light photodetector. *ACS applied materials & interfaces*. 2013;5(19):9362-6.

65. Lu R, Ge C, Zou Y, Zheng K, Wang D, Zhang T, et al. A localized surface plasmon resonance and light confinement-enhanced near-infrared light photodetector. *Laser & Photonics Reviews*. 2016;10(4):595-602.
66. Lu R, Christianson C, Weintrub B, Wu JZ. High photoresponse in hybrid graphene–carbon nanotube infrared detectors. *ACS applied materials & interfaces*. 2013;5(22):11703-7.
67. Zheng D, Fang H, Long M, Wu F, Wang P, Gong F, et al. High-performance near-infrared photodetectors based on p-type SnX (X= S, Se) nanowires grown via chemical vapor deposition. *ACS nano*. 2018;12(7):7239-45.
68. Shen G, Chen H, Lou Z. Growth of aligned SnS nanowire arrays for near infrared photodetectors. *Journal of Semiconductors*. 2020;41(4):042602.
69. Sharma A, Bhattacharyya B, Srivastava AK, Senguttuvan TD, Husale S. High performance broadband photodetector using fabricated nanowires of bismuth selenide. *Scientific reports*. 2016;6(1):1-8.
70. Wang Z, Safdar M, Jiang C, He J. High-performance UV–visible–NIR broad spectral photodetectors based on one-dimensional In₂Te₃ nanostructures. *Nano letters*. 2012;12(9):4715-21.
71. Liu HY, Qiu Y, Jin CY, Walther T, Cullis AG. 1.55 μ m InAs quantum dots grown on a GaAs substrate using a GaAsSb metamorphic buffer layer. *Appl Phys Lett*. 2008;92(11):111906.
72. Koblmüller G, Abstreiter G. Growth and properties of InGaAs nanowires on silicon. *physica status solidi (RRL)–Rapid Research Letters*. 2014;8(1):11-30.
73. Wolfstetter A, Geyer N, Nguyen-Duc T, Kanungo PD, Zakharov ND, Reiche M, et al. Comparison of the top-down and bottom-up approach to fabricate nanowire-based silicon/germanium heterostructures. *Thin Solid Films*. 2010;518(9):2555-61.
74. Zeng X, Zhang W, Zou X, Su X, Yartsev A, Borgström MT. In situ passivation of Ga_xIn_(1-x)P nanowires using radial Al_yIn_(1-y)P shells grown by MOVPE. *Nanotechnology*. 2021;32(42):425705.
75. Okuno K, Mizutani K, Iida K, Ohya M, Sone N, Lu W, et al. Room temperature pulsed operation of nitride nanowire-based multi-quantum shell laser diodes by MOVPE. *Applied Physics Express*. 2021.
76. Kakkerla RK, Hsiao C, Anandan D, Singh SK, Chang S, Pande KP, et al. Growth and crystal structure investigation of InAs/GaSb heterostructure nanowires on Si substrate. *IEEE Transactions on Nanotechnology*. 2018;17(6):1151-8.

77. Yang X, Du W, Ji X, Zhang X, Yang T. Defect-free InAsSb nanowire arrays on Si substrates grown by selective-area metal–organic chemical vapor deposition. *Nanotechnology*. 2018;29(40):405601.
78. Ren D, Ahtapodov L, van Helvoort AT, Weman H, Fimland B. Epitaxially grown III-arsenide-antimonide nanowires for optoelectronic applications. *Nanotechnology*. 2019;30(29):294001.
79. Yip S, Li D, Li F, Wang W, Kang X, Meng Y, et al. Unusual phase-pure zinc blende and highly-crystalline As-rich InAs $1-x$ Sb x nanowires for high-mobility transistors. *Journal of Materials Chemistry C*. 2020;8(38):13189-96.
80. Fedorov VV, Bolshakov AD, Dvoretckaia LN, Sapunov GA, Kirilenko DA, Mozharov AM, et al. Self-Catalyzed MBE-Grown GaP Nanowires on Si (111): V/III Ratio Effects on the Morphology and Crystal Phase Switching. *Semiconductors*. 2018;52(16):2092-5.
81. Joyce HJ, Gao Q, Tan HH, Jagadish C, Kim Y, Zou J, et al. III–V semiconductor nanowires for optoelectronic device applications. *Progress in Quantum Electronics*. 2011;35(2-3):23-75.
82. Maliakkal CB, Jacobsson D, Tornberg M, Persson AR, Johansson J, Wallenberg R, et al. In situ analysis of catalyst composition during gold catalyzed GaAs nanowire growth. *Nature communications*. 2019;10(1):1-9.
83. Zhang Y, Aagesen M, Holm JV, Jørgensen HI, Wu J, Liu H. Self-catalyzed GaAsP nanowires grown on silicon substrates by solid-source molecular beam epitaxy. *Nano letters*. 2013;13(8):3897-902.
84. Koivusalo ES, Hakkarainen TV, Guina MD, Dubrovskii VG. Sub-Poissonian narrowing of length distributions realized in Ga-catalyzed GaAs nanowires. *Nano letters*. 2017;17(9):5350-5.
85. Matteini F, Dubrovskii VG, Rüffer D, Tütüncüoğlu G, Fontana Y, Morral AFI. Tailoring the diameter and density of self-catalyzed GaAs nanowires on silicon. *Nanotechnology*. 2015;26(10):105603.
86. Priante G, Glas F, Patriarche G, Pantzas K, Oehler F, Harmand J. Sharpening the interfaces of axial heterostructures in self-catalyzed AlGaAs nanowires: experiment and theory. *Nano letters*. 2016;16(3):1917-24.
87. Cirlin GE, Dubrovskii VG, Samsonenko YB, Bouravleuv AD, Durose K, Proskuryakov YY, et al. Self-catalyzed, pure zincblende GaAs nanowires grown on Si (111) by molecular beam epitaxy. *Physical Review B*. 2010;82(3):035302.
88. R Reznik R, P Kotlyar K, O Gridchin V, V Ubyivovk E, V Federov V, I Khrebtov A, et al. Low-Temperature In-Induced Holes Formation in Native-SiO_x/Si (111) Substrates for Self-Catalyzed MBE Growth of GaAs Nanowires. *Materials*. 2020;13(16):3449.

89. Colombo C, Spirkoska D, Frimmer M, Abstreiter G, i Morral AF. Ga-assisted catalyst-free growth mechanism of GaAs nanowires by molecular beam epitaxy. *Physical Review B*. 2008;77(15):155326.
90. Gao Q, Dubrovskii VG, Caroff P, Wong-Leung J, Li L, Guo Y, et al. Simultaneous selective-area and vapor–liquid–solid growth of InP nanowire arrays. *Nano letters*. 2016;16(7):4361-7.
91. Boras G, Yu X, Fonseka HA, Davis G, Velichko AV, Gott JA, et al. Self-Catalyzed AlGaAs Nanowires and AlGaAs/GaAs Nanowire-Quantum Dots on Si Substrates. *The Journal of Physical Chemistry C*. 2021.
92. Ma L, Zhang X, Li H, Tan H, Yang Y, Xu Y, et al. Bandgap-engineered GaAsSb alloy nanowires for near-infrared photodetection at 1.31 μm . *Semiconductor Science and Technology*. 2015;30(10):105033.
93. Huh J, Yun H, Kim D, Munshi AM, Dheeraj DL, Kauko H, et al. Rectifying single GaAsSb nanowire devices based on self-induced compositional gradients. *Nano letters*. 2015;15(6):3709-15.
94. Nalamati S, Sharma M, Deshmukh P, Kronz J, Lavelle R, Snyder D, et al. A Study of GaAs $_{1-x}$ Sb $_x$ Axial Nanowires Grown on Monolayer Graphene by Ga-Assisted Molecular Beam Epitaxy for Flexible Near-Infrared Photodetectors. *ACS Applied Nano Materials*. 2019;2(7):4528-37.
95. Zhang Y, Liu H. Nanowires for high-efficiency, low-cost solar photovoltaics. *Crystals*. 2019;9(2):87.
96. Neamen DA. *Semiconductor physics and devices: basic principles*. McGraw-hill; 2003.
97. Longshore RE. MCT properties, growth methods and characterization. In: *Handbook of Infra-red Detection Technologies*. Elsevier; 2002. p. 233-67.
98. Agnihotri SK, Samajdar DP, Prashant DV, Arefinia Z. Numerical analysis of InP based high efficiency radial junction nanowire solar cell. *Optical Materials*. 2021;119:111365.
99. Martinez GL, Curiel MR, Skromme BJ, Molnar RJ. Surface recombination and sulfide passivation of GaN. *J Electron Mater*. 2000;29(3):325-31.
100. Christesen JD, Zhang X, Pinion CW, Celano TA, Flynn CJ, Cahoon JF. Design principles for photovoltaic devices based on Si nanowires with axial or radial p–n junctions. *Nano letters*. 2012;12(11):6024-9.
101. Scofield AC, Lin A, Shapiro JN, Senanayake PN, Mariani G, Haddad M, et al. Composite axial/core-shell nanopillar light-emitting diodes at 1.3 μm . *Appl Phys Lett*. 2012;101(5):053111.

102. Calarco R, Marso M, Richter T, Aykanat AI, Meijers R, vd Hart A, et al. Size-dependent photoconductivity in MBE-grown GaN– nanowires. *Nano letters*. 2005;5(5):981-4.
103. Gutsche C, Niepelt R, Gnauck M, Lysov A, Prost W, Ronning C, et al. Direct determination of minority carrier diffusion lengths at axial GaAs nanowire p–n junctions. *Nano letters*. 2012;12(3):1453-8.
104. Dai X, Zhang S, Wang Z, Adamo G, Liu H, Huang Y, et al. GaAs/AlGaAs nanowire photodetector. *Nano letters*. 2014;14(5):2688-93.
105. Li H, Alradhi H, Jin Z, Anyebe EA, Sanchez AM, Linhart WM, et al. Novel Type-II InAs/AlSb Core–Shell Nanowires and Their Enhanced Negative Photocurrent for Efficient Photodetection. *Advanced Functional Materials*. 2018;28(8):1705382.
106. Wang X, Pan D, Han Y, Sun M, Zhao J, Chen Q. Vis–IR Wide-Spectrum Photodetector at Room Temperature Based on p–n Junction-Type GaAs_{1–x}Sb_x/InAs Core–Shell Nanowire. *ACS applied materials & interfaces*. 2019;11(42):38973-81.
107. Wang W, Yip S, Meng Y, Wang W, Wang F, Bu X, et al. Antimony-Rich GaAs_xSb_{1–x} Nanowires Passivated by Organic Sulfides for High-Performance Transistors and Near-Infrared Photodetectors. *Advanced Optical Materials*. 2021;9(22):2101289.
108. Sharma M, Deshmukh P, Kasanaboina P, Reynolds CL, Liu Y, Iyer S. Growth of defect-free GaAsSbN axial nanowires via self-catalyzed molecular beam epitaxy. *Semiconductor Science and Technology*. 2017;32(12):125003.
109. Ojha SK, Kasanaboina PK, Lewis Reynolds Jr C, Rawdanowicz TA, Liu Y, White RM, et al. Incorporation of Be dopant in GaAs core and core–shell nanowires by molecular beam epitaxy. *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena*. 2016;34(2):02L114.
110. Chia A, Boulanger JP, LaPierre RR. Unlocking doping and compositional profiles of nanowire ensembles using SIMS. *Nanotechnology*. 2013;24(4):045701.
111. Toginho Filho DO, Dias I, Duarte JL, Laureto E, Harmand JC. Photoluminescence properties of Te doped AlGaAsSb alloys. *Brazilian journal of physics*. 2005;35(4a):999-1005.
112. Jie JS, Zhang WJ, Jiang Y, Meng XM, Li YQ, Lee ST. Photoconductive characteristics of single-crystal CdS nanoribbons. *Nano letters*. 2006;6(9):1887-92.
113. Hoag DR, Boles TE, Brogle JJ. No title. Heterojunction PIN diode and method of making the same. 2004.
114. Boles T, Brogle J, Hoag D, Carlson D. AlGaAs anode heterojunction PIN diodes. *physica status solidi c*. 2013;10(5):786-9.

115. Ahmed R, Abbas S. Electrical and Optical Characteristics of InP Nanowires based pin Photodetectors. . 2010.
116. Thorlabs [Internet]. []. Available from: <https://www.thorlabs.com/>.
117. Xiang H, Xin C, Hu Z, Aigouy L, Chen Z, Yuan X. Long-Term Stable Near-Infrared–Short-Wave-Infrared Photodetector Driven by the Photothermal Effect of Polypyrrole Nanostructures. *ACS Applied Materials & Interfaces*. 2021;13(38):45957-65.
118. Siala S, Naydenkov M, Roucka R, Maros A, Gao L, Ding D, et al. Dilute nitride photodetector arrays for sensing applications. *Optical Components and Materials XVII*; International Society for Optics and Photonics; 2020.
119. Tan WC, Huang L, Ng RJ, Wang L, Hasan DMN, Duffin TJ, et al. A black phosphorus carbide infrared phototransistor. *Adv Mater*. 2018;30(6):1705039.
120. Kasanaboina PK, Ojha SK, Sami SU, Reynolds CL, Liu Y, Iyer S. Bandgap tuning of GaAs/GaAsSb core-shell nanowires grown by molecular beam epitaxy. *Semiconductor Science and Technology*. 2015;30(10):105036.
121. Ramaswamy P, Devkota S, Pokharel R, Nalamati S, Stevie F, Jones K, et al. A study of dopant incorporation in Te-doped GaAsSb nanowires using a combination of XPS/UPS, and C-AFM/SKPM. *Scientific reports*. 2021;11(1):1-14.
122. Stevie FA, Donley CL. Introduction to x-ray photoelectron spectroscopy. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*. 2020;38(6):063204.
123. Crist BV. A critical review of popular XPS data-banks. *Crit.Rev*. 1996;2:15.
124. Powell CJ. NIST Data Resources for X-Ray Photoelectron Spectroscopy. . 2000.
125. Chastain J, King Jr RC. Handbook of X-ray photoelectron spectroscopy. Perkin-Elmer Corporation. 1992;40:221.
126. Greczynski G, Hultman L. X-ray photoelectron spectroscopy: towards reliable binding energy referencing. *Progress in Materials Science*. 2020;107:100591.
127. Major GH, Fairley N, Sherwood PM, Linford MR, Terry J, Fernandez V, et al. Practical guide for curve fitting in x-ray photoelectron spectroscopy. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*. 2020;38(6):061203.
128. Teichert C, Beinik I. Conductive atomic-force microscopy investigation of nanostructures in microelectronics. In: *Scanning Probe Microscopy in Nanoscience and Nanotechnology 2*. Springer; 2011. p. 691-721.

129. Gutsche C, Regolin I, Blekker K, Lysov A, Prost W, Tegude FJ. Controllable p-type doping of GaAs nanowires during vapor-liquid-solid growth. *J Appl Phys*. 2009;105(2):024305.
130. Goktas NI, Fiordaliso EM, LaPierre RR. Doping assessment in GaAs nanowires. *Nanotechnology*. 2018;29(23):234001.
131. Suomalainen S, Hakkarainen TV, Salminen T, Koskinen R, Honkanen M, Luna E, et al. Te-doping of self-catalyzed GaAs nanowires. *Appl Phys Lett*. 2015;107(1):012101.
132. Schmidt V, Mensch PF, Karg SF, Gotsmann B, Das Kanungo P, Schmid H, et al. Using the Seebeck coefficient to determine charge carrier concentration, mobility, and relaxation time in InAs nanowires. *Appl Phys Lett*. 2014;104(1):012113.
133. Dubrovskii VG, Hijazi H, Goktas NI, LaPierre RR. Be, Te, and Si doping of GaAs nanowires: Theory and experiment. *The Journal of Physical Chemistry C*. 2020;124(31):17299-307.
134. LaPierre RR, Chia A, Gibson SJ, Haapamaki CM, Boulanger J, Yee R, et al. III–V nanowire photovoltaics: review of design for high efficiency. *physica status solidi (RRL)–Rapid Research Letters*. 2013;7(10):815-30.
135. Storm K, Halvardsson F, Heurlin M, Lindgren D, Gustafsson A, Wu PM, et al. Spatially resolved Hall effect measurement in a single semiconductor nanowire. *Nature nanotechnology*. 2012;7(11):718-22.
136. Chen H, Himwas C, Scaccabarozzi A, Rale P, Oehler F, Lemaître A, et al. Determination of n-type doping level in single GaAs nanowires by cathodoluminescence. *Nano letters*. 2017;17(11):6667-75.
137. Salehzadeh O, Kavanagh KL, Watkins SP. Controlled axial and radial Te-doping of GaAs nanowires. *J Appl Phys*. 2012;112(5):054324.
138. Li L. Electron holography of nanowires–Part 1. In: *Semiconductor Nanowires*. Elsevier; 2015. p. 221-51.
139. Wolf D, Lichte H, Pozzi G, Prete P, Lovergine N. Electron holographic tomography for mapping the three-dimensional distribution of electrostatic potential in III-V semiconductor nanowires. *Appl Phys Lett*. 2011;98(26):264103.
140. Hakkarainen T, Piton MR, Fiordaliso EM, Leshchenko ED, Koelling S, Bettini J, et al. Te incorporation and activation as n-type dopant in self-catalyzed GaAs nanowires. *Physical Review Materials*. 2019;3(8):086001.
141. Devaraj A, Perea DE, Liu J, Gordon LM, Prosa TJ, Parikh P, et al. Three-dimensional nanoscale characterisation of materials by atom probe tomography. *International Materials Reviews*. 2018;63(2):68-101.

142. Perea DE, Hemesath ER, Schwalbach EJ, Lensch-Falk JL, Voorhees PW, Lauhon LJ. Direct measurement of dopant distribution in an individual vapour–liquid–solid nanowire. *Nature nanotechnology*. 2009;4(5):315-9.
143. Du S, Burgess T, Gault B, Gao Q, Bao P, Li L, et al. Quantitative dopant distributions in GaAs nanowires using atom probe tomography. *Ultramicroscopy*. 2013;132:186-92.
144. Qu J, Choi W, Katal Mohseni P, Li X, Zhang Y, Chen H, et al. Direct observation of dopants distribution and diffusion in GaAs planar nanowires with atom probe tomography. *ACS Applied Materials & Interfaces*. 2016;8(39):26244-50.
145. Orrù M, Repiso E, Carapezzi S, Henning A, Roddaro S, Franciosi A, et al. A roadmap for controlled and efficient n-type doping of self-assisted GaAs nanowires grown by molecular beam epitaxy. *Advanced Functional Materials*. 2016;26(17):2836-45.
146. Kwoka M, Lyson-Sypien B, Kulis A, Zappa D, Comini E. Surface properties of SnO₂ nanowires deposited on Si substrate covered by Au catalyst studies by XPS, TDS and SEM. *Nanomaterials*. 2018;8(9):738.
147. Barnett CJ, Castaing A, Jones DR, Lewis AR, Jenkins LJ, Cobley RJ, et al. XPS investigation of titanium contact formation to ZnO nanowires. *Nanotechnology*. 2017;28(8):085301.
148. Khan MA, Wahab Y, Muhammad R, Tahir M, Sakrani S. Catalyst-free fabrication of novel ZnO/CuO core-shell nanowires heterojunction: Controlled growth, structural and optoelectronic properties. *Appl Surf Sci*. 2018;435:718-32.
149. Miyoshi K. Surface characterization techniques: An overview. CRC Press; 2004.
150. Park JH, Pozuelo M, Setiawan BP, Chung C. Self-catalyzed growth and characterization of In (As) P nanowires on InP (111) B using metal-organic chemical vapor deposition. *Nanoscale Research Letters*. 2016;11(1):1-7.
151. Timm R, Hjort M, Fian A, Borg BM, Thelander C, Andersen JN, et al. Interface composition of InAs nanowires with Al₂O₃ and HfO₂ thin films. *Appl Phys Lett*. 2011;99(22):222907.
152. Lin H, Liu N, Shi Z, Guo Y, Tang Y, Gao Q. Cobalt-doping in molybdenum-carbide nanowires toward efficient electrocatalytic hydrogen evolution. *Advanced Functional Materials*. 2016;26(31):5590-8.
153. Liang Y. Ge-doped ZnO nanowire arrays as cold field emitters with excellent performance. *Nanotechnology*. 2019;30(37):375603.
154. May BJ, Selcu CM, Sarwar A, Myers RC. Nanoscale current uniformity and injection efficiency of nanowire light emitting diodes. *Appl Phys Lett*. 2018;112(9):093107.

155. Asres GA, Järvinen T, Lorite GS, Mohl M, Pitkänen O, Dombóvari A, et al. High photoresponse of individual WS₂ nanowire-nanoflake hybrid materials. *Appl Phys Lett*. 2018;112(23):233103.
156. Du W, Yang X, Pan H, Ji X, Ji H, Luo S, et al. Controlled-direction growth of planar InAsSb nanowires on Si substrates without foreign catalysts. *Nano letters*. 2016;16(2):877-82.
157. McKibbin SR, Colvin J, Troian A, Knutsson JV, Webb JL, Otnes G, et al. Operando surface characterization of InP nanowire p–n junctions. *Nano letters*. 2019;20(2):887-95.
158. Parida S, Sahoo AR, Madapu KK, Jaya SM, Dhara S. Role of the surface density of states in understanding size-dependent surface band bending in GaN nanowires. *Appl Surf Sci*. 2020;510:145502.
159. Abbas S, Kumar M, Kim D, Kim J. Translucent Photodetector with Blended Nanowires–Metal Oxide Transparent Selective Electrode Utilizing Photovoltaic and Pyro-Phototronic Coupling Effect. *Small*. 2019;15(10):1804346.
160. Mikulik D, Ricci M, Tutuncuoglu G, Matteini F, Vukajlovic J, Vulic N, et al. Conductive-probe atomic force microscopy as a characterization tool for nanowire-based solar cells. *Nano Energy*. 2017;41:566-72.
161. Koren E, Berkovitch N, Rosenwaks Y. Measurement of active dopant distribution and diffusion in individual silicon nanowires. *Nano letters*. 2010;10(4):1163-7.
162. Xia H, Yao B, Lu Z, Chen P, Li T. Photoconductive study and carrier dynamics of vertically aligned GaAs nanowires. *Progress in Natural Science: Materials International*. 2013;23(1):85-8.
163. Geydt P, Alekseev PA, Dunaevskiy MS, Haggrén T, Kakko J, Lähderanta E, et al. Influence of surface passivation on electric properties of individual GaAs nanowires studied by current–voltage AFM measurements. *Lithuanian Journal of Physics*. 2016;56(2).
164. Sun X, Wang X, Wang P, Sheng B, Li M, Su J, et al. Identifying a doping type of semiconductor nanowires by photoassisted kelvin probe force microscopy as exemplified for GaN nanowires. *Optical Materials Express*. 2017;7(3):904-12.
165. Ramaswamy P, Pokharel R, Parakh M, Jones K, Li J, Iyer S. Be-doping assessment in Self-Catalyzed MBE Grown GaAs Nanowires. *CLEO: Science and Innovations; Optical Society of America*; 2021.
166. Costa IM, Colmenares YN, Pizani PS, Leite ER, Chiquito AJ. Sb doping of VLS synthesized SnO₂ nanowires probed by Raman and XPS spectroscopy. *Chemical Physics Letters*. 2018;695:125-30.

167. Pulzara-Mora C, Pulzara-Mora A, Forero-Pico A, Ayerbe-Samaca M, Marques-Marchan J, Asenjo A, et al. Structural, morphological and magnetic properties of GaSbMn/Si (111) thin films prepared by radio frequency magnetron sputtering. *Thin Solid Films*. 2020;705:137971.
168. Cossu G, Ingo GM, Mattogno G, Padeletti G, Proietti GM. XPS investigation on vacuum thermal desorption of UV/ozone treated GaAs (100) surfaces. *Appl Surf Sci*. 1992;56:81-8.
169. Ghita RV, Logofatu C, Negrila C, Trupina L, Cotirlan-Simioniuc C. Surface Modification of III-V compounds substrates for processing technology. *Nanoscaled Films Layers*. 2017;115.
170. Tereshchenko OE, Bakulin AV, Kulkova SE, Ereemeev SV. Backward reconstructions on GaAs (001) surface induced by atomic hydrogen reactions: Surfactant-assisted low-temperature surface ordering. *The Journal of Physical Chemistry C*. 2013;117(19):9723-33.
171. Assebban M, Gibaja C, Fickert M, Torres I, Weinreich E, Wolff S, et al. Unveiling the oxidation behavior of liquid-phase exfoliated antimony nanosheets. *2D Materials*. 2020;7(2):025039.
172. Hofmann S. Typical Applications of AES and XPS. In: *Auger-and X-Ray Photoelectron Spectroscopy in Materials Science*. Springer; 2013. p. 451-85.
173. Reese MO, Perkins CL, Burst JM, Farrell S, Barnes TM, Johnston SW, et al. Intrinsic surface passivation of CdTe. *J Appl Phys*. 2015;118(15):155305.
174. Kim CK, Zhou H, Kowalewski T, Matyjaszewski K, Kim HK. Soft-templated tellurium-doped mesoporous carbon as a Pt-free electrocatalyst for high-performance dye-sensitized solar cells. *ACS applied materials & interfaces*. 2018;11(2):2093-102.
175. Hwang JO, Lee DH, Kim JY, Han TH, Kim BH, Park M, et al. Vertical ZnO nanowires/graphene hybrids for transparent and flexible field emission. *Journal of Materials Chemistry*. 2011;21(10):3432-7.
176. Borghs G, Bhattacharyya K, Deneffe K, Van Mieghem P, Mertens R. Band-gap narrowing in highly doped n-and p-type GaAs studied by photoluminescence spectroscopy. *J Appl Phys*. 1989;66(9):4381-6.
177. Padovani FA, Stratton R. Field and thermionic-field emission in Schottky barriers. *Solid-State Electronics*. 1966;9(7):695-707.
178. Parakh M, Johnson S, Pokharel R, Ramaswamy P, Nalamati S, Li J, et al. Space charge limited conduction mechanism in GaAsSb nanowires and the effect of in situ annealing in ultra-high vacuum. *Nanotechnology*. 2019;31(2):025205.
179. Gan X, Zheng X, Wu Y, Lu S, Yang H, Arimochi M, et al. GaAs tunnel junction grown using tellurium and magnesium as dopants by solid-state molecular beam epitaxy. *Japanese Journal of Applied Physics*. 2014;53(2):021201.

180. Hamon G, Paillet N, Alvarez J, Larrue A, Decobert J. Te doping of GaAs and GaInP using diisopropyl telluride (DIPTe) for tunnel junction applications. *J Cryst Growth*. 2018;498:301-6.
181. Massies J, Grandjean N. Surfactant effect on the surface diffusion length in epitaxial growth. *Physical Review B*. 1993;48(11):8502.
182. Czaban JA, Thompson DA, LaPierre RR. GaAs core– shell nanowires for photovoltaic applications. *Nano letters*. 2009;9(1):148-54.
183. Bennett BR, Magno R, Papanicolaou N. Controlled n-type doping of antimonides and arsenides using GaTe. *J Cryst Growth*. 2003;251(1-4):532-7.
184. Zhou N, Wang R, Zhou X, Song H, Xiong X, Ding Y, et al. P-GaSe/N-MoS₂ vertical heterostructures synthesized by van der Waals epitaxy for photoresponse modulation. *Small*. 2018;14(7):1702731.
185. Hajimammadov R, Bykov A, Popov A, Juhasz KL, Lorite GS, Mohl M, et al. Random networks of core-shell-like Cu-Cu₂O/CuO nanowires as surface plasmon resonance-enhanced sensors. *Scientific reports*. 2018;8(1):1-8.
186. Salerno M, Dante S. Scanning Kelvin probe microscopy: challenges and perspectives towards increased application on biomaterials and biological samples. *Materials*. 2018;11(6):951.
187. Tomioka K, Ikejiri K, Tanaka T, Motohisa J, Hara S, Hiruma K, et al. Selective-area growth of III-V nanowires and their applications. *J Mater Res*. 2011;26(17):2127-41.
188. Hall RN. Electron-hole recombination in germanium. *Physical review*. 1952;87(2):387.
189. Shockley W, Read Jr WT. Statistics of the recombinations of holes and electrons. *Physical review*. 1952;87(5):835.
190. Demichel O, Heiss M, Bleuse J, Mariette H, Fontcuberta i Morral A. Impact of surfaces on the optical properties of GaAs nanowires. *Appl Phys Lett*. 2010;97(20):201907.
191. Dhaka V, Perros A, Naureen S, Shahid N, Jiang H, Kakko J, et al. Protective capping and surface passivation of III-V nanowires by atomic layer deposition. *AIP Advances*. 2016;6(1):015016.
192. Signorello G, Sant S, Bologna N, Schraff M, Drechsler U, Schmid H, et al. Manipulating surface states of III–V nanowires with uniaxial stress. *Nano letters*. 2017;17(5):2816-24.
193. Van Weert M, Wunnicke O, Roest AL, Eijkemans TJ, Yu Silov A, Haverkort J, et al. Large redshift in photoluminescence of p-doped InP nanowires induced by Fermi-level pinning. *Appl Phys Lett*. 2006;88(4):043109.

194. Katzenmeyer AM, Léonard F, Talin AA, Wong P, Huffaker DL. Poole– Frenkel effect and phonon-assisted tunneling in GaAs nanowires. *Nano letters*. 2010;10(12):4935-8.
195. Chang C, Chi C, Yao M, Huang N, Chen C, Theiss J, et al. Electrical and optical characterization of surface passivation in GaAs nanowires. *Nano letters*. 2012;12(9):4484-9.
196. Tajik N, Peng Z, Kuyanov P, LaPierre RR. Sulfur passivation and contact methods for GaAs nanowire solar cells. *Nanotechnology*. 2011;22(22):225402.
197. Alekseev PA, Dunaevskiy MS, Ulin VP, Lvova TV, Filatov DO, Nezhdanov AV, et al. Nitride surface passivation of GaAs nanowires: impact on surface state density. *Nano letters*. 2015;15(1):63-8.
198. Dai X, Zhang S, Wang Z, Adamo G, Liu H, Huang Y, et al. GaAs/AlGaAs nanowire photodetector. *Nano letters*. 2014;14(5):2688-93.
199. Sköld N, Karlsson LS, Larsson MW, Pistol M, Seifert W, Trägårdh J, et al. Growth and Optical Properties of Strained GaAs– Ga x In1-x P Core– Shell Nanowires. *Nano letters*. 2005;5(10):1943-7.
200. Riikonen J, Sormunen J, Koskenvaara H, Mattila M, Sopanen M, Lipsanen H. Passivation of GaAs surface by ultrathin epitaxial GaN layer. *J Cryst Growth*. 2004;272(1-4):621-6.
201. Kasu M, Makimoto T, Kobayashi N. Anisotropic surface morphology of GaAs (001) surfaces passivated with nitrogen radicals. *Appl Phys Lett*. 1996;68(7):955-7.
202. Fujieda S, Mizuta M, Matsumoto Y. Low-temperature metalorganic chemical vapour deposition of AlN for surface passivation of GaAs. *Advanced Materials for Optics and Electronics*. 1996;6(3):127-34.
203. Lipsanen H, Sopanen M, Taskinen M, Tulkki J, Ahopelto J. Enhanced optical properties of in situ passivated near-surface Al x Ga1– x As/GaAs quantum wells. *Appl Phys Lett*. 1996;68(16):2216-8.
204. Kwo J, Murphy DW, Hong M, Opila RL, Mannaerts JP, Sergent AM, et al. Passivation of GaAs using (Ga₂O₃)_{1–x}(Gd₂O₃)_x, 0 ≤ x ≤ 1.0 films. *Appl Phys Lett*. 1999;75(8):1116-8.
205. Aierken A, Riikonen J, Mattila M, Hakkarainen T, Sopanen M, Lipsanen H. GaAs surface passivation by ultra-thin epitaxial GaP layer and surface As–P exchange. *Appl Surf Sci*. 2007;253(14):6232-5.
206. Beaudry R, Watkins SP, Xu X, Yeo P. Photoreflectance study of phosphorus passivation of GaAs (001). *J Appl Phys*. 2000;87(11):7838-44.

207. Schroth P, Al Humaidi M, Feigl L, Jakob J, Al Hassan A, Davtyan A, et al. Impact of the shadowing effect on the crystal structure of patterned self-catalyzed GaAs nanowires. *Nano letters*. 2019;19(7):4263-71.
208. Bosund M, Mattila P, Aierken A, Hakkarainen T, Koskenvaara H, Sopanen M, et al. GaAs surface passivation by plasma-enhanced atomic-layer-deposited aluminum nitride. *Appl Surf Sci*. 2010;256(24):7434-7.
209. Hinkle CL, Sonnet AM, Vogel EM, McDonnell S, Hughes GJ, Milojevic M, et al. GaAs interfacial self-cleaning by atomic layer deposition. *Appl Phys Lett*. 2008;92(7):071901.
210. Timm R, Hjort M, Fian A, Thelander C, Lind E, Andersen JN, et al. Interface composition of atomic layer deposited HfO₂ and Al₂O₃ thin films on InAs studied by X-ray photoemission spectroscopy. *Microelectronic Engineering*. 2011;88(7):1091-4.
211. Ko H, Takei K, Kapadia R, Chuang S, Fang H, Leu PW, et al. Ultrathin compound semiconductor on insulator layers for high-performance nanoscale transistors. *Nature*. 2010;468(7321):286-9.
212. Troian A, Knutsson JV, McKibbin SR, Yngman S, Babadi AS, Wernersson L, et al. InAs-oxide interface composition and stability upon thermal oxidation and high-k atomic layer deposition. *AIP Advances*. 2018;8(12):125227.
213. D'Acunto G, Troian A, Kokkonen E, Rehman F, Liu Y, Yngman S, et al. Atomic layer deposition of hafnium oxide on InAs: Insight from time-resolved in situ studies. *ACS Applied Electronic Materials*. 2020;2(12):3915-22.
214. Klejna S, Elliott SD. First-principles modeling of the “clean-up” of native oxides during atomic layer deposition onto III–V substrates. *The Journal of Physical Chemistry C*. 2012;116(1):643-54.
215. Ye PD, Wilk GD, Yang B, Kwo J, Gossmann H, Frei M, et al. GaAs-based metal-oxide semiconductor field-effect transistors with Al₂O₃ gate dielectrics grown by atomic layer deposition. *J Electron Mater*. 2004;33(8):912-5.
216. Xuan Y, Lin H, Peide DY. Simplified Surface Preparation for GaAs Passivation Using Atomic Layer-Deposited High- κ Dielectrics. *IEEE Trans Electron Devices*. 2007;54(8):1811-7.
217. Frank MM, Wilk GD, Starodub D, Gustafsson T, Garfunkel E, Chabal YJ, et al. HfO₂ and Al₂O₃ gate dielectrics on GaAs grown by atomic layer deposition. *Appl Phys Lett*. 2005;86(15):152904.
218. Timm R, Fian A, Hjort M, Thelander C, Lind E, Andersen JN, et al. Reduction of native oxides on InAs by atomic layer deposited Al₂O₃ and HfO₂. *Appl Phys Lett*. 2010;97(13):132904.

219. Milojevic M, Aguirre-Tostado FS, Hinkle CL, Kim HC, Vogel EM, Kim J, et al. Half-cycle atomic layer deposition reaction studies of Al₂O₃ on In_{0.2}Ga_{0.8}As (100) surfaces. *Appl Phys Lett*. 2008;93(20):202902.
220. Brennan B, Milojevic M, Hinkle CL, Aguirre-Tostado FS, Hughes G, Wallace RM. Optimisation of the ammonium sulphide (NH₄)₂S passivation process on In_{0.53}Ga_{0.47}As. *Appl Surf Sci*. 2011;257(9):4082-90.
221. Chen X, Xia N, Yang Z, Gong F, Wei Z, Wang D, et al. Analysis of the influence and mechanism of sulfur passivation on the dark current of a single GaAs nanowire photodetector. *Nanotechnology*. 2018;29(9):095201.
222. Mahmoodnia H, Salehi A, Mastelaro VR. XPS Study of Long-Term Passivation of GaAs Surfaces Using Saturated Ammonium Sulfide Solution under Optimum Condition. *Russian J Electrochem*. 2021;57(5):471-7.
223. Ren D, Azizur-Rahman KM, Rong Z, Juang B, Somasundaram S, Shahili M, et al. Room-temperature midwavelength infrared InAsSb nanowire photodetector arrays with Al₂O₃ passivation. *Nano letters*. 2019;19(5):2793-802.
224. Lebedev MV, Kunitsyna EV, Calvet W, Mayer T, Jaegermann W. Sulfur passivation of GaSb (100) surfaces: comparison of aqueous and alcoholic sulfide solutions using synchrotron radiation photoemission spectroscopy. *The Journal of Physical Chemistry C*. 2013;117(31):15996-6004.
225. Fu Y, Peralagu U, Millar DA, Lin J, Povey I, Li X, et al. The impact of forming gas annealing on the electrical characteristics of sulfur passivated Al₂O₃/In_{0.53}Ga_{0.47}As (110) metal-oxide-semiconductor capacitors. *Appl Phys Lett*. 2017;110(14):142905.
226. Cuypers D, Fleischmann C, van Dorp DH, Brizzi S, Tallarida M, Müller M, et al. Sacrificial self-assembled monolayers for the passivation of GaAs (100) surfaces and interfaces. *Chemistry of Materials*. 2016;28(16):5689-701.
227. Mancheno-Posso P, Muscat AJ. Self-assembly of alkanethiolates directs sulfur bonding with GaAs (100). *Appl Surf Sci*. 2017;397:1-12.
228. Fang X, Yao L, Fang D, Zhao H, Guo Z, Zhang H, et al. Enhanced Band Edge Luminescence in GaAs with Sulfur Passivation. *Integrated Ferroelectr*. 2021;219(1):47-54.
229. Oigawa H, Fan J, Nannichi Y, Sugahara H, Oshima M. Universal passivation effect of (NH₄)₂S_x treatment on the surface of III-V compound semiconductors. *Japanese Journal of Applied Physics*. 1991;30(3A):L322.
230. Jeng M, Wang H, Chang L, Cheng Y, Chou S. Barrier height enhancement of Ag/n-GaAs and Ag/n-InP Schottky diodes prepared by P₂S₅/(NH₄)₂S_x and HF treatments. *J Appl Phys*. 1999;86(11):6261-3.

231. Ren D, Azizur-Rahman KM, Rong Z, Juang B, Somasundaram S, Shahili M, et al. Room-temperature midwavelength infrared InAsSb nanowire photodetector arrays with Al₂O₃ passivation. *Nano letters*. 2019;19(5):2793-802.
232. Dalapati GK, Tong Y, Loh W, Mun HK, Cho BJ. Electrical and Interfacial Characterization of Atomic Layer Deposited High- κ Gate Dielectrics on GaAs for Advanced CMOS Devices. *IEEE Trans Electron Devices*. 2007;54(8):1831-7.
233. D'Acunto G, Troian A, Kokkonen E, Rehman F, Liu Y, Yngman S, et al. Atomic layer deposition of hafnium oxide on InAs: Insight from time-resolved in situ studies. *ACS Applied Electronic Materials*. 2020;2(12):3915-22.
234. Troian A, Knutsson JV, McKibbin SR, Yngman S, Babadi AS, Wernersson L, et al. InAs-oxide interface composition and stability upon thermal oxidation and high-k atomic layer deposition. *AIP Advances*. 2018;8(12):125227.
235. Black LE, Cavalli A, Verheijen MA, Haverkort J, Bakkers E, Kessels W. Effective surface passivation of InP nanowires by atomic-layer-deposited Al₂O₃ with PO_x interlayer. *Nano letters*. 2017;17(10):6287-94.
236. Kobayashi M, Chen PT, Sun Y, Goel N, Majhi P, Garner M, et al. Synchrotron radiation photoemission spectroscopic study of band offsets and interface self-cleaning by atomic layer deposited HfO₂ on In_{0.53}Ga_{0.47}As and In_{0.52}Al_{0.48}As. *Appl Phys Lett*. 2008;93(18):182103.
237. He G, Gao J, Chen H, Cui J, Sun Z, Chen X. Modulating the interface quality and electrical properties of HfTiO/InGaAs gate stack by atomic-layer-deposition-derived Al₂O₃ passivation layer. *ACS applied materials & interfaces*. 2014;6(24):22013-25.
238. Parakh M, Ramaswamy P, Devkota S, Kuchoor H, Dawkins K, Iyer S. Passivation efficacy study of Al₂O₃ dielectric on self-catalyzed molecular beam epitaxially grown GaAs_{1-x}Sb_x nanowires. *Nanotechnology* - Conditionally Accepted. 2022.
239. Parakh M. GaAsSb/GaAs Ensemble Axial Nanowire Configured Avalanche Near-Infrared Photodetectors [dissertation]. North Carolina A&T State University.
240. Sah RE, Tegenkamp C, Baeumler M, Bernhardt F, Driad R, Mikulla M, et al. Characterization of Al₂O₃/GaAs interfaces and thin films prepared by atomic layer deposition. *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena*. 2013;31(4):04D111.
241. Liu J, Clavel M, Hudait MK. Tailoring the Valence Band Offset of Al₂O₃ on Epitaxial GaAs_{1-y}Sb_y with Tunable Antimony Composition. *ACS applied materials & interfaces*. 2015;7(51):28624-31.

242. Huh J, Yun H, Kim D, Munshi AM, Dheeraj DL, Kauko H, et al. Rectifying single GaAsSb nanowire devices based on self-induced compositional gradients. *Nano letters*. 2015;15(6):3709-15.
243. Ahmad E, Karim MR, Hafiz SB, Reynolds CL, Liu Y, Iyer S. A two-step growth pathway for high Sb incorporation in GaAsSb nanowires in the telecommunication wavelength range. *Scientific reports*. 2017;7(1):1-12.
244. Kasanaboina PK, Ahmad E, Li J, Reynolds Jr CL, Liu Y, Iyer S. Self-catalyzed growth of dilute nitride GaAs/GaAsSbN/GaAs core-shell nanowires by molecular beam epitaxy. *Appl Phys Lett*. 2015;107(10):103111.
245. Iyer S, Nalamati SRK, Li J, inventors; GaAs_{1-x}Sb_x NANOWIRES ON A GRAPHITIC SUBSTRATE. 2022 .
246. Li X, Ni S, Jiang Y, Li J, Wang W, Yuan J, et al. AlInGaAs multiple quantum well-integrated device with multifunction light emission/detection and electro-optic modulation in the near-infrared range. *ACS omega*. 2021;6(12):8687-92.
247. Shi Y, Wu Z, Dong X, Chen P, Wang J, Yang J, et al. A silicon-based PbSe quantum dot near-infrared photodetector with spectral selectivity. *Nanoscale*. 2021;13(28):12306-13.
248. Chun DH, Choi YJ, In Y, Nam JK, Choi YJ, Yun S, et al. Halide perovskite nanopillar photodetector. *ACS nano*. 2018;12(8):8564-71.
249. Zhang Y, Zhang Y, Ma H, Feng Y, Wang S, Li Z. High-responsivity, self-driven visible-near infrared Sb₂Se₃ nanorod array photodetector. *Optics Express*. 2021;29(24):39549-59.
250. Cao B, Liu Q, Zheng Y, Tang X, Chai J, Ma S, et al. Wafer-Scale InN/In₂S₃ Core-Shell Nanorod Array for Ultrafast Self-Powered Photodetection. *Advanced Functional Materials*. 2021:2110715.
251. Keru G, Ndungu PG, Nyamori VO. A review on carbon nanotube/polymer composites for organic solar cells. *Int J Energy Res*. 2014;38(13):1635-53.
252. Pal B, Sarkar KJ, Das S, Banerji P. Near-infrared detection in Si/InP core-shell radial heterojunction nanowire arrays. *J Alloys Compounds*. 2021;885:160943.
253. Casadei A, Krogstrup P, Heiss M, Röhr JA, Colombo C, Ruelle T, et al. Doping incorporation paths in catalyst-free Be-doped GaAs nanowires. *Appl Phys Lett*. 2013;102(1):013117.
254. Uccelli E, Arbiol J, Magen C, Krogstrup P, Russo-Averchi E, Heiss M, et al. Three-dimensional multiple-order twinning of self-catalyzed GaAs nanowires on Si substrates. *Nano letters*. 2011;11(9):3827-32.

255. Krogstrup P, Popovitz-Biro R, Johnson E, Madsen MH, Nygård J, Shtrikman H. Structural phase control in self-catalyzed growth of GaAs nanowires on silicon (111). *Nano letters*. 2010;10(11):4475-82.
256. Russo-Averchi E, Heiss M, Michelet L, Krogstrup P, Nygard J, Magen C, et al. Suppression of three dimensional twinning for a 100% yield of vertical GaAs nanowires on silicon. *Nanoscale*. 2012;4(5):1486-90.
257. Matteini F, Tütüncüoğlu G, Rüffer D, Alarcón-Lladó E, i Morral AF. Ga-assisted growth of GaAs nanowires on silicon, comparison of surface SiO_x of different nature. *J Cryst Growth*. 2014;404:246-55.
258. Matteini F. Growth of GaAs nanowires on Si (111) for photovoltaic applications [dissertation]. EPFL; 2016.
259. Kang Y, Tang J, Wang P, Lin F, Fang X, Fang D, et al. High density GaAs nanowire arrays through substrate processing engineering. *Materials Research Express*. 2018;6(3):035012.
260. Somaschini C, Bietti S, Trampert A, Jahn U, Hauswald C, Riechert H, et al. Control over the number density and diameter of GaAs nanowires on Si (111) mediated by droplet epitaxy. *Nano letters*. 2013;13(8):3607-13.
261. Wen L, Pan D, Liao D, Zhao J. Foreign-catalyst-free GaSb nanowires directly grown on cleaved Si substrates by molecular-beam epitaxy. *Nanotechnology*. 2020;31(15):155601.
262. Zhang Y, Sanchez AM, Aagesen M, Huo S, Fonseka HA, Gott JA, et al. Growth and Fabrication of High-Quality Single Nanowire Devices with Radial p-i-n Junctions. *Small*. 2019;15(3):1803684.
263. Zhang Y, Sun Z, Sanchez AM, Ramsteiner M, Aagesen M, Wu J, et al. Doping of self-catalyzed nanowires under the influence of droplets. *Nano letters*. 2018;18(1):81-7.
264. Sun SZ, Armour EA, Zheng K, Schaus CF. Zinc and tellurium doping in GaAs and Al_xGa_{1-x}As grown by MOCVD. *J Cryst Growth*. 1991;113(1-2):103-12.
265. Houngh Y, Low TS. Te doping of GaAs and Al_xGa_{1-x}As using diethyltellurium in low pressure OMVPE. *J Cryst Growth*. 1986;77(1-3):272-80.
266. Jin Y. Influence of N Incorporation on the Electronic Properties of Dilute Nitride (IN) GaAsN Alloys.[dissertation]. ; 2010.
267. Devkota S, Parakh M, Ramaswamy P, Kuchoor H, Penn A, Reynolds L, et al. A Study on the Effects of Gallium Droplet Consumption and Post Growth Annealing on Te- Doped GaAs Nanowire Properties grown by Self-Catalyzed Molecular Beam Epitaxy. *Catalysts - Under Review*. 2022.

268. Tejwani MJ, Kanber H, Paine BM, Whelan JM. Growth and diffusion of abrupt beryllium-doped profiles in gallium arsenide by organometallic vapor phase epitaxy. *Appl Phys Lett*. 1988;53(24):2411-3.
269. Kang Y, Li H, Tang J, Jia H, Hou X, Li X, et al. Structural and optical properties of Be-doped high-quality self-catalyzed GaAs nanowires. *Optical Materials Express*. 2021;11(8):2422-31.
270. Dheeraj DL, Munshi AM, Christoffersen OM, Kim DC, Signorello G, Riel H, et al. Comparison of Be-doped GaAs nanowires grown by Au- and Ga-assisted molecular beam epitaxy. *J Cryst Growth*. 2013;378:532-6.
271. Nie R, Zhao Z, Deng X. Roles of electrode interface on the performance of organic photodetectors. *Synth Met*. 2017;227:163-9.
272. Li C, Zhu J, Du W, Huang Y, Xu H, Zhai Z, et al. The photodetectors based on lateral monolayer MoS₂/WS₂ heterojunctions. *Nanoscale Research Letters*. 2021;16(1):1-9.
273. Costas A, Florica C, Preda N, Apostol N, Kuncser A, Nătescu A, et al. Radial heterojunction based on single ZnO-Cu_xO core-shell nanowire for photodetector applications. *Scientific reports*. 2019;9(1):1-9.
274. Yang S, Zhou D, Lu H, Chen D, Ren F, Zhang R, et al. High-performance 4H-SiC pin ultraviolet photodiode with p layer formed by Al implantation. *IEEE photonics technology letters*. 2016;28(11):1189-92.
275. Joly R, Girod S, Adjeroud N, Grysan P, Polesel-Maris J. Evidence of Negative Capacitance and Capacitance Modulation by Light and Mechanical Stimuli in Pt/ZnO/Pt Schottky Junctions. *Sensors*. 2021;21(6):2253.
276. Brubaker MD, Genter KL, Roshko A, Blanchard PT, Spann BT, Harvey TE, et al. UV LEDs based on p-i-n core-shell AlGa_N/Ga_N nanowire heterostructures grown by N-polar selective area epitaxy. *Nanotechnology*. 2019;30(23):234001.
277. Cai J, Chen X, Hong R, Yang W, Wu Z. High-performance 4H-SiC-based pin ultraviolet photodiode and investigation of its capacitance characteristics. *Opt Commun*. 2014;333:182-6.
278. Caputo D, De Cesare G, Irrera F, Palma F, Tucci M. Characterization of intrinsic a-Si: H in p-i-n devices by capacitance measurements: Theory and experiments. *J Appl Phys*. 1994;76(6):3534-41.
279. Moloi SJ, McPherson M. The current and capacitance response of radiation-damaged silicon PIN diodes. *Physica B: Condensed Matter*. 2009;404(21):3922-9.

280. Bao X, Xu J, Li C, Qiao H, Zhang Y, Li X. Temperature and frequency dependence of negative differential capacitance in a planar GaN-based pin photodetector. *J Alloys Compounds*. 2013;581:289-92.
281. Cheng CJ, Si JJ, Zhang XF, Ding JX, Lu ZX, Sun WG, et al. Capacitance characteristics of back-illuminated Al_{0.42}Ga_{0.58}N/Al_{0.40}Ga_{0.60}N heterojunction p-i-n solar-blind UV photodiode. *Appl Phys Lett*. 2007;91(25):253510.
282. Park YS, Park CM, Lee JW, Cho HY, Kang TW, Yoo K, et al. Electrical transport properties of a nanorod GaN p-n homojunction grown by molecular-beam epitaxy. *Journal of Applied Physics*. 2008.
283. Cheng CJ, Zhang XF, Lu ZX, Ding JX, Zhang L, Zhao L, et al. Temperature dependence on current-voltage characteristics of Ni/Au–Al_{0.45}Ga_{0.55}N Schottky photodiode. *Appl Phys Lett*. 2008;92(10):103505.
284. Ganjipour B, Sepehri S, Dey AW, Tizno O, Borg BM, Dick KA, et al. Electrical properties of GaSb/InAsSb core/shell nanowires. *Nanotechnology*. 2014;25(42):425201.