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**A Study on GaAs/GaAsSbN Schottky and GaAs/GaAsSb Core-Shell Avalanche Nanowire
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Dedication

This work is dedicated to my father, my late mother, my advisor and all my family and friends
that inspired me to move forward.

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List of publications

Journal publications/submitted/in preparation as a result of this Ph.D. work

- ❖ **Pokharel, Rabin**, Priyanka Ramaswamy, Shishir Devkota, Mehul Parakh, Kendall Dawkins, Aubrey Penn, Matthew Cabral, Lewis Reynolds, and Shanthi Iyer. "Epitaxial High-Yield Intrinsic and Te-Doped Dilute Nitride GaAsSbN Nanowire Heterostructure and Ensemble Photodetector Application." *ACS Applied Electronic Materials* 2, no. 9 (2020): 2730-2738.
<https://pubs.acs.org/doi/abs/10.1021/acsaelm.0c00450>
A provisional patent is filed for this work • **“MBE growth of high-quality dilute nitride GaAsSbN for room temperature near-infrared photodetection application”,
Invention disclosure completed. Disclosure no: JSNN0034 0821**
- ❖ Johnson, Sean, **Pokharel, Rabin**, Lowe, Michael, Kuchoor, Hirandeep, Nalamati, Surya, Davis, Klinton, Rathnayake, Hemali, and Shanthi Iyer. "Study of patterned GaAsSbN nanowires using a sigmoidal model." *Scientific Reports* 11, no. 1 (2021): 1-14. <https://doi.org/10.1038/s41598-021-83973-9>.
- ❖ Yuan, Long, **Pokharel, Rabin**, Devkota, Shisir, Kuchoor, Hirandeep, Dawkins, Kendall, Lee, Min-Cheol, Huang, Yue, A. Yarotski, Dmitry, Iyer, Shanthi, and P. Prasankumar, Rohit, “Revealing Charge Carrier Dynamics and Transport in Te-Doped GaAsSb and GaAsSbN Nanowires by Correlating Ultrafast Terahertz Spectroscopy and Optoelectronic Characterization”, *Nanotechnology*, (2022) Under review.
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- ❖ **Pokharel, Rabin**, Shisir Devkota, Mehul Parakh, Kendall Dawkins, and Shanthi Iyer, "Core-shell GaAs/GaAsSb nanowire separate absorption multiplication region APD for NIR photodetection," manuscript under preparation for submission to a suitable scientific journal.

List of related journal publications as co-author

- ❖ Parakh, Mehul, Sean, Johnson, **Pokharel, Rabin**, Priyanka Ramaswamy, Surya Nalamati, Jia Li, and Shanthi Iyer. "Space charge limited conduction mechanism in GaAsSb nanowires and the effect of in situ annealing in ultra-high vacuum." *Nanotechnology* 31, no. 2 (2019): 025205.
<https://doi.org/10.1088/1361-6528/ab47aa>
- ❖ Ramaswamy, Priyanka, Shisir Devkota, **Pokharel, Rabin**, Surya Nalamati, Fred Stevie, Keith Jones, Lew Reynolds, and Shanthi Iyer. "A study of dopant incorporation in Te-doped GaAsSb nanowires using a combination of XPS/UPS, and C-AFM/SKPM." *Scientific Reports* 11, no. 1 (2021): 1-14.
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- ❖ Parakh, Mehul, **Pokharel, Rabin**, Dawkins, Kendall, Devkota, Shishir, Li, Jia, and Iyer Shanthi, "Ensemble GaAsSb/GaAs axial configured nanowire-based separate absorption, charge and multiplication avalanche near-infrared photodetectors", Under review for publication in *Nanoscale advances* (2022).

Abbreviations

MBE	Molecular beam epitaxy
MOCVD	Metalorganic chemical vapor deposition
MOVPE	Metal organic vapor phase semiconductor
VLS	Vapor liquid solid
VS	Vapor solid
ZB	Zinc blende
WZ	Wurzite
UHV	Ultra high vacuum
Si	Silicon
SiO ₂	Silicon dioxide
ML	Monolayer
GaAs	Gallium Arsenide
GaAsSb	Gallium Arsenide Antimonide
GaAsSbN	Gallium Arsenide Antimonide Nitride
GaAsSbNTe	Gallium Arsenide Antimonide Nitide Telluride
AlGaAs	Aluminium gallium arsenide
APD	Avalanche Photodiode
SAM	Separate Absorption Multiplication
BEP	Beam Equivalent Pressure
E _g	Band gap energy
CB	Conduction band
VB	Valance band
DN	Dilute nitride

SEM	Scanning electron microscope
TEM	Transmission electron microscope
EDS	Electron dispersive x-ray spectroscopy
EBL	Electron beam lithography
SAED	Selective area diffraction pattern
HRTEM	High resolution transmission electron microscopy
PL	Photoluminescence
FEM	Finite element method
NIR	Near infrared region
IR	Infrared region
I-V	Current-voltage
LFN	Low frequency noise
SMU	Source measure unit
TO	Transverse optical
LO	Longitudinal optical
PMMA	Poly methyl methacrylate
QD	Quantum dot
SL	Super lattice
S/V	Surface to volume ratio
SMU	Source measure unit
DUT	Device under

Abstract

III-V semiconductor nanowire-based infrared photodetectors are the critical components of next-generation devices for quantum information science and photonic integrated circuit due to their small size, low power, high sensitivity, and speed. The ability to achieve effective strain relaxation without creating extended defects allows interesting heteroepitaxial growths and novel NW configuration structures. This work intends to leap the reliable NW-based device demonstration in two material systems, namely GaAsSbN and GaAsSb/GaAs on Si in respective Schottky and avalanche photodetector device configurations. Schottky photodetectors have a low forward voltage drop and swift switching action and are attractive for technologies such as focal planar arrays and image sensors. Avalanche photodetectors (APDs) are highly desired in next-generation optical transmission systems, computing systems, and other weak light signal devices requiring high-speed, low-cost, low-power, and sensitivity.

The first part of this work will discuss the NW growth optimization and device performance aspects of dilute nitride GaAsSbN NWs in axial configuration. Multiple strategies are adopted to address the challenge of device demonstration in dilute nitride NWs, namely (i) investigating N-incorporation to improve optical and morphological properties, (ii) suppressing defects and inhomogeneities, and (iii) resolving the challenge of large-scale implementation and bandgap tuning using patterned growth. The underlying difficulties for NW growth and approaches for overcoming them in achieving improved quality material growth are presented. A study of n-type doping incorporation using GaTe captive source and device performance aspects of these NWs have been investigated, and finally, a study on the patterned growth of these NWs is presented. We demonstrate a room temperature (RT) photoluminescence in the non-patterned ensemble dilute

nitride NWs, with an ensemble NW device responsivity reaching 3800 A/W at -1V bias at an illumination of 1100 nm wavelength. We identify rich prospects for this material system in near-infrared bandgap engineering applications.

The second part of the work is focused on the GaAsSb/GaAs material system APDs consisting of separate absorption, charge, and multiplication region (SCAM) structures. GaAsSb is an important material system in the near-infrared (NIR) region, wavelength-tunable up to 1.7 μm , and is growth compatible with GaAs material, which is another extensively researched III-V material system. The proposed core-shell (CS) architecture is intended to maximize light absorption, suppress the multiplication noise, and achieve spectral sensing spanning a large portion of the NIR region. We identify the critical challenges and demonstrate creative solutions to achieve RT photodetection using epitaxial growth of the GaAsSb/GaAs material system. The design of APD is guided by E-field simulation using finite element method simulation using COMSOL Multiphysics. The SCAM APD is achieved with a punch-through voltage of $\sim 5\text{V}$ and breakdown voltage as low as $\sim 20\text{ V}$ at RT. Positive temperature dependence of the breakdown voltage and dark current of the device, along with the C-V measurement, confirm the avalanche mechanism in the device as the dominant gain mechanism in the NW device. The device showed a broad spectral response from 633 nm to 1200 nm, with a cut-off wavelength of 1300 nm. The device exhibited—a low capacitance below pico-Farads and a unity gain responsivity of $\sim 0.2\text{ A/W}$. Gain value exceeding 100 at a reverse bias of 18 V and 1200 nm wavelength is achieved at room temperature. In summary, this dissertation examines the challenges and their mitigation in epitaxial growth of dilute nitride GaAsSbN material system in axial NW ensemble configuration and core-shell GaAs/GaAsSb ensemble NW based APDs on Si to build a foundation for next-generation near-infrared photodetector devices for low light level detection.

Chapter 1

Introduction

1.1 Overview

Semiconductor photodetectors have enabled numerous technologies demanding durability, high sensitivity, quick response, and low cost. Commercially dominating photodetectors include PIN and APD devices that provide high detection efficiency from visible to infrared spectrum. Moreover, there are inevitable performance tradeoffs in currently dominating thin-film photodetectors, which are unavoidable. A tremendous advancement made in growth techniques of semiconductor materials has enabled the fabrication of devices consisting of varieties of alloys with varying structural designs extending from 2-D structures to 1-D NWs with radial and axial architectures and to more complex configurations, namely embedded 0-D quantum dots (QDs) in these low dimensional structures. Nanowire photodetectors are the emerging technology that has proven potential for representing state-of-art technology, and tremendous growth has been seen in this sector, making it one of the most exciting sectors capable of circumventing the tradeoffs in device metrics in current planar technology. Introduction of defects due to lattice mismatch with Si substrate and slow response speed due to bulk volume compared to small NW volume are the significant advantages over thin-film technology. An attractive feature of NW architecture is the unique ability to synthesize NWs in the crystal phase that is unfavorable thermodynamically in their bulk and 2-D counterparts. Semiconductor NW growth has, thus, extended beyond the conventional boundary and utilizes several combination of material systems that were previously limited in planar geometry configurations [3].

NWs also offer dimension-controlled bandgap engineering, enhanced light trapping, the ability to exploit rich surface state properties, and a variety of possible architectures (e.g., axial and core-shell configurations). Axially configured nanowires are advantageous for achieving a sharp interface between materials while also effectively overcoming lattice-mismatch constraints in highly mismatched alloys. Growth of nanowire inserts and quantum well inserts is easily achievable in axial configuration, which enables enhancement of optical properties like light extraction efficiency and suppresses light scattering [4]. This configuration is desirable for electron transport applications. Core-shell (CS) configured nanowires have an edge in achieving, broader material composition and growth design, carrier collection efficiency, and passivation [5, 6]. This configuration allows one to take advantage of thin-film configuration as well as nanowire configuration due to Vapor-Solid (VS) growth mechanism followed in the shell growth. Although the growth and device fabrication cost of nanowire devices is a major significant factor to be considered, an unprecedented enhancement in performance is possible, which can ultimately balance the scale with currently dominating thin-film technology. Among the variety of materials available in the near-infrared spectrum, $\text{GaAs}_{1-x}\text{Sb}_x$ encompasses wavelength range from 870 nm (GaAs) to 1700 nm (GaSb), in which a variety of next-generation optoelectronic applications is possible, including but not limited to optical telecommunications, quantum computing, and photonic circuits [6-9]. GaAsSb material demonstrates high optical absorption and superior carrier mobility, making it a suitable candidate for photodetector, and has successfully been grown in both axial and core-shell configurations [6, 9-11]. A significant reduction of the bandgap energy is achieved with the addition of a small amount of nitrogen into the host lattice of GaAsSb. Incorporation of $\sim 1\%$ Nitrogen into the GaAs lattice is found to reduce

the bandgap by 150 meV^{-1} [12]. This enables simultaneous tuning of the valence and the conduction band, facilitating bandgap engineering in the near-infrared regime. In contrast, the nanowire configuration empowers the growth of such alloys directly on the Si substrate by overcoming the lattice mismatch constraints. Thus, CMOS-compatible photodetector devices with tunable bandgap can be achieved, promising a wide range of optoelectronic applications. Further, nitrogen incorporation is believed to perturb the conduction band (CB) of GaAs introducing traps and potential fluctuations. This provides an opportunity to study free carriers' interaction with the localized states [13-15], the degree of which can be controlled by tuning the N concentration.

Semiconductor photodetectors are fabricated in various configurations depending upon their applications (e.g., Schottky, PIN, Avalanche photodetectors, etc.), and the design considerations and applications differ based on the category. For example, Schottky photodetectors use the basic structure and technology of a standard Schottky barrier diode and operate in two photon-detection modes, namely electron pair generation, and carrier emission. Electron pair generation mode is dependent on band-to-band energy gap excitation, and the carrier emission occurs from metal to semiconductor over the Schottky barrier, also called internal photoemission. Schottky detectors have a low forward voltage drop and a swift switching action since they are unipolar devices, and their speed is only limited by junction capacitance. Schottky configured photodetectors are particularly compatible with mature silicon technology and can be directly integrated into a single chip and have widely been used in the charge-coupled device (CCD) as the image sensor photodetector. The CCD itself forms a shift register to allow data to be transferred from the array of Schottky detectors out of the overall chip in a managed way, which provides a method of extracting huge data files from the large variety of photodetectors with a sensible number of leads on the integrated circuit. These advantages have made Schottky photodetectors a desirable technology for focal planar arrays. Another unique class of photodetectors is avalanche photodetectors, which operate relatively in a higher reverse bias voltage and take advantage of the internal current gain effect due to impact ionization (or

avalanche effect). This gives the advantage of higher gain, response time and signal to noise ratio in APD devices (only when the internal gain produced by the APD boosts the signal level without drastically affecting the overall system noise [16]) compared to PIN devices at the expense of higher operating voltage, complex circuitry, and hence higher cost. As the output of PIN diodes is linear compared to the operation of APDs, APDs generally produce a higher noise level. Thus, avalanche photodetectors are generally used where the level of gain is of foremost importance and cannot replace PIN photodetectors in applications requiring low voltages and higher reliability. PIN diodes are particularly attractive for attenuators, RF switches, lower sensitivity photodetectors, and high-voltage power electronics applications such as high-voltage rectifiers [17-19]. The large depletion region in PIN diodes makes them attractive for high-voltage applications. The multiplication gain due to impact ionization can be very high in an APD and has a strong dependence on the applied electric field, temperature, and doping. APDs represent one of the significant technologies representing most advancement in applications requiring detection of few photons such as LiDARs, fiber-optic telecommunication, long-range fiber-optic telecommunication, and quantum sensing for control algorithms. Various material systems have been used so far, including silicon, germanium, InGaAs, and HgCdTe-based diodes in the near-infrared region. Moreover, InGaAs are the dominating material system in the near-infrared region, encompassing 0.9-1.7 μm , due to their high absorption coefficient and lower multiplication noise, the ability to operate at higher temperatures compared to HgCdTe-based diodes. GaAsSb is another competing direct bandgap III-V material system having comparable absorption to InGaAs and the bandgap to encompass the telecommunication range.

1.2 III-V compound semiconductor materials for photodetection

III-V compound semiconductors are obtained by combining group III elements (e.g., Ga, Al, In) with group V elements (e.g., N, As, Sb, P), and a variety of combinations are possible. The combination of III and V group materials is crystallized either in a diamond lattice (e.g., Si), which is often referred to as a zinc-blende structure. Or they can be bonded in a hexagonal lattice known

as wurtzite. III-V compound semiconductor detectors are particularly desirable due to the range of wavelengths they can cover and a broad choice of materials available for various energy gaps required in the wavelength spectrum. III-V materials have shown very high absorption properties, high electron mobility, low exciton binding energy, and direct bandgap properties (as opposed to Si, which has indirect bandgap) that enable high-speed detections and can be used to emit light, which is a crucial advantage over Si.

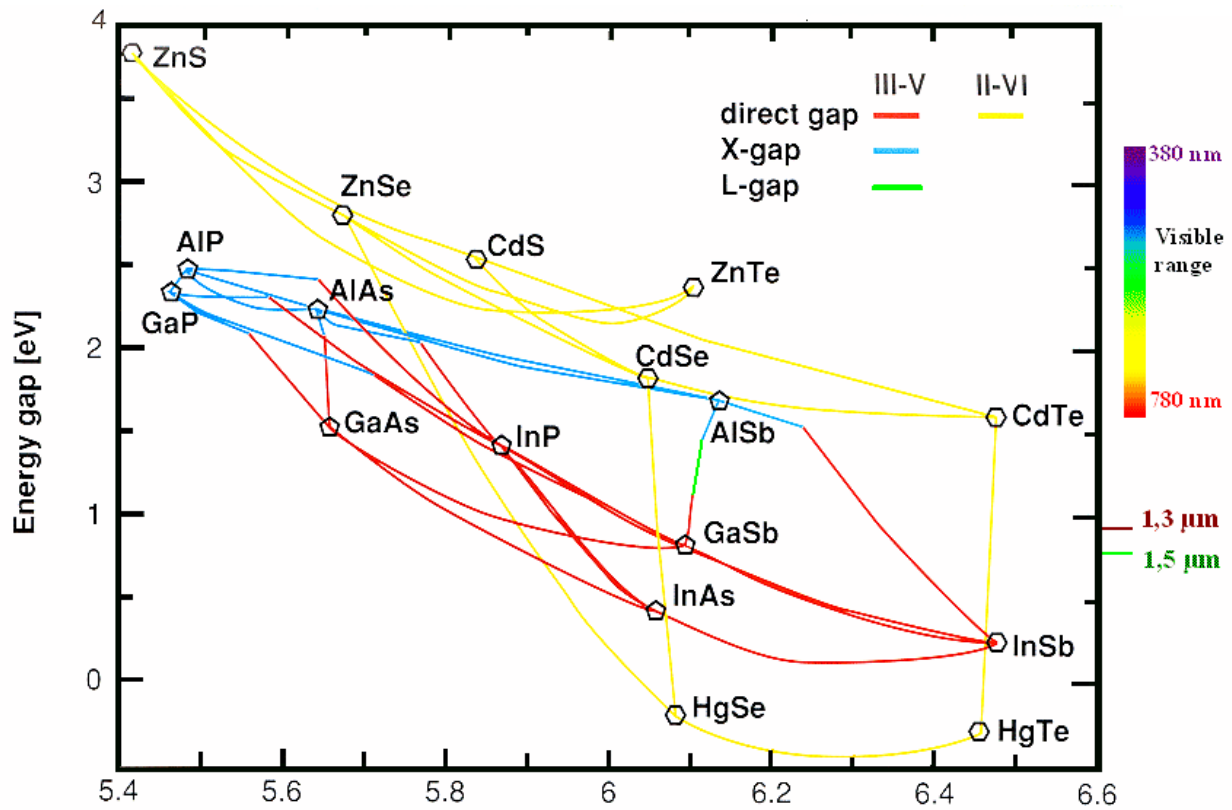


Figure 1.1: Various III-V semiconductors bandgap vs. lattice constant. Gap vs. lattice constant [1]. (reprinted with permission from Dr. Helmut Foll, *Semiconductors I*, 5.1.4 wavelength engineering, “bandgap vs the lattice constant”).

Figure 1.1 shows the variety of III-V semiconductors and their wavelength range of coverage indicated by the color bar at the right. The choice of materials is dependent on both the bandgap of material which determines the wavelength it covers and their optical properties attainable in an

alloy configuration. Particularly, the current state-of-art infrared photodetectors is mainly based on the semiconductor detectors such as Si (0.4-1.1 μm), InGaAs (1.1-1.7 μm), Ge (0.7-1.7 μm), InAs (0.9-3.5 μm), HgCdTe (2-10.6 μm) and GaAsSb (0.7- 1.7 μm). These detectors have been studied for decades with gradual developments, and the focus has been to improve the responsivity, noise levels, temperature range of operation, and detectivity. As the materials are grown on a certain substrate, the choice of substrate is another crucial factor to be considered for the growth of high-quality alloys free of defects.

The majority of semiconductors employed in IR detections belong to the III-V group. With a direct bandgap between 0.35 eV for InAs to 1.43 eV for GaAs, InGaAs are established as one of the prominent materials for the SWIR spectral range. The major competitor for this material in this field is GaAsSb, apart from Germanium (Ge) and Si-Ge, which covers most of the SWIR range, including the telecommunication wavelength range of 1.33-1.55 μm . GaAsSb has very good absorption properties comparable to InGaAs (Sb) and is an excellent candidate for fabricating low-cost optoelectronics, given the cost of Indium (In) is high. Further, as the new wave of interesting developments has come from low dimensional detectors in these material systems [20-23] (e.g., nanowires, nanorods, quantum dots), the growth of InGaAs material (consists of two group III elements In, Ga) has a narrow window compared to GaAsSb. This stems from the difference between different group III elements having quite different optimized growth conditions, thus posing difficulty to provide the optimum growth environment in nanowires for more than one group-III element at the same time [24]. Moreover, group-V elements have high vapor pressure and short diffusion length and participate in nanowire growth by impinging directly on the catalyst droplet from the vapor phase, making them less sensitive to the growth conditions compared to group III elements. Thus, keeping a single group III element and changing group-V elements such

as GaAs, GaAsSb, and GaAsSbN (Te) heterojunctions could be more reproducible and cheaper alternatives to grow.

1.3 Growth mechanism and crystal structure of nanowires

III-V semiconductor nanowires growth is done either by top-down or bottom-up approaches, and some use a combination of both [25-27]. The top-down method of fabrication involved direct writing or etching of lithographically defined patterns on a bulk substrate or a layered structure [28], and this technique can be used from ordered arrays of NWs by accurate size, spacing, and position control. Bottom-up approaches, in contrast, involve the growth of nanowires on a substrate, usually using catalytic approaches. This approach offers much flexibility in terms of material/structure design and benefits from the effective strain relaxation compared to the bottom-up approach of synthesis. Also, the surface defects and roughness of the nanostructures can be avoided using the bottom-up approach, which helps to attain better quality materials.

The majority of nanowires are grown using bottom-up vapor-liquid-solid (VLS) or Vapor-solid-solid (VSS) mechanisms (which is rather uncommon). For the growth of NWs by the VLS mechanism, the precursor (Au, Cu, Ga, In, etc.) acts as a catalyst for mass transfer from the vapor phase to the liquid phase due to constant vapor pressure onto the metal precursor deposited on the substrate surface. This liquid alloy system is then pushed beyond equilibrium resulting in supersaturation of the liquid droplet, forming a solid surface layer-by-layer under the liquid droplet. The metal droplet acts as a seed particle for the subsequent growth of supplied species compositions. The catalyst particles should have very low solubility with the substrate, must form a liquid solution with the crystalline material to be grown at the growth temperature, should be a low vapor pressure material in order to sustain the growth, and should have a suitable contact angle with the substrate, and the solid-liquid interface must have well-defined crystallographic ally in

order to yield highly directional NW growth [29]. The axial, radial growth rates and density of nanowires depend on the initial droplet size and contact angle, growth species and kinetics associated with them, type and surface energy of the substrate, and temperature of growth. Besides these, there are various factors that can alter the growth conditions and quality of film deposited, like vacuum conditions, unwanted growth species present, annealing, growth species sources purity, the ratio of growth species (V/III ratio), the thickness of silicon dioxide layer on the substrate, etc.

Highly anisotropic nanowires can be produced using the VLS growth mechanism. A variety of growth mechanisms are reported in the literature for the synthesis of III-V NWs by the VLS mechanism, namely metal-assisted (e.g., Au, Cu) growth by molecular beam epitaxy (MBE), metalorganic vapor phase epitaxy (MOVPE), metal-assisted organic chemical vapor deposition (MOCVD), energy transfer methods such as pulsed laser ablation[30] and self-catalyzed growth using MBE and MOVPE which uses precursors such as Gallium (Ga) and Indium (In). Metal-assisted VLS growth, particularly using Au as a precursor, was commonly used in past decades until self-assisted growth started replacing it. The growth of nanowires using Au was favorable due to its inert nature and the formation of a low melting point eutectic droplet [31, 32]. Moreover, the process incompatibility of gold-assisted nanowires with CMOS technology and the formation of deep trap states due to gold contamination limited the applications and performance of devices. Thus, self-catalyzed nanowires growth using the VLS mechanism is the more common and widely used method for the synthesis of 1D nanowires. The growth of nanowires requires stringent control of numerous growth parameters during nanowire growth, and the reproducible, high-quality alloys growth calls for careful control of these parameters. The growth parameters for instance include the choice of precursor, growth temperature, flux ratios, growth environment and so on. Further

considerations must be given during the nanowire growth, namely the adjustment of growth rates, diffusion of the dopants, surface energy fluctuations during growth, substrate choice, and processing, etc. A variety of nanowire structures such as tapered, cylindrical, and inverse tapered structures is possible via careful control of growth parameters in the given growth window.

Elemental semiconductors and III-V compounds (except group III nitrides) adopt a face-centered-cubic (FCC) structure in bulk and even in the nanostructured forms. This especially holds true for III-V compounds, which frequently adopt a hexagonal wurtzite (WZ) or the standard zinc-blende (ZB) structure or a combination of both that can coexist [33, 34], and they can manifest in a variety of electrical and optical properties [35]. For example, in GaAs [36-38] and InP [39, 40] nanowires, WZ structure is found to be dominant; for GaAsSb nanowires [11, 41], ZB crystal structure is mostly favored since the addition of Sb in GaAs lowers the droplet surface energy of the droplet. The change of crystal structure is also found in nanostructured forms compared to the bulk since the surface energy is greatly altered in the case of nanostructures, and the change in crystal structure might be viable. An instance is the growth of GaN nanowires [42] which exhibited the ZB phase, although GaN exhibit only the WZ phase in bulk. Since the growth of nanowires is believed to proceed layer-by-layer in the direction of growth, a subtle change in the sequence of layers easily can lead to a change between two crystal phases [43]. Further, nanowire diameter, droplet size and surface energy during nucleation, droplet contact angle, and changes in the V/III growth ratio can have influences the crystal structure during the growth of NWs [35]. Doping might induce a significant change in the growth conditions causing a dramatic change in crystal structures[44, 45]. ZB and WZ structures only differ subtly in their stacking sequence, and the energetic difference between these two arises from the difference in the third nearest neighbor in

a cubic lattice, which is shorter for the WZ segment compared to ZB [46]. Moreover, ZB and WZ phases have shown different band structures [47-49], and the bandgap of ZB is believed to be comparatively smaller. An uncontrolled mixture of these phases in nanowires can have a degrading implication on the optical and electrical properties since stacking faults, and twin planes can scatter carriers or trap them. But the selective control or tuning of the crystal phases can result in interesting properties of materials [50, 51]. The majority of nanowires are found to exhibit structural defects, and high purity crystal structure is generally an exception but achievable with stringent growth parameter tuning and control.

1.4 III-V dilute nitride materials and nitrogen incorporation in nanowires.

The family of dilute nitride material systems has been studied closely for more than two decades now, while group III-nitride nanowire structures have been studied since 1969 when the first synthesis of gallium nitride (GaN) was made using hydride vapor-phase epitaxy process on sapphire substrate by Maruska and Tietjen [52] at Corporation of America Laboratories, New Jersey, USA. Since then, tremendous development in III-nitride semiconductors can be seen, including materials like GaN, AlN, InN, and their alloys, and stands among the most important materials for modern electronics and optoelectronic sectors [53]. The Nobel prize in physics was awarded to Profs. Isamu Akasaki, Hiroshi Amano, and Shuji Nakamura for GaN-based LEDs in 2014. The areas of applications have extended to not only LEDs but also radiofrequency (RF) electronics, display technology, power electronics applications, and many other optoelectronic sectors.

The incorporation of N in the lattice of GaAs is unlike the crystal growth of most III-V semiconductors. Growth kinetics in N-incorporation is also quite different from arsenides, phosphides, and antimonides, where in their case surface is usually terminated or stabilized by one

of the above-mentioned group V elements [54]. This also brings to the point that N does not compete in the same manner as another group V species for the group-V lattice site. For example, during the growth of GaAsN, the amount of N incorporated appears to be independent of the As-flux, and substrate temperature and only dependent on group-III growth rate[55]. Other than this, the amount of N-incorporation can be varied by changing plasma conditions, RF power, flow rate, and excitation power, as shown in other studies [56, 57], and these are also important parameters for controlling the structural and optical quality of material grown by MBE.

The first novel quaternary alloy InGaAsN was grown lattice-matched to GaAs, introduced by Kondow et al. [58] in 1996. Using this configuration, lasers were fabricated for operation in 1.33 to 1.55 μm wavelength region with temperature characteristics better than existing InP-based lasers. A good review of the commencement in the progress of dilute nitride quaternary alloys is done by Henini [59], which unveils the motivation behind quaternary dilute nitride alloy systems. Dramatic decrease of the bandgap of GaAs with a small atomic fraction of N and near-lattice-matching property of quaternary alloys like GaInNAs and GaInNAsSb [60] with GaAs increased tremendous research interest for 1.33-1.55 μm region optoelectronic applications. Furthermore, these quaternary alloys offered numerous processing advantages over conventional InGaAsP grown on InP substrates, namely larger refractive index difference for lattice-matched alloys and highly selective oxidation of AlAs to form AlO_x used to provide current and optical confinement [59]. The development of quaternary dilute nitride structures was crucial in realizing edge-emitting lasers and vertical-cavity surface-emitting lasers. InGaAsN was developed as a suitable material for multijunction solar cell design, which led to an increase in the efficiency of solar cells from 36 to 38% at ten suns [61]. Moreover, short minority carrier diffusion length, low mobility, and short

lifetime of carriers [62-65] posed serious limitations demanding higher quality growth of these material systems.

Apart from the material system discussed above, GaAsSbN and InGaAsSbN are other families of III-V dilute nitride material systems, and numerous studies have been recorded so far [10, 55, 59, 60, 66-77], most of them being directed to the former one. Moreover, GaAsSbN is more attractive for solar cells and optoelectronic applications due to the stronger band bowing property in GaAsSb and GaAsSbN systems requiring less incorporation of N compared to InGaAs and InGaAsN, respectively. The preference for the GaAsSbN material system also arises from a cost-effectiveness point of view since Indium, with the growing demand of supply and limited supply, increases the cost of the device in practical applications. Furthermore, one more element in InGaAsSbN growth requires more stringent control compared to the GaAsSbN counterpart [60, 69-71], which might pose a challenge in mass manufacturing and quality control. GaAsSbN also has the edge over InGaAsN in thermal stability as well since GaAsSbN has only a single group III element, thus free from InN/GaN bond change during heat treatment [78] due to the large difference in the diffusion rates of In and Ga [79-81]. This attribute is also advantageous for obtaining a better quality of nanowires/thin films during post-growth annealing with lesser blue-shift in emission wavelength [59, 74, 75, 77]. Apart from this, longer electron lifetime suppressed Auger recombination and compositional homogeneity in GaAsSbN NW configuration compared to InGaAsN NWs can be exploited to enhance the structural and optical properties.

Dilute nitrides predominantly exhibit ZB crystal structure and very few WZ inclusions (less than 5-10% of total volume) [82-86]. TEM studies have shown that structural defects, namely twin planes and stacking faults, are usually increasing as the NW growth proceeds and might contain short WZ inclusions [85, 86]. Also, note that a similar crystalline structure was observed in GaAs

NWs; it can be concluded that polymorphism is not necessarily induced by N incorporation but rather by non-optimized growth conditions. Thus, an optimized growth condition is crucial in obtaining a single-phase high quality dilute nitride alloy in NW configuration, which is one of the major focus areas of this dissertation.

1.5 Avalanche photodetectors encompassing near-infrared regime

Avalanche photodetectors are based on the principle of avalanche effect, which occurs as a result of band-to-band carrier impact ionization at a large electric field at the expense of high reverse bias voltages. This enables the multiplication of photogenerated carriers, which are accelerated in the high electric field depletion region to gain sufficient energy for the creation of new electron-hole pairs from their bound state. The cascade effect of the electron-hole pair generation in the high-electric field region leads to large concentrations of impact-ionized carriers, thus giving rise to high internal gain in the photodetector.

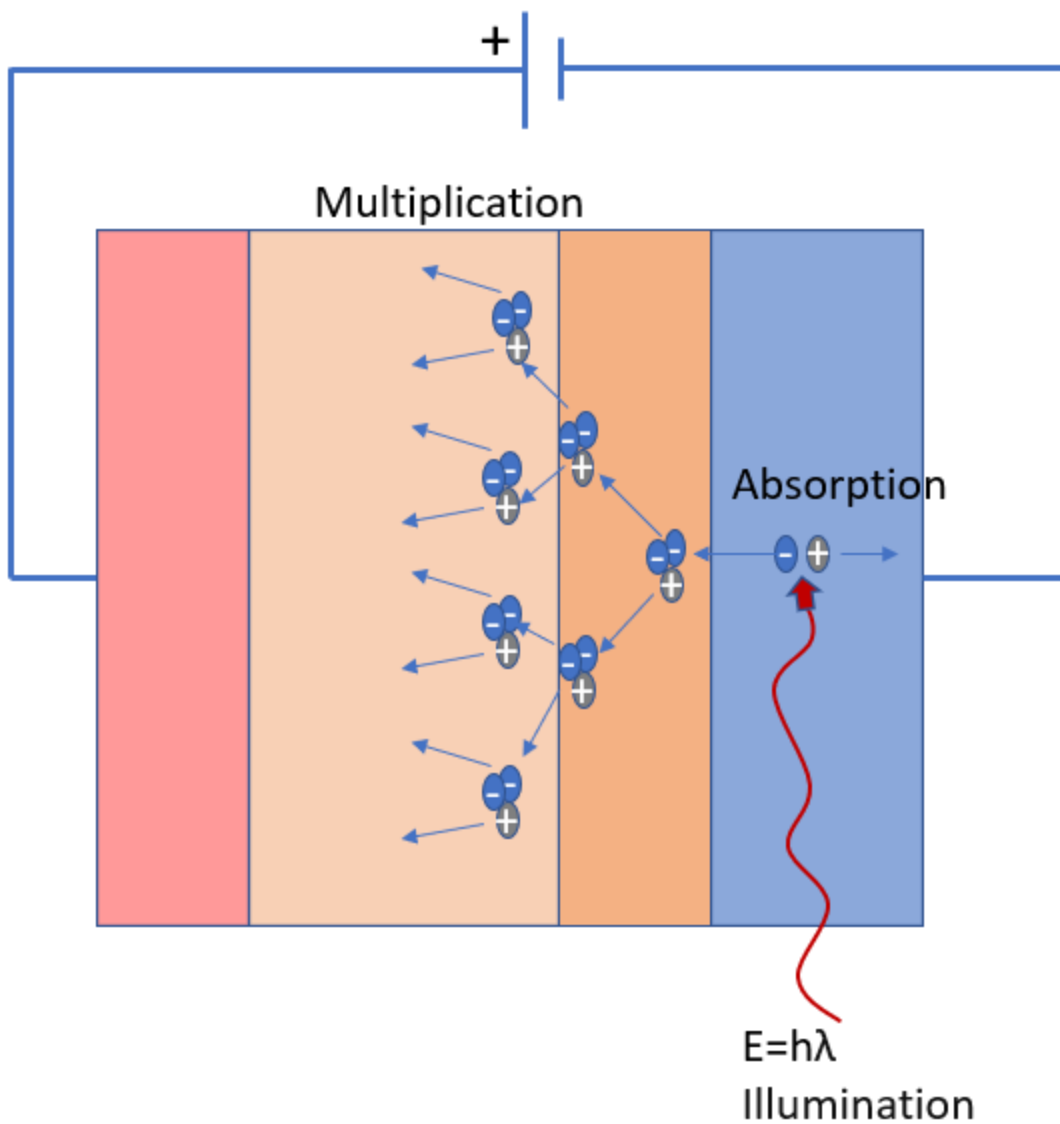


Figure 1.2: A schematic of a carrier multiplication process in a separate absorption multiplication layer APD.

Avalanche photodetectors are one interesting implementation of the photodetectors, which encompasses a wide field of applications in the near-infrared region. Compared to traditional PIN photodetectors, the carrier multiplication process largely increases the sensitivity of APDs at the expense of a high electric field [87]. Traditionally APDs consists of multiplication and charge control layers to control the E-field in the device suitable for carrier multiplication. With

the necessity of decreasing signal detection noise, a separate absorption region can be found in modern-day APDs to suppress the noise induced by photon absorption-related phenomena. Depending on the wavelength of operation, a variety of material systems are used in near-infrared APDs namely Si, GaAs, GaAsSb, InP, InAs, InP, InAsSb, InGaAs, and InGaAsSb [88, 89]. In the planar configuration, APDs suffer from low sensitivity to photon flux, high breakdown voltage, high excess noise, and low gain-bandwidth products limiting their applications in modern-day devices. A variety of techniques have been explored to overcome the limitations of these planar APDs namely the use of mesa structures, dual charge control layers, and use of advance band structures thus improving the excess noise, breakdown voltage and device performance limitations [90-93]. Moreover, the inability to overcome lattice mismatch with conventional Si substrates leads to poor crystalline quality of most APDs. Thin-film APDs still suffer from the higher dark current due to increased device volume and hence compromise in the device sensitivity will be inherent. Due to the presence of a large device area, reduction in breakdown voltage is still a challenge in thin-film APDs which introduces complexity in integration with modern-day electronics.

Nanoscale APDs have an edge over the conventional thin-film APDs due to their small footprint that enables overcoming lattice mismatch and increased flexibility in bandgap engineering to tune their optoelectronic properties. A high surface-to-volume ratio enables superior optical trapping features, reduced phonon scattering, and increased selection of material combination while possessing the ability to be integrated into existing COMS technology [94]. In nanowire configuration, axial and core-shell configurations can be used for segmented homo-structure or heterostructure growths. The axial heterostructure is advantageous in achieving sharp interface heterojunctions [95, 96], thus reducing the defect concentration in

the device. Core-shell configured devices have an edge in decoupling light absorption and carrier generation, thus enhancing the device sensitivity [91]. Suitably optimized nanoscale 1D APDs, thus, can have distinct advantages over conventional thin-film APDs by overcoming the challenge of lattice mismatch and process incompatibility (resulting from the difference in lattice mismatch constants and thermal expansion coefficients), lowering the breakdown voltage, introducing nanoscale features namely quantum heterostructures and nanophotonic resonances, and lowering the device overall noise. These advantages can be leveraged to achieve highly sensitive photodetector devices capable of replacing the current technology with further device miniaturization to fit the need for ever-shrinking modern-day circuitry.

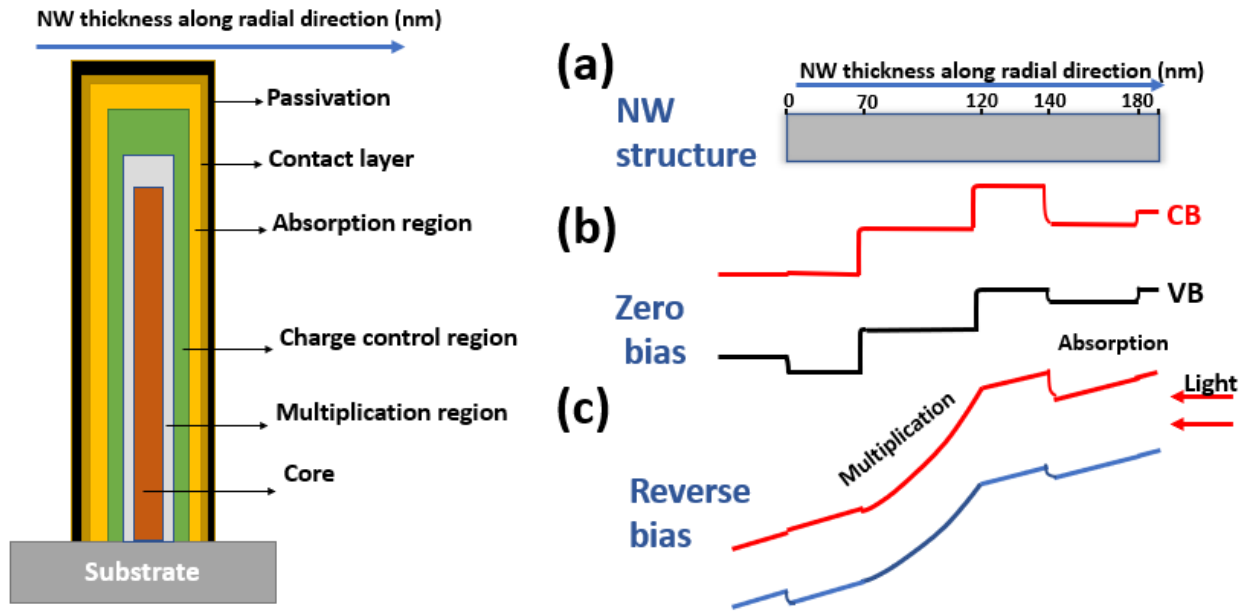


Figure 1.3: A schematic of core-shell NW avalanche photodetector (left), NW band structure along a radial direction at zero bias and reverse bias conditions (right).

A schematic of SCAM NW APD is shown in figure 1.3, which consists of the three distinct regions namely absorption, multiplication, and charge control regions. The incoming light energy is absorbed corresponding to the bandgap energy of the absorption region (figure 1.3 (c)), which generates electron-

hole pairs as shown in figure 1.2. The generated electron-hole pairs are accelerated to the multiplication region in the presence of a high reverse bias E-field, causing an avalanche of generated electron-hole pairs under a suitable E-field. The charge control region facilitates control of the mobility of the carriers passing through it, thus facilitating the avalanche generation of carriers. A separate absorption region APD is advantageous in achieving low levels of dark current and reducing the carrier tunneling probability in the presence of high reverse bias. As the carriers are absorbed and multiplied in separate regions, the overall noise is reduced in the device thus increasing the device sensitivity.

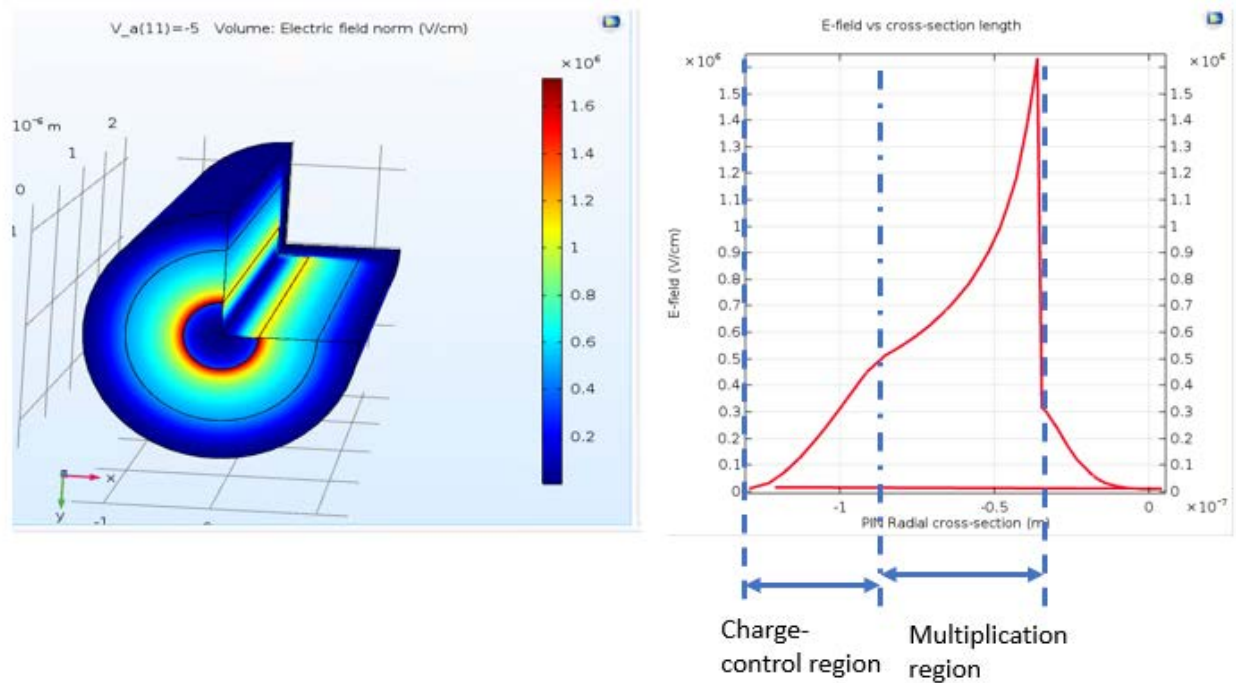


Figure 1.4: E-field schematic around the multiplication region for reverse bias condition; the figure on the left shows a simulated E-field and the right shows a plot of E-field corresponding to the simulated GaAs N-I-P structure.

The E-field is graded inside the device which is tuned by the doping and thicknesses of the underlying structures. This helps to achieve a suitable saturation velocity for carriers entering the multiplication region, thus facilitating the avalanche multiplication. An example of a simulated E-field (figure 1.4) shows a graded distribution of the E-field in the charge-control and

multiplication regions in the GaAs APD structure. In a working NW APD device, there are numerous aspects, besides the doping and thicknesses of the underlying structure, that need to be addressed to achieve a successful avalanche process. These aspects will be covered in the following chapters.

1.6 Applications of nanowires, III-V nanowire photodetectors, and III-V dilute nitrides.

In the past couple of decades, nanowire's attention has stemmed from their promising potential to replace the currently dominating thin-film technology in a wide-ranging application covering optoelectronic to chemical and biological fields. NWs have demonstrated an excellent candidate for photodetectors [88, 89, 97] light-emitting diodes (LEDs) [98-101], lasers [102-104], solar cells [105-107], and also in-field chemical [108-110] and biological advancements [111-113]. This is enabled by the excellent geometry of nanowires for exploring novel physics and chemical properties with reduced dimensions.

Photodetectors are one of the most important fields of applications of 1D inorganic NWs. High responsivity, fast response, high specific detectivity, flexibility in spectral selection, flexibility, and low power consumption are the prominent characteristics that nanowire-based electronics are capable of demonstrating [114]. These superior characteristics are enabled by the light confinement, which increases internal quantum efficiency, prolonged carrier lifetimes, and shortened transit time of carriers due to smaller volume [115, 116]. The development of next-generation high-performance optoelectronic systems can, thus, be facilitated by the NWs due to their small dimensions, flexibility, and compatibility with semiconductor technology today. The flexibility of NW devices stems from the ability to position and control the growth and spacing between nanowires and the ability to be grown on a variety of lattice-mismatched substrates allowing devices to have exciting nanoscale features and performance, robustness against bends

and twists, and be employed on various configurations. The ability to be grown on largely lattice-mismatched substrates allow a variety of NWs to be grown directly on Si substrate, making integration with current matured CMOS technology easier and more cost-effective. With a variety of NW heterostructures and configurations possible, a carefully designed NW grown on Si substrate has a strong potential to have an edge over thin-film counterparts, overcoming the limitations of lattice mismatch, power consumption, process incompatibility, sensitivity, and speed. Quantum heterostructures inclusion[4, 117] and nanophotonic resonances [118-120] have unlocked further perks in the development of NWs as next-generation photodetectors.

The infrared region of photodetection holds a very special significance and groundbreaking applications. Ranging from 750 nm to more than a 10 μm light wavelength, IR detection is divided into three regions, namely near-IR ($\sim 0.7\text{-}2.5\ \mu\text{m}$), mid-wave-IR ($\sim 2.5\text{-}4.5$), and far-IR (above 4.5 μm to hundreds μm), and they can have different applications. Applications include night vision, long-haul space communications, weather monitoring, quantum computing, weather monitoring, pollution measurement, surveillance, and so on [121-123]. III-V narrow bandgap semiconductors are especially of interest in this wavelength region due to their wide detection range, lower dielectric constant, limited self-diffusion at normal temperature, and fairly weak dependence between band edge and composition[121, 124]; thus considered the optimal candidates among different class of semiconductors for high-performance IR detectors at room temperature (RT). Among the regions of IR, the near-infrared region is a very interesting wavelength region encompassing niche applications such as surveillance, quantum computing, optical data transfer, night vision, near-infrared spectroscopy for biomedical applications, etc. In recent years, near-IR detectors based on a variety of III-V NWs have been investigated and demonstrated, which include binary, ternary, and quaternary materials like InGaAs [125-127], InAs [100, 128-130], InP [131-

134], GaAsSb [98, 135, 136], GaAsSbN [101], etc. Efforts have been made to suppress dark current, enhance photo response and photoconductive gain, increase photocurrent to dark current ratio, and increase light absorption efficiency in such detectors.

Dilute nitride III-V nanowires, and material systems share a common applicability field with general NWs extending the region of application from far-infrared to near-infrared region and robust design of devices owing to their unique properties. Dilute nitride III-V nanowires exhibit a duality in their electronic and transport properties [55] and thus shows both bulk-like (homogenous) and fluctuating (heterogenous) characteristics. Homogenous characteristics are, for example, a shift of conduction band with temperature and pressure, showing new-bulk-like absorption edges like E_+ and split E_- , which are explained by models such as “band anti-crossing.” On the other hand, heterogeneous characteristics include localization centers formation and alloy fluctuations, Stoke’s shift between emission and absorption, blueshift of emission peak with increased excitation, asymmetric emission peaks, etc. They are more apparent in photoluminescence characteristics and are more relevant to photo-emitting device fabrication such as LEDs and lasers [55].

Having a distinguishing feature of simultaneous reduction in bandgap and lattice parameter with a nominal amount of incorporation, nitride alloys in nanowire architecture offers numerous advantages like the independent tuning of energy bands, reducing strain in GaAsSb ternary material systems allowing vertical nanowire (NW) growth, and they are thermally more stable than other methods in for telecommunication lasers and high-efficiency solar cells[137]. In comparison to the conventional counterparts, III-nitrides NWs can be void of dislocations and piezoelectric polarization field to a great extent [138], owing to the effective lateral strain relaxation due to a large surface-to-bulk-volume ratio. The addition of Nitrogen in GaAs(Sb)/InGaAs(Sb) material

system has opened the door for numerous other optoelectronic applications which are based on GaAs technologies operating on the important wavelength window of 1.3-1.55 μm for data and telecommunications optoelectronics [137]. The 1.55- μm emission range is attractive for metro-area and “last-mile” applications [139]. The innovative design of solar cells is possible with a dilute nitride III-V material system for increasing the efficiency of cells as high as 50% using the monolithic approach of fabrication of tandem solar cells with four or more junctions [140]. Another interesting property of nitride-based alloy is the large refractive index difference for lattice-matched alloys, enabling DBR mirrors to be epitaxially grown with QW active regions, which can lead to the integration of photonic crystal with lasers, optical multipliers, detectors etc. within a single alloy material system which can lead to the fabrication of a revolutionary ICs technology [55]. One more distinct advantage that (In)GaAsSbN offers over other dilute nitride material systems is the reduction of the miscibility gap, thus allowing alloys to be grown at a higher temperature. This is important for suppressing the defects' point of view.

1.7 Motivation

A reliable NW-based device demonstration remains a challenge compared to the progress in thin-film counterparts. Major delimiting factors for the realization of an NW device include the growth and crystal quality of NWs, sharp interfaces, precise doping control, surface defects, effective passivation, and compositional homogeneity in the NW structure.

Despite the potential dilute nitride materials holds in fulfilling the existing gap, dilute nitride nanowires suffer from inherent defects formation, degradation density, and optical properties rapidly with increasing N-incorporation and more stringent need for growth parameters control with the addition of one more atom in the host lattice. Addressing the issues associated with dilute nitride NWs from the viewpoint of device fabrication can be divided into several aspects such as

resolving the challenge of large-scale implementation using patterned growth, investigating N-incorporation to improve optical and morphological characteristics, suppressing defects and surface states to demonstrate an NW ensemble photodetector (PD) operating at RT.

Next-generation fiber optical transmission systems, computing systems, and other weak light signal devices need high-speed, low cost, low power, and sensitive avalanche photodiodes (APDs) operating at room temperature. The growth and fabrication technology we have today allows us to engineer different nanostructured heterostructures with sharp interfaces with the ability to overcome the bottleneck of film technology that has enabled present APDs. As discussed in earlier sections, GaAs/GaAsSb-based NW APD has the potential to the realization of next-generation PD in the near-infrared region encompassing the telecommunication wavelength range. For attaining a reliable NW APD, the challenge, however, remains significantly high. Starting from the NW growth with precise thickness, doping, material quality, and composition homogeneity, the challenge extends to appropriate passivation, contact formation, annealing, and repeatability of such nanostructured APDs.

The above-listed possibilities and challenges on the dilute GaAsSbN material system and GaAs/GaAsSb based material for core-shell avalanche photodetector call for the following objectives to overcome the gap that exists in N-incorporation in III-V NWs for device applications and the development of GaAs/GaAsSb CS NW APD.

1.8 Objectives

This dissertation focuses on two aspects: 1) Growth and improvement of dilute nitride GaAsSbN alloy for photodetector application and 2) Realization of core-shell GaAs/GaAsSb based nanowire

APD. To address both aspects, a variety of approaches shall be adopted, a brief description of which are as follows:

1.8.1 Enhancement of optical and morphological characteristics of dilute nitride NWs in an axial configuration for ensemble NW photodetector device.

As discussed in earlier sections, the growth of dilute nitride GaAsSbN in Si <111> has plenty of challenges when it comes to attaining good nanowire density, morphological properties, overcoming defects, and optical properties for device applications. A variety of methodology and techniques, including axial inserts, tuning RF plasma source, the methods of N-firing, etc., will be explored to gain insights into the behavior of N-incorporation in GaAsSb material system. Our previous studies on dilute nitride GaAsSbN material systems in axial and core-shell configuration [10, 141] revealed further work and techniques necessary to attain the target emission wavelength of 1.3 μm , one of the main focuses of this dissertation.

1.8.2 Demonstration of ensemble W photodetector device in dilute nitride GaAsSbN (Te) material system.

Dilute nitride-based photodetector device demonstration is the main goal of this work. Ensemble NW device on dilute nitride shall be demonstrated in axial configuration targeting a good spectral response for near-infrared region wavelength up to 1100 nm. Te-doping of nanowires using GaTe captive source is studied to enhance the device performance by increasing $I_{\text{photo}}/I_{\text{dark}}$ ratio. The incorporation of Te in nanowires is found to compensate for the point defects in dilute nitride NWs. This is the first demonstration of the device on axial GaAsSbN (Te) NW Schottky device on Si<111> substrate to the best of our knowledge.

1.8.3 Study of critical parameters for best vertical yield on selected area growth (patterned growth) of GaAsSbN NWs growth and bandgap engineering using pitch length.

The selective area growth of NW not only requires growth parameter tuning but also is influenced by substrate preparation, substrate loading, and other processing parameters namely, electron beam lithography (EBL), reactive ion etching (RIE), Patterned growth on GaAsSb has been established by our group [142] with near 100% hole occupancy and pitch-dependence bandgap. Moreover, the addition of N comes with a bigger challenge to control the growth parameters and growth kinetics. My focus on obtaining patterned growth will be on tuning the growth and understanding growth kinetics aspects, and this work shall be the first reported work on selective area growth of dilute nitride GaAsSbN NWs on Si <111>. A growth model based on previous work on patterned growth of GaAsSb [143] shall be improvised to estimate the length, diameter, and incorporation dependence of various growth species on pitch length.

1.8.4 Study of GaAs/GaAsSb NW growth, doping for C-S APD structure.

Growth of CS GaAs/GaAsSb nanowire in separate absorption multiplication structures involves multiple shell structures around a core. The optimization of the growth of each shell layer, along with the doping optimization, is necessary for designing an appropriate electric field to cause an avalanche breakdown. The fluctuation in doping or unoptimized structure has several implications like tunneling, early avalanche, etc., which might give rise to undesirable Zener breakdown or poor APD. Further, passivation and contact layer growth optimization are crucial in realizing high-quality NW APD. Thus, all the parameters involved in the epitaxial growth of a SAM APD NW structure will be studied to yield an optimum NW APD.

1.8.5 Demonstration of GaAs/GaAsSb CS NW APD on Si <111> substrate.

After successful optimization of ensemble NW growth, demonstration to GaAs/GaAsSb NW APD shall require numerous process iterations involving nanowire growth, annealing, device fabrication processes, and characterizations. The absorption region consists of the GaAsSb segment, which will be tuned for Sb composition for the required target absorption wavelength. The device will be optimized for maximum absorption of target wavelength and high gain characteristics, and low multiplication noise. Critical parameters affecting the avalanche characteristics and the delimiting factors in achieving high-performance device characteristics will be delineated. The underlying challenges for achieving room temperature (RT) photodetection have been addressed to achieve a stable RT photodetection reaching 1.3 μm wavelength with an internal gain exceeding 150 at 1060 nm wavelength. This is the first work on core-shell GaAs/GaAsSb-based nanowire APD. The successful ensemble growth of the APD structure shall be a foundation for extending the work to patterned NW APD growth to demonstrate a high-performance device.

Characterization techniques involved in all these studies include scanning electron microscopy (SEM), μ -photoluminescence (PL), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, room temperature, and low-temperature I-V, and low-frequency noise (LFN) measurements. These tools have been used for obtaining information regarding the NW structure, optical properties, vibrational properties, composition, and NW defects, as well as in calculating and estimating device parameters and performance metrics. Correlating the information from this wide range of instrumentation has enabled us to explore the material properties from numerous

aspects as well as support and validate the results and findings relating to the objectives of this dissertation.

1.9 Dissertation outline

This dissertation work is organized into six chapters, and discussed briefly below:

Chapter 1 provides an overview of III-V nanowires, dilute nitride material system, the basics of APDs, and the applications of these different material systems in the near-infrared region. The motivation behind the research on dilute nitride GaAsSbN material system and GaAs/GaAsSb separate absorption multiplication APD (SAM-APD) is briefly discussed. These discussions are followed by a brief summary of the critical issues and objectives for fulfilling research goals. The chapter is concluded with the achievements of all the accomplished works.

Chapter 2 presents a detailed overview of the growth and characterization tools, and experimental methods adopted in the research works following the chapter.

Chapter 3 delineates the study of dilute nitride nanowire growth optimization in intrinsic and doped configuration and the study of material properties in each setting. The study has been extended to demonstrate a Schottky device sensitive in the near-infrared region up to 1100 nm. Various characterization tools data and analyses are presented to support the findings of this work. This work has been published in the **Journal of Applied Electronic materials (Pokharel, Rabin, et al., ACS Applied Electronic Materials 2.9 (2020): 2730-2738)**. An extension of this work has been submitted for publication in **Nanotechnology Journal (Yuan and Pokharel et.al, Nanotechnology IOP Sci, 2022)**

Chapter 4 presents the study on selective growth and bandgap tuning of dilute nitride nanowires on patterned Si substrate. Critical parameters for growth optimization in the patterned configuration are discussed and the effect of these parameters on bandgap tuning of this alloy is

discussed. Underlying issues and approaches for improving vertical yield are discussed. This work has been published in the **Scientific Reports Journal (Johnson et.al, Scientific Reports (2021). DOI: 10.1038/s41598-021-83973-9)**

Chapter 5 presents a study on GaAs/GaAsSb based separate absorption multiplication avalanche photodetector (SAM-APD) from growth optimization to device fabrication. Various challenges faced and systematic approaches adopted to achieve room-temperature photodetection are presented in the chapter. The manuscript for this work is under preparation for publication in the **Nanotechnology Journal of IOP science (Pokharel et al., Nanotechnology IOP Sci, 2022)**

Chapter 6 summarises the important findings of this dissertation and the future scope of the works.

1.10 Achievements

This dissertation focused on two material systems NWs namely GaAsSbN in axial intrinsic and Te-doped configuration, and GaAs/GaAsSb core-shell configuration. Axial GaAsSbN (Te) NWs are studied to achieve a Schottky device and selective growth, and Core-shell configured GaAs/GaAsSb NWs are studied to achieve advanced avalanche photodetector spanning near-infrared regions up to 1.3 μm . The achievements and important findings of all these works are underlined below:

- (i) First report on the successful optimization of dilute nitride intrinsic and doped NWs to demonstrate high quality and vertical yield showcasing room temperature photoluminescence.
- (ii) First report on NW device demonstration of dilute nitride GaAsSbN NWs up to 1100 nm wavelength with high device responsivity.

- (iii) A study of material properties of doped GaAsSbN NWs in comparison to GaAsSb material for the ultrafast photo-detection application.
- (iv) First report on selective area epitaxy of dilute nitride GaAsSbN NWs aiming to study the pitch-dependent bandgap tuning in this alloy system.
- (v) A detailed study on the critical growth parameters and novel approaches to overcome the underlying issues in material growth limitations towards complex heterostructure employing GaAs and GaAsSb material system in core-shell configuration for high-quality APD device structure that exhibits clear avalanche mechanism.
- (vi) Demonstration of room temperature avalanche photodetection reaching 1.3 μm wavelength in GaAs/GaAsSb core-shell configured nanowires.

Chapter 2

Experimental Details

2.1 Overview

A brief description of the growth techniques, characterization tools, and methods used in nanowire devices growth, device fabrication, and characterization will be discussed in this Chapter. All the nanowire configurations discussed in the following chapters are grown using a bottom-up approach using VLS or VS mechanisms using MBE. The process of device fabrication includes a wide variety of tools and methods, including spin coating, reactive ion etching, chemical etching, and physical vapor deposition (PVD) of metallic contacts. Furthermore, analysis of the device performances and verification of the characteristics is done by a combination of characterization tools, including scanning electron microscope (SEM) imaging, selected area electron diffraction (SAED) pattern, high-resolution transmission electron microscopy (HR-TEM), micro-photoluminescence (μ -PL), DC-IV characterization across different temperature ranges, low-frequency noise (LFN) measurements, and capacitance-voltage (CV) measurements. All of the tools used in device growth, fabrication, and characterization are discussed in the following sections.

2.2 Device growth and fabrication tools

2.2.1 Molecular beam epitaxy (MBE)

MBE is an epitaxial method of thin-film deposition and growth of nanowires of single crystals in ultra-high vacuum (UHV) ambient. A combination of pumping systems consisting of roughing pumps, turbomolecular pumps (TMP), ion pumps, and cryo-pump makes it possible to achieve a UHV environment required for the deposition of high-purity films onto the substrate. The growth

proceeds by deposition of atomic beam or clusters of atoms onto a heated substrate target. The deposition rate of MBE is typically less than 3,000 nm per hour, allowing the films to grow epitaxially, and the deposition using this technique requires a proportionally better vacuum to achieve the same impurity levels as other deposition techniques. The kinetic energy of incoming growth species drives the growth process in MBE, which allows for the growth of highly crystalline material combinations. MBE is widely used in semiconductor device manufacture in a variety of configurations and is also considered one of the fundamental tools for the development of nanotechnologies.

Modern MBE systems are built with a variety of characterization tools attached to the system, making it a versatile tool for research to industrial production. By using computer-automated shutters and growth timings, intricate material structures can be grown using MBE. Quantum wells and quantum dots are an example of precisely controlled structures that can be grown using MBE, which are now an essential part of modern semiconductor devices in applications, such as semiconductor lasers and light-emitting diodes (LEDs).

A Veeco EPI, 930 solid sources MBE is used to grow III-V nanowires used in this study, as shown in figure 2.1.

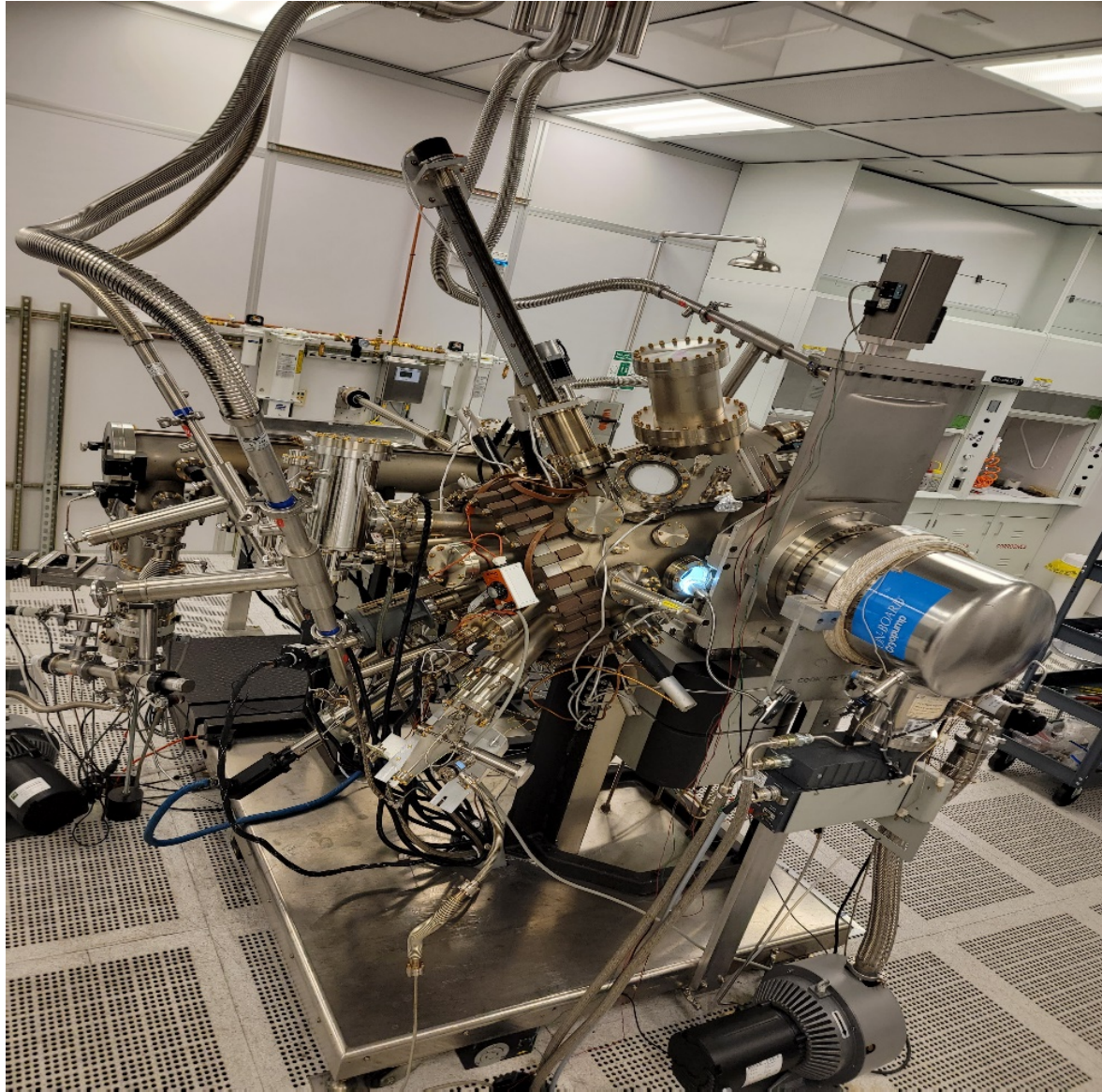


Figure 2.1: Veeco EPI, 930 solid source MBE system used in the growth of nanowires.

The system consists of Knudsen effusion cells to hold Al, In, GaTe, and Be solid sources, one SUMO cell to have Gallium (Ga), and two valved-crackers for Arsenic (As) and Antimony (Sb) sources, and a UNI-Bulb plasma nitrogen source. A SUMO cell consists of the dual filament in a hot lip configuration, the temperature of which is controlled by the power ratio in tip and base segments. A higher tip temperature can be achieved by adjusting the power ratio, allowing the reduction of oval defects and Ga droplet formation in the crucible. A resistive heating effusion

cells are used to hold Al, Te, and Be sources used in the growth. For group V species (As and Sb), valved crackers are used, which allows for controlling the cracking temperature of the species allowing control over tetramers, dimers, and monomers leaving the cell. An accurate beam equivalent pressure (BEP) can be set by controlling the needle valves in these cracker cells. An optical pyrometer is used to monitor the temperature of growth, which works on the principle of thermal radiation. The heat emitted by the substrate is focused onto the radiation thermocouple detector, which is ultimately converted to a voltage that is calibrated to accurately display high temperatures. During growth, the substrate is rotated at an optimized rotation per minute to increase deposition uniformity.

2.1.1.1 Growth details of dilute nitride ensemble and patterned GaAsSbN using MBE.

The growth of dilute nitride $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ ($x < 10\%$, $y < 1\%$) nanowire (NW) on p-type Si (111) was carried out via the VLS mechanism. The details of dilute nitride GaAsSbN growths are described in detail by Ahmad et al. [144] and Manish et al. [10]. Also, NWs consisted of gallium arsenide (GaAs) stem of 200 nm length followed by 300 nm long gallium arsenide antimonide (GaAsSb) segment grown at substrate temperatures of 620 °C and 590 °C, respectively, unless stated otherwise. Again, in most of the NWs, the commencement of the dilute nitride segment began with the firing of the nitrogen (N) plasma at this stage. A Ga cell temperature with arsenic (As) cracker cell temperature set for As_4 species was preset to a V/III ratio of 20 to yield a nominal GaAs thin film growth rate of 0.5 monolayer/second (ML/s). For antimonide growth, an As to Sb ratio of 4:1 was used with a cracked As_4 BEP set to 5×10^{-6} Torr, and for nitride growth, N plasma corresponding to 2.5 ML/s at a BEP of 1.8×10^{-7} Torr was used at 300 W RF-power. The passivating layer consisted of a GaAs shell of ~8 nm grown at 465 °C, which was in-situ annealed for 10 minutes in an ultra-high vacuum at the same temperature.

For patterned growth, a SiO₂ layer of 150 Å⁰ was patterned with square arrays of 50 × 50 patterned holes on p-type Si <111> substrate using Elionix ELS-7500 EX Electron Beam Lithography System. The patterned samples were coated with PMMA via spin coating at 3000 rpm for the 40s, followed by soft baking at 180 °C for 2 minutes. The optimized patterned hole diameter was set to 200nm, and the pitch length varied from 200 to 1200 nm. The cell temperatures and growth rates for axial growth of patterned samples were the same except for the stem growth part. A GaAs stem followed by two different compositions of GaAsSb stem were studied for patterned growth prior to the GaAsSbN core growth. The additional details of the stem growth shall be discussed in chapter 4.

2.1.1.2 Growth of separate absorption multiplication layer avalanche photodetectors (SAM-APD) on n-Si<111> substrates.

Samples were grown on an epi-ready Arsenic (As) doped Si (111) substrate via vapor-liquid-solid (VLS) mechanism using molecular beam epitaxy (MBE) using As₄ and Sb₂ species at a varying growth temperature from 550C to 615C. A Ga cell temperature with arsenic (As) cracker cell temperature set for As₄ species was preset to a V/III ratio of 10 to yield a nominal GaAs thin film growth rate of 0.25 monolayer/second (ML/s). Before sample growth, a native oxide of 15 Å⁰ was grown and is baked at 200C for 8 hours and heated at 615C for 5 minutes before Ga pre-deposition of 10 secs. The GaAs core is grown at a temperature of 615/600C at a BEP ratio of 10, followed by intrinsic and P-doped GaAs segment growth at 550C at a BEP of 12. The substrate temperature was increased to 580C for the growth of the GaAsSb absorption layer and P⁺ GaAsSb contact layer. Finally, a low-doped passivation layer of AlGaAs was grown at 465C for 8 minutes, followed by an intrinsic GaAs segment growth of 2 minutes. Grown samples were in-situ annealed for 10 minutes in an ultra-high vacuum at 465 °C.

A Su-8 polymer is spin-coated and etched to the desired height to expose NW tips before the chemical treatment to remove the passivation layer. Finally, Metal contacts were made to the exposed NW tips and Si surface, which serves as a top and bottom contact of the designed device. Two types of contact configurations were studied for the device performance study, and the details of the study are explained in chapter 5.

2.2.2 Electron beam physical vapor deposition (or EB-PVD)

EB-PVD is a form of physical vapor deposition (PVD) in which the target anode (source material to be deposited) is bombarded with an electron beam that results in the atoms from the target transforming into a gaseous phase, and hence precipitating into solid form onto the desired target. The nanowire ensemble device was deposited with Ti/Au of thicknesses 20 and 200nm to make a front contact. In comparison, the back contact was deposited with Ni/Au of thickness 20nm and 200nm, respectively, using the Kurt J. Laskar PVD75 system.

A schematic of the deposited contacts on GaAsSbN(Te) NWs is shown in figure 2.2 below.

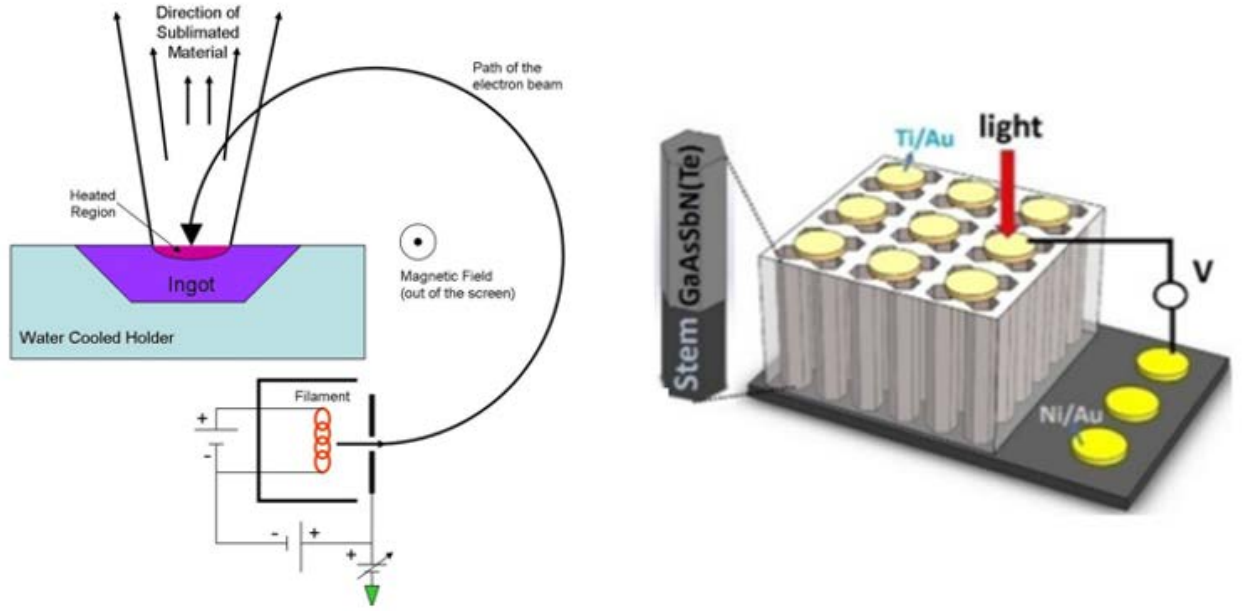


Figure 2.2: Schematic of an electron beam deposition (left), schematic of an NW ensemble device after contact deposition (right).

Prior to contact deposition, the MBE-grown nanowires were spin-coated with a non-conducting PMMA or SU-8 layer, which served as a filler and passivation layer. The resulting structure was followed by oxygen plasma treatment or deep reactive ion etching (DRIE) to expose the nanowire tips. The exposed NW tips were confirmed using SEM and chemically etched to expose the contact layer onto which the contacts were deposited using the PVD system.

2.2.3 Electron beam lithography (EBL)

EBL is a high resolution (sub-10 nm) and low throughput mask-less lithography method of preparing nanoscale pattern arrays in a substrate. This form of lithography is often used in low-volume semiconductor device fabrication and research and development purposes. It uses a focused beam of electrons to draw shapes onto an electron-sensitive film (resist) by changing the solubility of the resist upon exposure. For patterned growth of nanowires, EBL can be used to prepare patterns of holes in oxide-covered Si, acting as a template for positioning the NW arrays. A polymethyl methacrylate (PMMA) layer deposited on the SiO_2 layer acts as a resist layer that is

chemically modified upon exposure to the electron beam. Thus, selective removal of the PMMA resist facilitates the transfer of the pattern to the oxide layer using reactive ion etching (RIE).

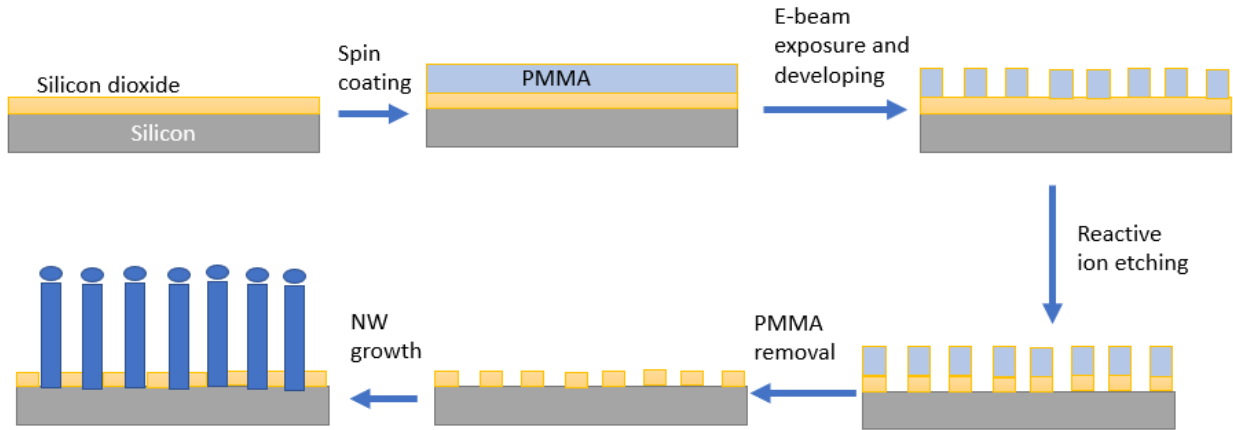


Figure 2.3: Steps for patterned growth on Si substrate using electron beam lithography and reactive ion etching tools.

A silicon dioxide thickness of $150 \text{ \AA}$ was grown using dry thermal oxidation before the deposition of the PMMA layer by spin coating. After etching using RIE, the PMMA layer was removed using oxygen plasma etching. The final pattern of silicon dioxide on silicon substrate was chemically treated using piranha solution to remove organic impurities and finally etched using 1% HF solution to desired oxide thickness for optimizing the NW hole occupancy.

2.2.4 Reactive ion etching (RIE)

RIE is a common etching technology typically used in micro and nano fabrication. It is a type of dry etching technique that uses chemically reactive plasma to etch a desired material in the wafers. The plasma is generated under a low vacuum condition (achieved by a combination of vacuum pumps) by an oscillating electromagnetic field, and the generated plasma reacts with the wafer surface. The type and concentration of gas (or gases) used for generating plasma depends on the etch process and the material to be etched. Sulfur hexafluoride is a commonly used gas used for etching silicon. Gases with Fluorine are good at etching silicon, while metal etching is preferable

with Chlorine based gases. Due to the mostly vertical delivery of reactive ions, RIE can yield anisotropic etch profiles as opposed to wet etching techniques. A general etching schematic of an RIE system is shown in figure 2.

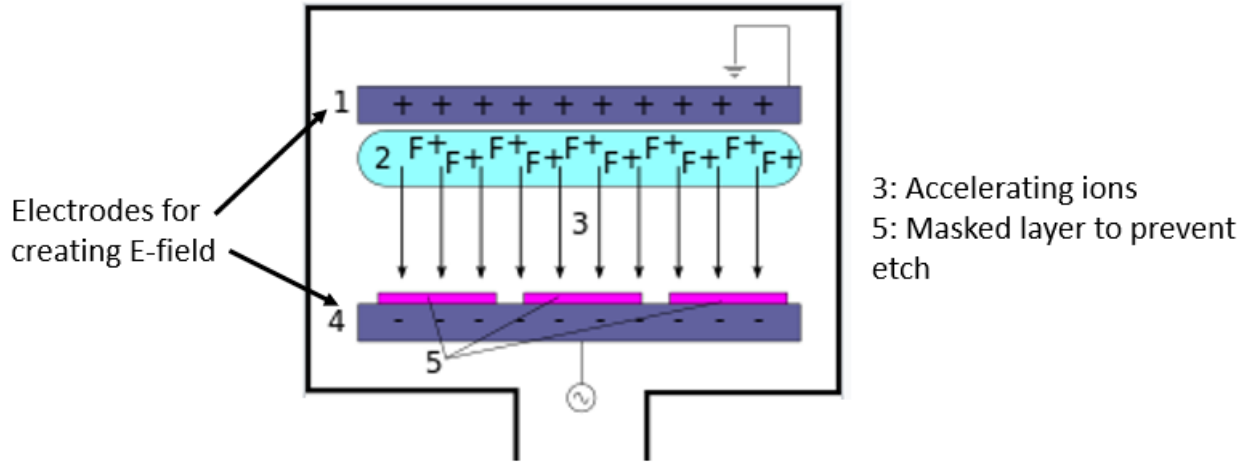


Figure 2.4: RIE operating schematic- ionized atoms are accelerated vertically towards the sample surface due to an electric field, which causes very anisotropic etching.

For the patterned NW substrate preparation process, RIE is used to etch the SiO_2 layer masked by PMMA after the E-beam exposure and development step, as shown in figure 2.3. For the ensemble NW device fabrication process, RIE is used to etch the Su-8 polymer to desired height after spin coating the PMMA onto the NW sample.

2.3 Characterization tools

2.3.1 Photoluminescence spectroscopy

Photoluminescence (PL) is light emission from a matter following the absorption of light (photons). This is an important technique for measuring the band gap, purity, and crystalline quality of the semiconductors, which can be quantified in terms of material disorders in the system. In a typical PL experiment of a semiconductor, the excitation source is greater than the material bandgap energy. The absorbed electrons and holes (excitons) undergo energy and momentum

relaxation towards the bandgap minimum, and finally, the electrons and holes recombine by emitting the photons. This energy release is measured in terms of PL intensity, and the material disorder can be quantified in terms of the full-width half maxima (FWHM) of the PL spectra. The position of PL peak energy corresponds to the direct bandgap of the material.

The PL spectroscopy used in the characterization of our NWs consists of a low vibration closed-cycle optical cryostat from Montana Cryostation consisting of a sample chamber extended away from the cryostat. A fiber-coupled confocal microscope from Horiba Jobin Yvon Inc was used to focus a 633 nm He-Ne laser excitation source onto the sample. The obtained PL signal was dispersed using a 0.32 nm double grating monochromator equipped with an InGaAs detector cooled with liquid nitrogen. The signal is detected using the conventional lock-in technique in the temperature range of 4K to 300 K.

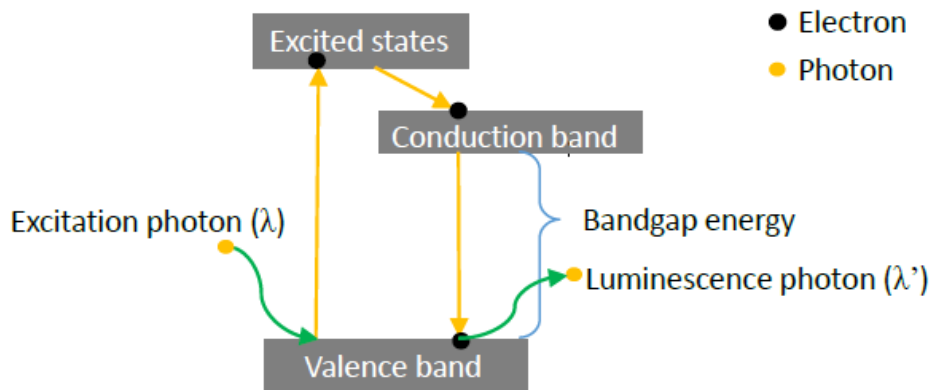


Figure 2.5: The process of photoluminescence.[145]

2.3.2 Scanning electron microscope (SEM)

SEM is one of the most widely used and versatile techniques for observing the surface morphology of a sample. The image is produced by scanning the surface of the sample with a focused beam of electrons at various depths within the sample. By analyzing a variety of signals produced following

the illumination of a focused beam of electrons, which may include secondary electrons, back-scattered electrons, transmitted electrons, characteristics X-rays and light, and absorbed current on the specimen, etc., the image is produced. While it is not common to have all the types of signal detectors in an SEM system, typically, the secondary and backscattered electrons are used to study the surface morphology, and x-rays are used to study the chemical composition of the sample using EDAX. A schematic of an SEM is shown in the figure below.

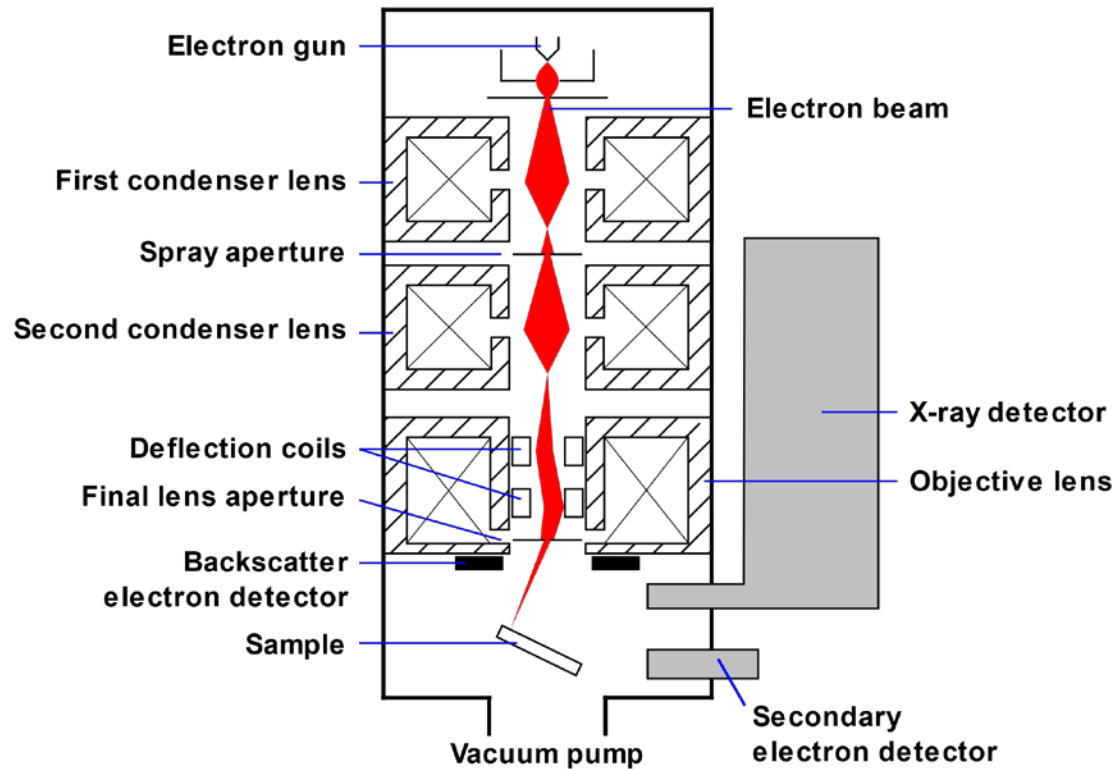


Figure 2.6: A schematic of a Scanning Electron Microscope. [145]

For our samples, the surface morphology of NWs was characterized using Carl Zeiss Auriga-BU FIB field emission scanning electron microscopy (SEM) and equipped with Burker EDS. Typically, a 45⁰-sample stage tilt angle was used to image the NWs, while a 0⁰ tilt was used to image and analyze the tilting and fallen nanowires in the sample. For imaging, samples were placed

in an Aluminum stub using double-sided copper tape for attaching a sample. A typical accelerating voltage of 5 kV and a working distance between 5-10 nm were used for imaging the NW samples. For compositional analysis using EDX, a higher operating voltage of ~20 kV was used.

2.3.3 Raman spectroscopy

Raman spectroscopy technique is commonly used to analyze a structural fingerprint of the molecules by measuring the vibrational modes of the molecules present in the sample. This technique relies on the inelastic scattering of photons, which is known as Raman scattering. Depending on the sample to be analyzed, a monochromatic light source in either visible, near-infrared, or near ultraviolet range is used to shine on the sample resulting in molecular vibrations, phonons, or other excitations in the system which alters the laser phonons upon interaction. The elastic radiation at the wavelength corresponding to the laser line (Raleigh scattering) is filtered out, and the remaining is collected onto a detector enabling the detection of molecules. A schematic of the Raman spectroscopy process is shown in figure 2.7.

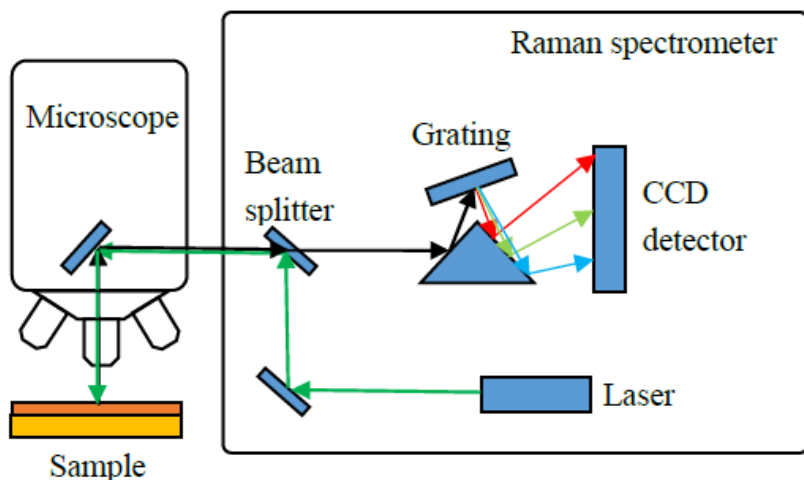


Figure 2.7: A schematic of the Raman spectroscopy process [145]

For the NW samples, Raman spectroscopy was carried out in a Horrible Jobin Yvon LabRam ARAMIS Raman microscope consisting of a 633 nm He-Ne laser excitation. The signal was

detected using a multichannel air-cooled charge-coupled device. Before measuring the vibrational characteristics of the sample, a standard Si sample was used to calibrate the system. The measurements were carried out at the Joint School of Nanoscience and Nanoengineering (JSNN) as well as in Shared Materials Instrumentation Facility (SMIF) at Duke University.

2.3.4 Atomic force microscopy (AFM).

AFM is a very-high-resolution type of scanning probe microscopy that is widely used for nanoscale device imaging, electrical and optical characterizations, and force measurements. AFM consists of a cantilever with a sharp tip (the type and thickness can be selected as per the requirements) that is used to scan the sample surface. It is a versatile technique and can be used both in contact and contactless modes, thus having applications in a wide range of disciplines, including solid-state physics, semiconductor science and technology, molecular engineering, surface chemistry, and many more.

Among numerous modes of AFM, conductive atomic force microscopy (C-AFM) was used for extracting single vertical NW I-V characteristics on Si (111) substrate using Asylum MFP-3D Origin. Ti/Ir-coated Si cantilever of 25 nm radius and spring constant of 2.8 N/m AFM probe was used. An infrared laser with 860 nm wavelength and power density of 37 W/cm² was used for simulating illumination conditions. Topography and corresponding current mapping were carried out under a specific bias of 600 mV at a scan rate of 0.2 Hz [146, 147]. The AFM tip served as the top contact of the NW tip, and the bottom contact was made on the Si substrate using a gold contact, while the voltage bias ranging from -1 V to 1 V under laser illumination and dark was applied to the substrate for I-V characterization.

2.3.5 Transmission electron microscopy (TEM)

TEM is a major analytical tool used in physics, chemical, and biological sciences. This technique of microscopy used a beam of electrons transmitted through the sample specimen to form an image due to the interaction of electrons with the sample, as the beam is transmitted through the specimen. A very high accelerating voltage greater than 100 kV is used to achieve light transmission through the sample. The image is focused onto the imaging device such as photographic film, a fluorescent screen, or another form of sensor to achieve a high resolution. Due to the smaller de Broglie wavelength of electrons, TEMs are capable of imaging at a high resolution capturing fine details like a single column of atoms.

For NW samples, high-resolution transmission electron microscopy (HRTEM), field TEM, and SAED patterns of NW samples were characterized on a JEOL 2010F microscope operated at 200 kV. The NW samples were first sonicated in acetone solution, and a few drops were placed in a lacey Carbon Cu grid and allowed to dry at RT. STEM was characterized using a probe aberration-corrected FEI Titan G2 system at Analytical Instrumentation Facility (AIF) at North Carolina State University (NCSU).

2.3.6 Electrical characterization

Nanowire devices following the device fabrication process were electrically characterized using a two-probe method using Keithley-4200 semiconductor parameter analyzer systems integrated with a radiation shield equipped Lake Shore TTPX probe station. A microHR (LSH-T250) Horiba spectrometer equipped with a tungsten-halogen lamp excitation source was used for studying the device's photoresponse. For ensemble NW devices, the deposition of Ni/Au and Ti/Au thin films with an active area of $7.9 \times 10^{-7} \text{ m}^2$ for each patch served as back and front contacts, respectively.

An optical illumination area of $2 \times 10^{-5} \text{ m}^2$ was used. A schematic of the I-V measurement system using the Keithley source measure unit with pre-amplifiers (to achieve low-current source measure capabilities) is shown in figure 2.8.

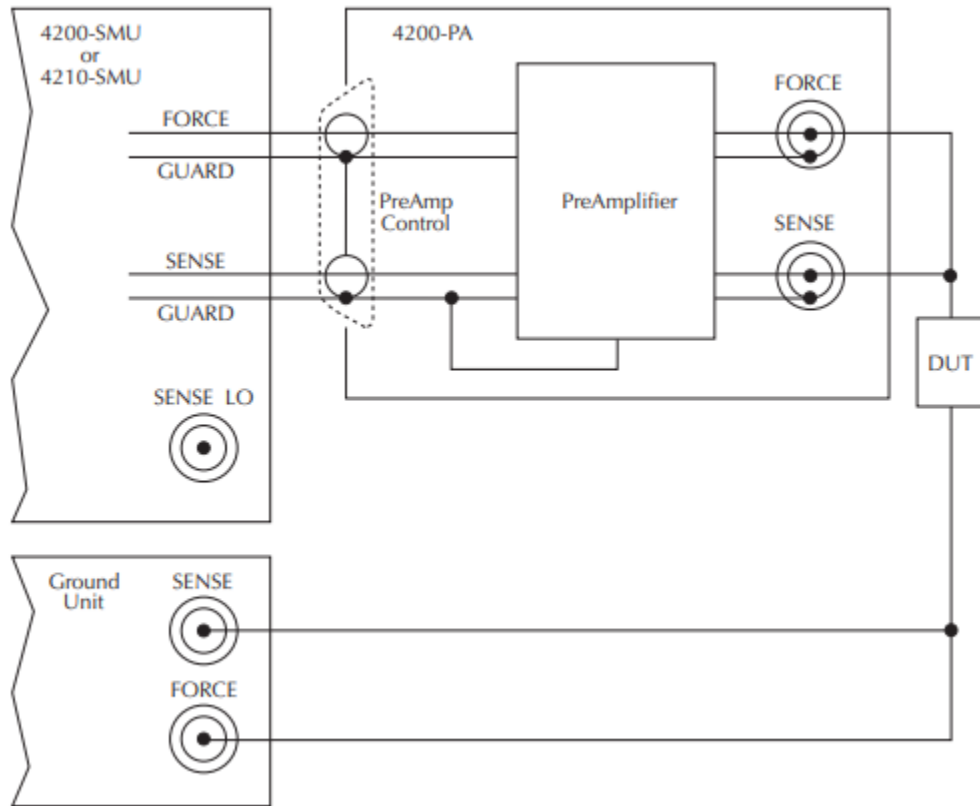


Figure 2.8: A schematic of Keithley 4200 SCS IV measurement system using source measure unit (SMU) equipped with 4200-PA remote pre-amplifiers. DUT refers to the NW device under test.

2.3.7 Low-frequency noise (LFN) measurement

In general, noise is any non-signal-related voltage or current in a system. Measurement of noise gives a lot of information regarding the material and/or device quality, and often performance of the device can be evaluated. In a semiconductor, noise is generally expressed as noise spectral density, which is a term used to describe the noise content in a unit of bandwidth. Different categories of noise can be deduced from a noise spectrum, namely Internal noise, Johnson noise,

shot noise, etc. and analysis of the contribution of these noises is crucial in evaluating the performance of a semiconductor device.

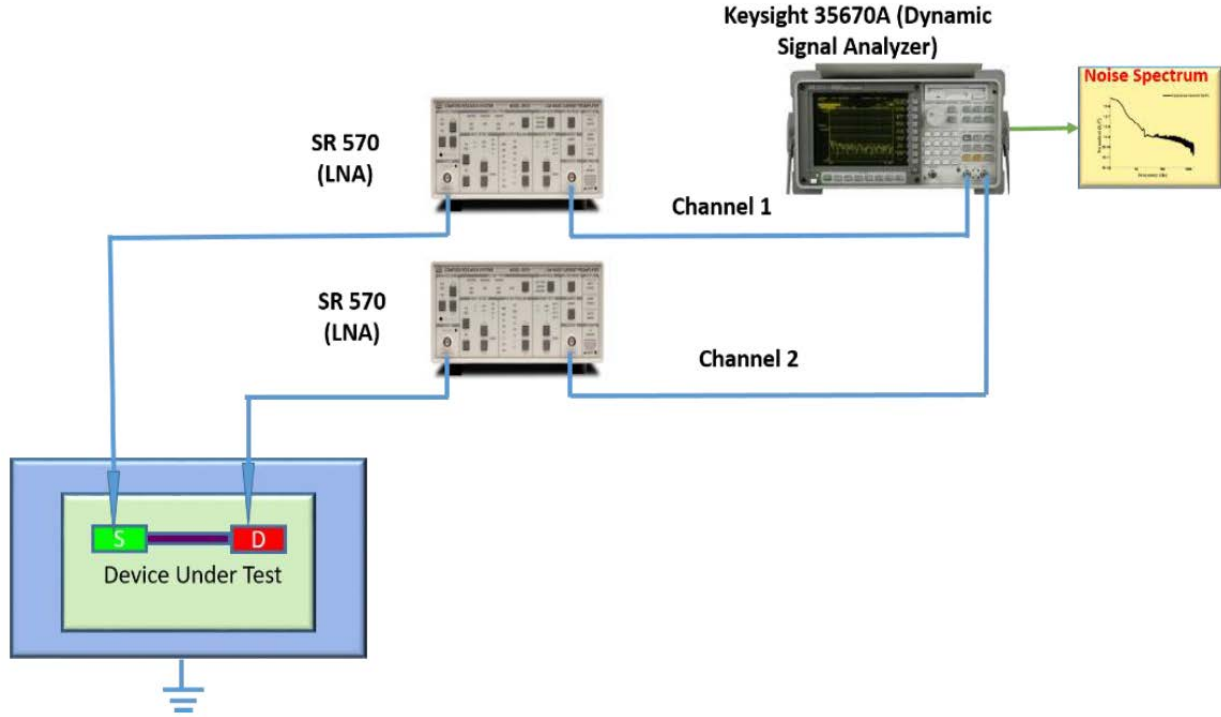


Figure 2.9: A schematic of low-frequency noise measurement setup.

For our NW devices, noise spectrum measurements were carried out using two independent low noise current preamplifiers (SR 570 from Stanford Research Systems) equipped with Keysight 35670 dynamic signal analyzer. The source-drain bias was provided by the internal batteries of these two amplifiers, and its output terminals were connected to two different channels of the dynamic signal analyzer. Measurements were carried out between 1Hz to 6400 Hz, and the data were averaged over 100 sets of readings.

2.4 Conclusion

This chapter provided the details of all the experimental tools and methods used, from NW growth to device fabrication and characterizations. Most of the growth and fabrication tools were used at the Joint School of Nanoscience and nanoengineering (JSNN) facilities at Greensboro. A part of the work, including E-beam Lithography and development and RIE for patterned substrates, was performed at Analytical Instrumentation Facility (AIF) at North Carolina State University.

Chapter 3

Intrinsic and Te-doped dilute nitride GaAsSbN nanowire photodetector

3.1 Introduction

Dilute nitride-based semiconductor NWs encompass the unique ability to tune the bandgap due to significant bandgap bowing caused by the interaction of N-induced energy levels with the conduction band (CB) [148]. Simultaneous tuning of the conduction and valence band energy levels can be achieved with dilute nitride mixed arsenide-antimonide-based semiconductors paving the way toward bandgap tuning in the telecommunication wavelength range. Enhancement of electron effective mass) [149, 150] and increased thermal stability of N-based alloys due to superior carrier confinement [144], along with the advantages of NW configuration, can aid in exploring the unique capabilities of this material system.

A previous study [10] on dilute nitride arsenide-antimonide-based NWs demonstrated a 4K PL emission reaching 1.23 μm , with room to optimize the NW growth and quality for device demonstration in the NIR region. Here, we present modified approaches to the NW growth with a focus on NW density and optical quality of the epitaxially grown NWs, by overcoming the limitations posed by N-incorporation on NW growth conditions and the material quality. A clear RT photoluminescence is demonstrated, which is not normally observed in this material system. The study has been extended to study the effect of Te-incorporation in NW for possible improvement in the device performances.

3.2 Optimization of undoped NW growth.

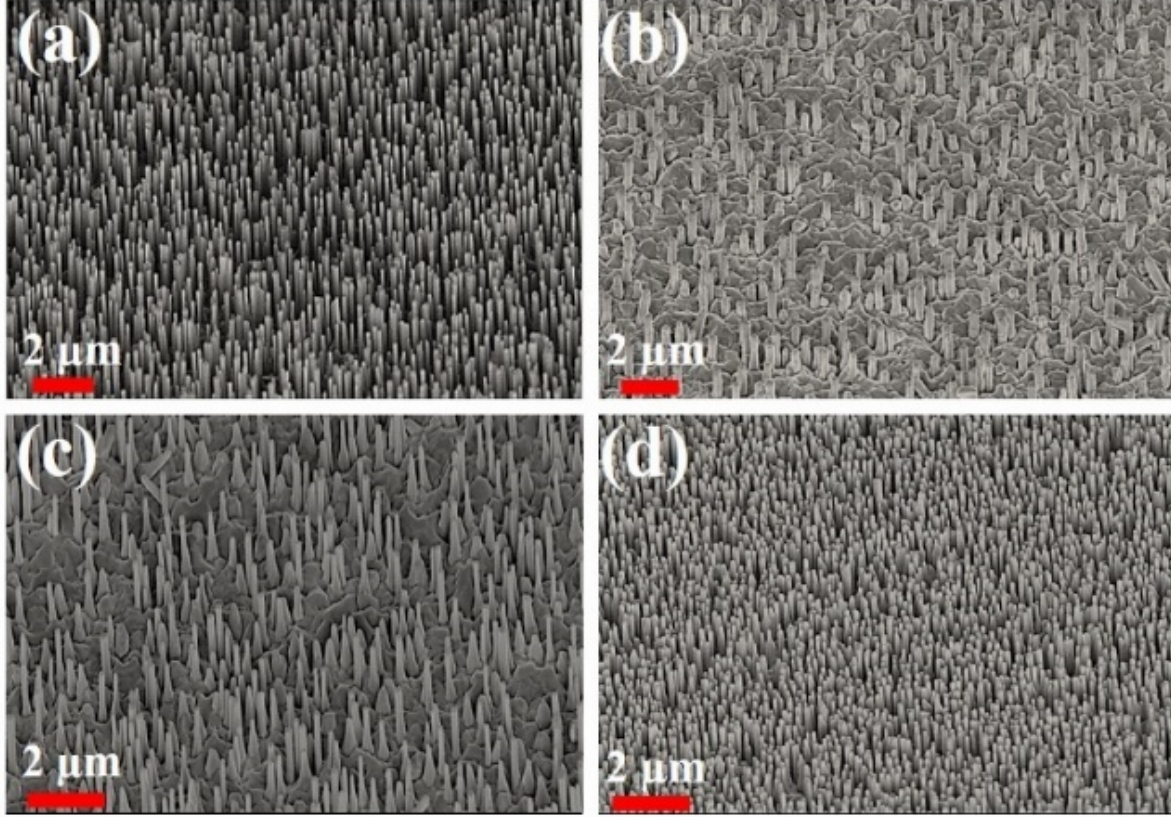


Figure 3.1: Tilted (450) SEM images: (a) Reference intrinsic GaAsSb NWs, (b) N-plasma exposure from the beginning of the growth, (c) N-plasma exposure after the stem growth, and (d) sample has been grown with exposure to plasma intermittently during the growth resulting in dilute nitride inserts.

As-grown dilute nitride arsenide-antimonide NWs showed depletion in the vertical yield and NW compared to the reference non-nitride counterparts (referred to as 7R sample hereafter) grown on p-Si $\langle 111 \rangle$ substrates. The growth details of 7R samples are discussed elsewhere [151], and the SEM images of the 7R sample are presented in figure 4.1 (a). As-grown dilute nitride NWs with N-flux impinging from the beginning of the growth are shown in figure 4.1 (b), which resulted in a high radial growth rate of ~ 10 nm/min and an axial growth rate of ~ 35 nm/min (this sample will

be referred to as DN hereafter) with a concomitant decrease in NW nucleation density and increase in 2D growths. This observation is consistent with an earlier study by Sharma et al.[10]. To mitigate the adverse effect of N-plasma at the nucleation state, NW growth was initiated on a GaAs/GaAsSb stem of approximate length 500 nm (referred to as DS sample hereafter). Improvement in NW density was seen with a simultaneous decrease in 2D growths, with an axial and radial growth rate of 40 nm/min and 8 nm/min, respectively. To study the effect of continuous N-plasma exposure on NWs, we attempted to minimize the exposure of the NW to the direct N-plasma via growth of nitride inserts. NWs were grown with four equal lengths of GaAsSbN inserts (each of ~80 nm) in GaAsSb barrier layers (each of ~500nm), and a dramatic increase in NW nucleation density was observed compared with the reference 7R sample. The axial and radial growth rates of ~80nm/min and ~6nm/min were achieved for this configuration (referred to as IN sample hereafter).

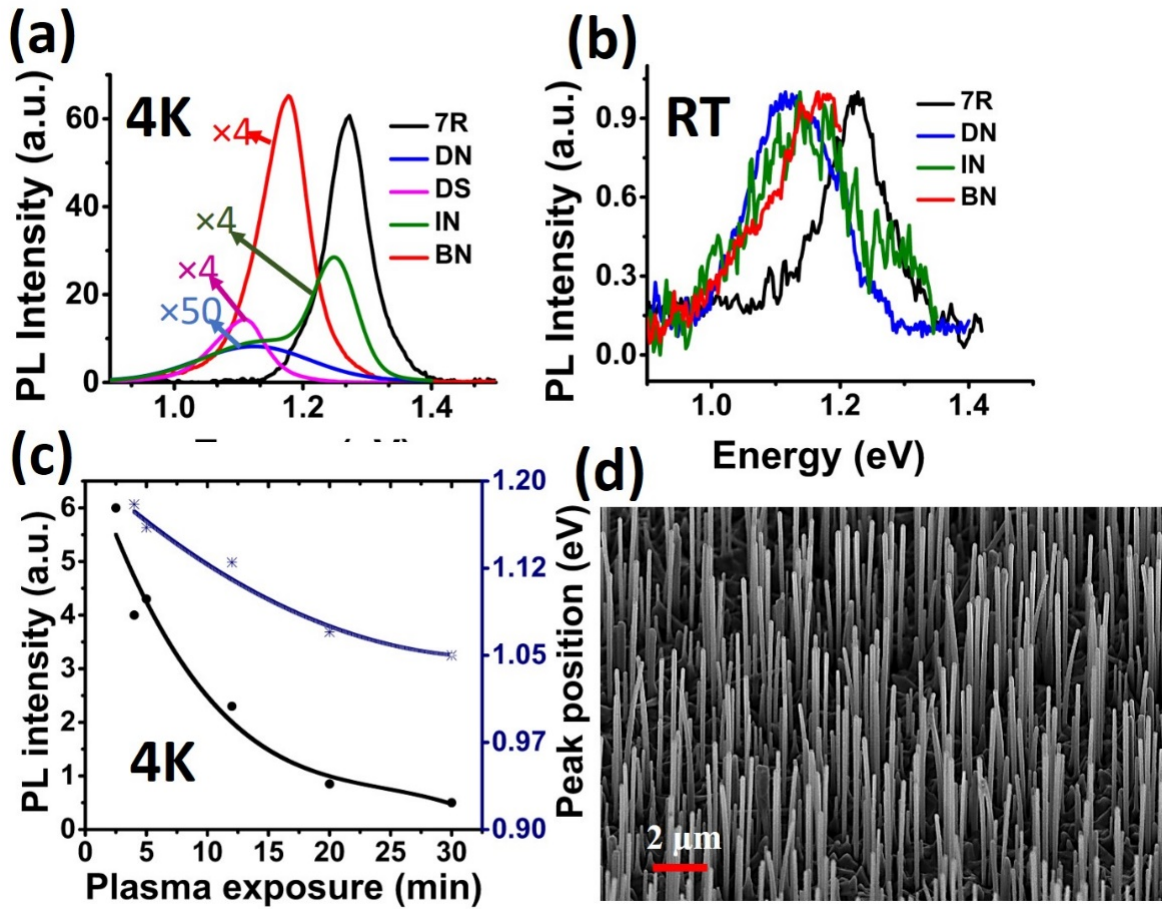


Figure 3.2: (a) PL intensity and peak positions at 4K of 7R, DN, DS, IN, and BN dilute nitride samples (DN, DS, IN, and BN sample peaks are multiplied by factors indicated in the figure). (b) normalized peak positions of samples at RT (excluding DN sample due to the lack of any distinct RT peak), (c) effect of duration of direct N-plasma exposure on 4K μ -PL intensity, and PL peak energy shift, and (d) 45° tilted SEM image of BN sample.

Next, the PL spectrum of the grown samples was examined at 4K and Rt, as shown in figure 4.2.

(a) and (b) respectively. Dilute nitride NWs manifest significantly lower PL emission spectrum intensity than the reference non-nitride samples. Amongst the dilute nitride samples shown, the DN sample did not exhibit a clear RT PL spectrum, while a broad 4K PL spectrum was observed. This is a clear indication of the inferior quality of these NWs. Compared to the DN sample, the DS sample showed an improvement in quality with a visible RT PL peak with a reduction in

FWHM of the 4K PL spectrum. It is to be noted that both the samples exhibited similar bandgap emission peaks, and we can surmise that they have equivalent N-incorporation, while the DS sample exhibited improvement in the material quality. Further improvement in PL emission intensity and FWHM was achieved with a reduction in direct N-plasma exposure time in IN sample (comparison presented in figure 4.2 (a)). In addition to the more prominent peak at 1.25 eV, a distinct broad lower energy peak at 1.14 eV can be discerned for IN sample corresponding to GaAsSb and GaAsSbN bandgap emissions. All the dilute nitride samples showed a weak temperature-induced bandgap shift of 6-10 meV from RT to 4K temperatures. The comparison of the PL peak positions and FWHM of the samples under study is shown in table 4.1.

Table 3.1: Photoluminescence peak positions and FWHM at 4K of 7R, DN, IN, DS, and BN samples.

Sample	Peak1 (eV)	FWHM1 (meV)	Peak2 (eV)	FWHM2 (meV)
7R	1.25	85	-	-
DN	1.1	200	-	-
DS	1.12	120		
IN	1.14	220	1.25	80
BN	1.18	110	-	-
Te-BN	1.18	80		

Nitrogen impingement on the Si substrate was found to enhance the nucleation rate [152], whereas Sb tends to lower the Ga diffusion length and As adatom mobility due to the surfactant effect, hence lowering the chemical potential of the droplet to be nucleated. This effect is most likely to promote the coalescence of neighboring islands resulting in 2D growths, which compete with the NW growth. Thus, the observation of higher 2D growths for the DN sample is justified due to the increased contribution of incoming flux toward 2D growth and less towards the NW growth. In the other case of the DS sample, the growth of the GaAs/GaAsSb segment before the N-incorporated GaAsSb segment enables the separation of the

nucleation stage from the growth of dilute nitride NWs. The presence of Sb in the stem growth also facilitates a larger diameter compared to only the GaAs segment, which is required for subsequent GaAsSbN growth. Thus, an increase in NW density can be expected for this sample, as shown in the result. Although the DS sample exhibited an increase in the nucleation density (figure 1(c)), a tapered NW morphology was observed, which is attributed to the rapid consumption of the droplet under Sb and N fluxes imposing a barrier for other growth species incorporation and hence termination of the growth [153]. Replacement of Sb by N atoms at the NW sidewall surface due to the Sb-N exchange mechanism leads to diffusion of N-atoms towards the NW core occupying Sb vacancy sites [154]. This interdiffusion is likely to reduce the Ga adatom diffusion length that drives the lowering of the replenishment rate of the melt, suppressing the VLS mechanism. The result is a direct reduction of the axial growth rate and an increase in radial growth rate facilitated through a step-mediated growth mode [155]. This was overcome in IN sample by limiting the exposure to direct N-plasma by intermittent exposure, thus reducing the tapering and parasitic 2D growths. The presence of RT PL in all the dilute nitride samples except DN and a gradual deterioration of PL emission at 4K from IN to DS to DN sample corroborate the reduction in NW quality. The effect of longer duration on N-plasma exposure is surmised in figure 2(c), which suggest a redshift in PL spectrum upon higher N-plasma exposure, signature of N incorporation. Increased N-plasma exposure is likely to favor higher Sb-N exchange mechanism and hence N-incorporation, and thus increase the N-induced potential fluctuations in the CB of the alloy [57, 156].

From the above discussions, we hypothesize that the deterioration in the NW quality is due to direct N-plasma exposure. Thus, to minimize the effect of plasma damage and study the incorporation of Nitrogen upon background exposure, the growth of NWs was carried out with the N-shutter closed. This methodology of growth resulted in a significant enhancement of the growth rates in the axial direction and minimization of growth rate in the radial direction at a comparable NW density compared to IN sample. An axial growth rate of ~ 130 nm/min and a radial growth rate of ~ 5 nm/min was observed with a concomitant decrease in the undesired 2D growths and an

increase in NW uniformity, shown in figure 2d (referred to as BN hereafter). A remarkable enhancement in PL emission intensity was observed with a significant reduction in FWHM of the peak (comparison presented in table 4.1) compared to the rest of the dilute nitride samples. Moreover, the 4K PL peak energy disclosed a slight blueshift relative to the direct N-exposure samples, while the gain in PL intensity was significant. Compared to the reference 7R sample, the PL spectrum of the BN sample still exhibited a red shift, as shown in figures 4.2 (a) and (b) for 4K and RT, respectively. This supports our hypothesis that circumventing the direct exposure of RF-plasma on the NWs leads to a reduction in the undesirable RF species affecting the NW qualitatively. We surmise that the plasma-induced damage due to the high kinetic energy of the ions as well as the unwanted plasma species reaching the NWs can be avoided by preventing direct exposure of plasma to NWs at the expense of less N-incorporation. It is to be noted that roughly 1% of the composition was Nitrogen in the alloy based on ~ 270 meV redshift in the PL spectrum compared to the 7R sample [56].

To further study the properties of the grown GaAsSbN alloy, HRTEM, SAED, and EDX tools were used. These characterizations were done at Analytical Instrumentation Facility (AIF) at North Carolina State University (NCSU). The image obtained from HRTEM, SAED patterns, and the compositional profile using EDX are shown in figure 4.3.

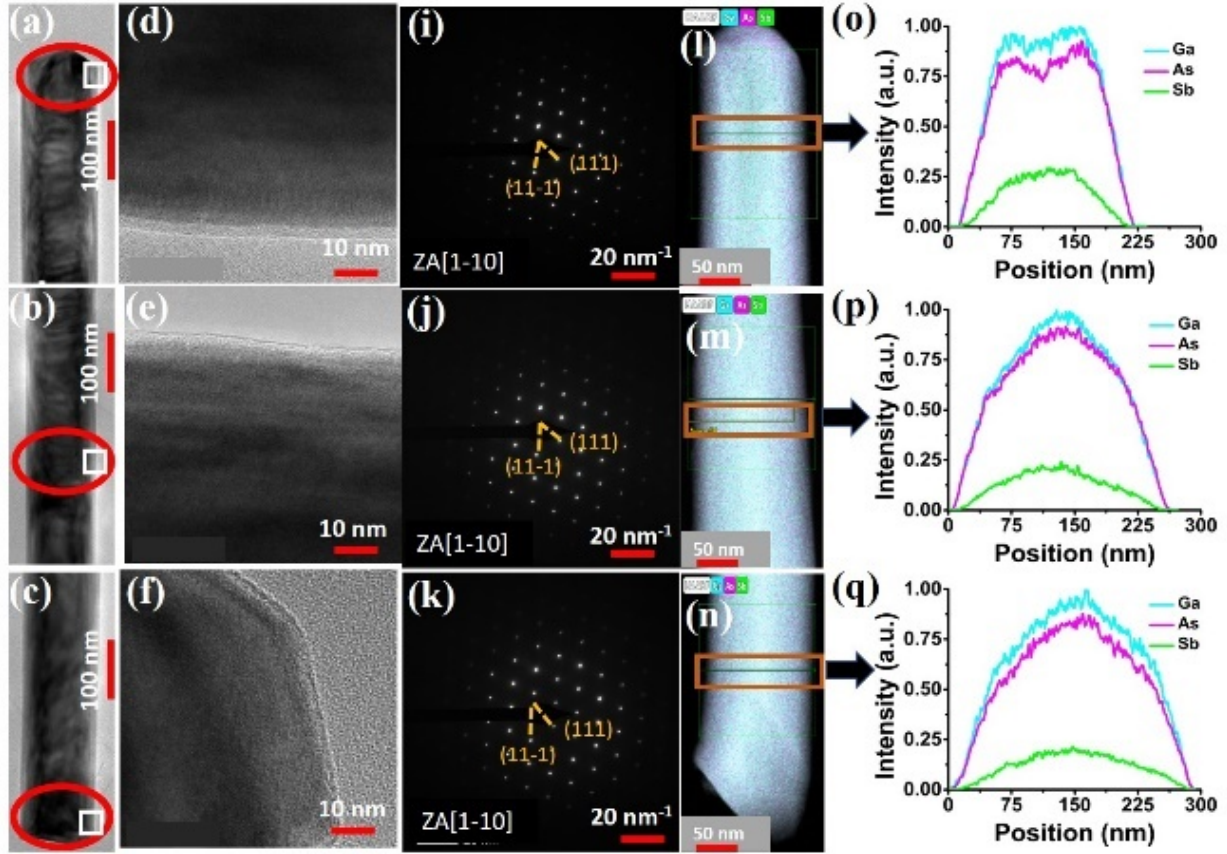


Figure 3.3: BN sample: (a, b, c) NW top, middle, and bottom segments scan locations; (d, e, f) HRTEM images at respective areas indicated by a white square on images a, b and c; (i, j, k) SAED patterns on respective sites pointed out by red circle on images a, b and c; (o,p,q) EDS radial composition profiles at the individual line positions in false color mapping of HAADF images shown in l,m, and n.

The SAED patterns indicate a pure zinc blende (ZB) crystal structure at the bottom, top and middle segments of the NWs. SAED patterns were devoid of satellite diffraction spots suggesting the absence of planar defects in the NWs. This is attested by the HRTEM images, which show a single ZB crystal structure at all the imaged portions of NWs. From EDX analysis (shown in figure 4.3 (o), (p), and (q)), the radial composition of Sb was found to be nearly consistent amongst all the segments. The top segment showed a mere increase in Sb incorporation, which is attributed to the temperature-dependent phenomenon of Sb incorporation [157] and/or self-induced compositional gradient [158]. In addition, as the segment of NWs towards the surface favored the N-Sb exchange

mechanism more, the incorporation of N shall be more towards the edges. This phenomenon is also likely to be responsible for the strain compensation in the NWs, leading to a planar-defect-free structure and vertical NWs.

3.3 Choice and optimization of Tellurium (Te) doping in NWs

The doping study of semiconductor heterostructures is crucial to the development of devices, and thus the study is expanded to study the doping incorporation on GaAsSbN using a GaTe captive source. The choice of the dopant source is grounded on the potential of using the GaTe source to achieve precise doping temperature control and a high level of doping that can reportedly be achieved at low temperature compared to the rest of the dopant sources [159, 160].

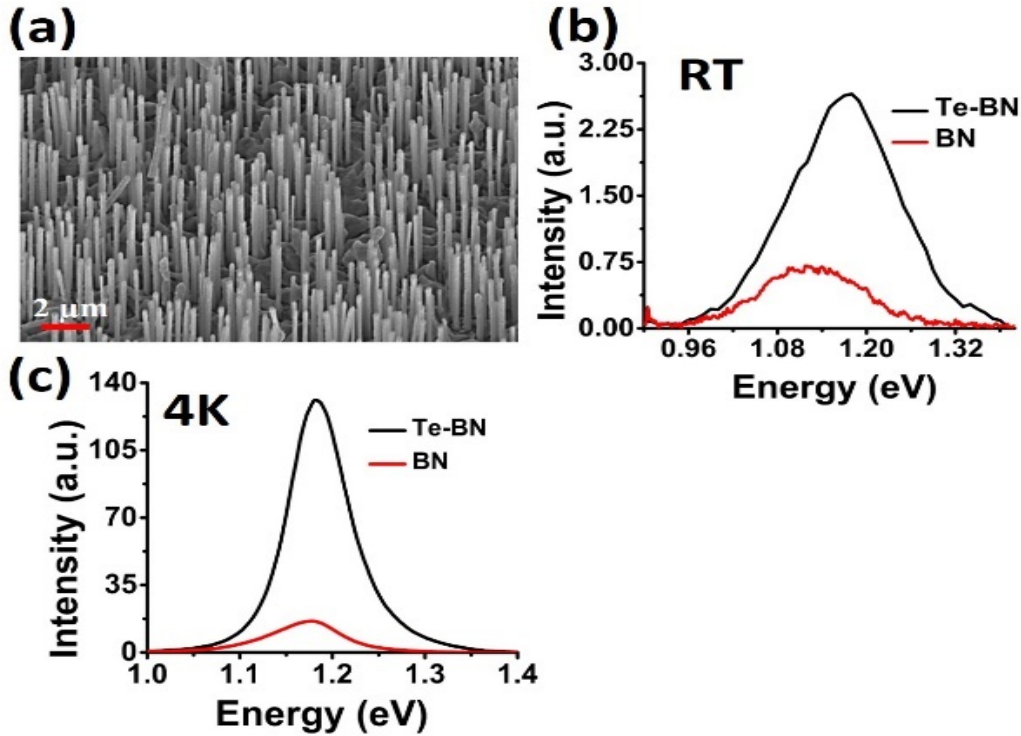


Figure 3.4: (a) SEM image of Te-BN sample, and (b, c) comparison of RT and 4K PL spectra of BN and Te-BN samples.

The optimization of doping temperature for optimum doping is based on achieving the suitable doping range for the annihilation of the intrinsic defects in the GaAsSb-based material system and

is discussed elsewhere [161]. The optimized BN samples were doped with Te dopant at a GaTe cell temperature of 540 °C. Figure 4.4 (a) shows the optimized Te-doped GaAsSbN NWs (referred to as Te-BN hereafter). The NWs exhibited an axial growth rate of 112 nm/min and a radial growth rate of 7 nm/min with an increase in NW diameter to ~215 nm, indicating the incorporation of Te, also consistent with work by Ahmad et al. [162]. Due to the surfactant nature of Te, we can expect an increase in radial growth rate and hence the increase in NW diameter compared to the BN sample. An increase in PL emission intensity at RT and 4K by four-fold and nine-fold, respectively, were observed (shown in figures 4.4 (b) and (c)), which corroborates the increase in free charge carrier's density via doping. Furthermore, a decrease in FWHM of the μ -PL spectrum peaks from 110 meV in BN sample to ~80 meV in Te-BN sample supports a hypothesis that there is a reduction in the defects and/or improvement in the compositional homogeneity of the grown NWs.

To support the hypothesis, a Raman characterization of the samples was done before and after the doping. Figure 4.5 (a) shows the comparison of Raman spectra of the BN and Te-BN sample along with the reference 7R sample. The Raman peaks for all the samples constitute GaAs TO, GaAs LO, and GaSb TO vibrational modes, which can be identified in figure 4.4 (b) for a Te-BN sample. TO and LO peaks at 265 cm^{-1} and 285 cm^{-1} , respectively for the reference 7R sample with a weak Raman peak at 235 cm^{-1} corresponding to the local vibrational mode of GaSb in GaAs, commonly observed in III-V ternary alloys [163, 164]. In contrast, the BN sample exhibited a large redshift of 6 cm^{-1} and 5 cm^{-1} , respectively, in TO and LO modes while exhibiting increased symmetry and broader line shape along with an increase in TO/LO ratio. This feature of large redshift with supporting evidence from the Raman spectra shapes is consistent with previously reported attributes of dilute nitride NWs attributed to phonon localization at N-induced point defects [10,

144, 165]. In sum, these Raman characteristics features point towards the evidence of N-incorporation induced defects in the NWs. On the other hand, the LO and TO modes in the Te-BN sample were observed close to the 7R samples at 263 cm^{-1} and 283 cm^{-1} , respectively, with a much less redshift of 2 cm^{-1} compared to a large red-shift in the BN sample. The rest of the characteristics feature of the Te-BN sample nearly approaches the 7R sample, with a note that the Raman scattering intensity is significantly low in the rest of the dilute nitride samples. These observations, with earlier observed enhancement in the PL spectrum intensity, suggest the compensation of either N-induced defects and/or acceptor-type vacancies in the GaAsSb(N) material system. It can be speculated that the competition between the formation of the Te-complex and N-induced point defects might lead to the suppression of the latter. A similar observation can be found in a report by Jin et al. [166] on the Si doping of the InGaAs material system. Piton et al. [167] reported a similar possibility where the suppression of structural defects was observed with Be-incorporation in GaAs NWs. Furthermore, a decrease in GaSb-like TO mode in the dilute nitride NWs of BN and Te-BN samples can be attributed to a reduction in Ga-Sb bonds in crystal lattice due to the earlier mentioned Sb-N exchange mechanism, in agreement with our previous work by Sharma et al. [10].

Next, we examined the structural integrity of the material system to examine the difference from the non-doped BN sample. The HRTEM, SAED patterns, and EDX plots of the Te-BN samples are presented in figure 4.6. As expected, the compositional homogeneity was intact in the doped samples, although there is no direct evidence that can be derived regarding the improvement in the crystal structure in terms of non-structural defects. Compositional uniformity was found to be consistent radially among the top, middle, and bottom segments and significantly consistent

throughout compared to the BN samples. NW tapering was observed in the samples, which is attributed to the presence of two surfactants, Sb and Te, as discussed earlier.

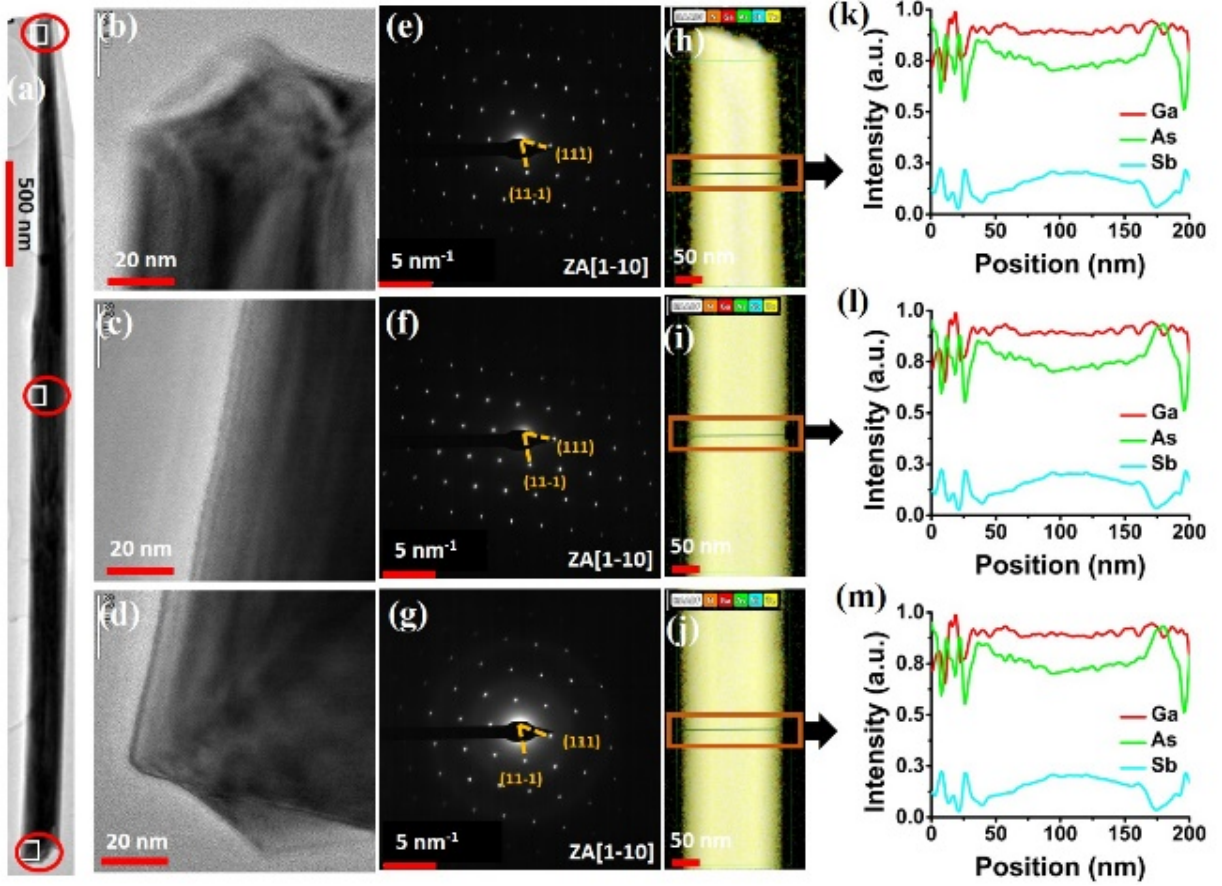


Figure 3.5: Te-BN sample: (a) NW image showing top, middle, and bottom segments; (b, c, d) HRTEM images at respective areas indicated by the white squares on the image a; (e, f, g) SAED patterns on respective locations indicated by red circle on the image a; (k, l, m) EDS radial composition profiles at the individual line positions in false color mapping of HAADF images shown in h, i, and j.

3.3 Electrical and optical characteristics of Single NWs

After a successful doping examination of the dilute nitride GaAsSbN samples, the electrical characteristics of the samples were examined for their applicability in NIR region photodetection. The samples were first characterized electrically using the AFM tool before device fabrication for further testing. Figures 4.7 (a), (b) and (c), (d) represent the topography and corresponding current mapping of the respective BN and Te-BN samples. The experimental detail of this process is

presented in chapter 2 earlier. From the topography mapping and the current mapping, we can observe an increase in NW diameter as well as the increase in an average current distribution in the Te-BN sample compared to BN and IN samples, both of which exhibited similar distribution in current mapping. Next, a comparison of the I-V plots under unilluminated and 870 nm illumination for IN, BN, and Te-BN single NWs is presented in figure 4.7 (e). Schottky behavior was common for all the samples, and the responsivity of ~ 12 mW/W, ~ 1 A/W, and ~ 5 A/W, respectively, were achieved at 1V reverse bias for IN, BN, and Te-BN samples with corresponding diameters of ~ 190 nm (± 11 nm), ~ 150 nm (± 9) and ~ 215 nm (± 14). As the Te-BN samples exhibited the highest PL spectra intensity, along with the highest responsivity, we speculate an increase in carrier lifetime from Te-doping due to defect compensation phenomena. Three primary non-radiative recombination mechanisms are responsible for carrier lifetime determination, namely Auger recombination, surface recombination, and Schottky-Reed-Hall (SRH) or trap-assisted recombination, amongst which the contributions from Auger and surface recombination are speculated to be similar for all the samples given they have NWs of near-identical material composition. In the case of Auger recombination, the effect is significant, particularly in non-equilibrium conditions with very high carrier density [168]. Thus, a reduction in the SRH recombination mechanism points towards the observed enhancement in photoconductivity and hence responsivity in Te-doped samples. This reduction in SRH recombination shall be induced by the compensation of N-induced defects and/or compensation of group-V vacancies, which also corroborates the earlier study using Raman spectroscopy. An aiding factor for the increase in NW responsivity in Te-BN samples is the increase in diameter of the Te-BN sample by approximately ~ 60 nm leading to a reduction in loss of carriers due to surface recombination, hence improving the NW channel conductivity.

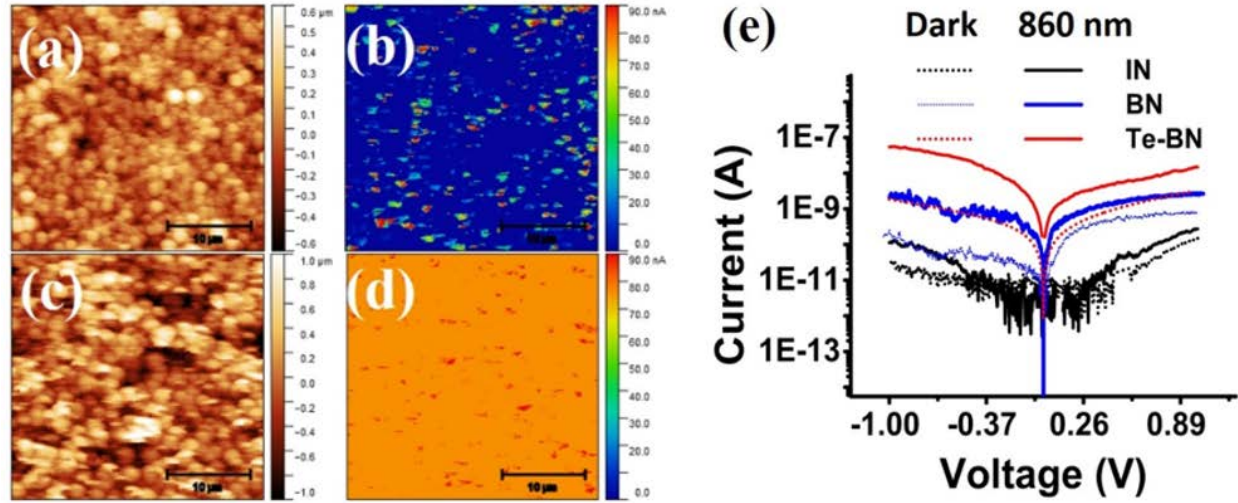


Figure 3.6: Surface topography and corresponding current map of (a, b) BN sample and (c, d) Te-BN sample, respectively. (e) Semi-log I - V characteristics of IN, BN, and Te-BN single nanowires (SNWs) grown on p -type Si (111) substrate in the dark and under 860 nm illumination using C-AFM.

Based on improved NW optical and electrical characteristics of the Te-BN sample compared to the rest of the dilute nitride samples, ensemble NW devices were fabricated using Au/Ni back contact and Au/Ti front contacts (the details of device fabrication can be found in chapter 2).

3.4 Electrical and optical characteristics Ensemble NWs

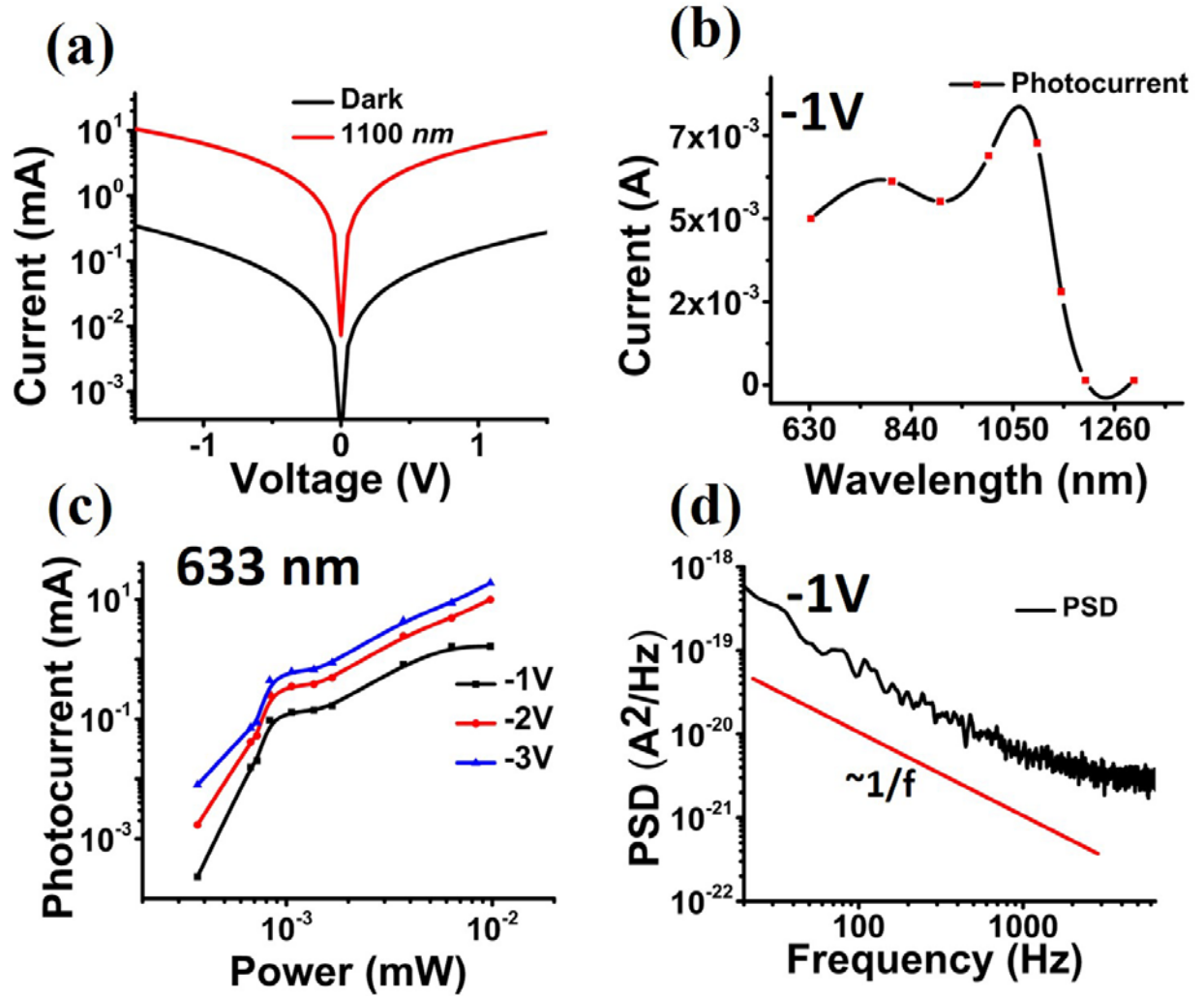


Figure 3.7 Te-doped GaAsSbN ensemble NWs: (a) Photoresponse at 1100 nm, (b) spectral response at 1V reverse bias, (c) power dependence of the sample with illumination power for different bias voltages at 633 nm laser illumination, and (d) power spectral density vs. frequency plot and $1/f$ fitting of noise in the frequency range of 10-3200 Hz.

In agreement with the single NW characteristics, a double Schottky behavior was observed for the sample as depicted in I-V characteristics in figure 4.8 (a). A fitting to the experimental I-V curve resulted in a respective ideality factor and barrier height of 5 and 0.83 eV, and 4.5 and 0.81 eV, respectively, in the forward and reverse bias. This result suggests the presence of the tunneling mechanism being dominant over the thermionic emission (TE) mechanism for carrier transport in these NWs. From I-V characteristics,

an excellent device responsivity of ~ 3800 A/W at -1V was calculated. The spectral response of the NWs was studied for a wavelength up to 1300 nm at 1V reverse bias (shown in figure 4.8 b). The NWs showed a good photoresponse up to a wavelength of 1100 nm and a rapid decrease in absorption following 1100 nm, finally cutting off at 1200 nm illumination wavelength. The power dependence of illumination on NW device at reverse bias ranging from 1V to 3V showed a super-linear behavior at low excitation below 10^{-3} mW and linear behavior above $\sim 10^{-3}$ mW (shown in figure 4.8 c). Surface recombination of the photoexcited carriers at the vicinity of the NW contacts and/or the lateral spreading of the photoexcited carriers is likely to cause a drastic decrease in photoexcitation current at lower excitation power [29, 30]. It should be noted that no intentional contact annealing was carried out for the NW devices. In order to further investigate the trap characteristics, the low-frequency noise (LFN) spectrum of the ensemble device was studied at 1V reverse bias (shown in figure 4.8 d). A $1/f$ dependence was seen in the noise characteristics taken up to a frequency of ~ 3 kHz, which is indicative of a dominant tunneling mechanism consistent with the earlier observation. The NEP and detectivity calculated for a bandwidth of 100 Hz are 3×10^{-11} W and 3.2×10^{10} Jones, respectively.

3.5 Conclusion

A systematic and comprehensive study of quaternary dilute nitride GaAsSbN NWs in intrinsic and doped settings is presented in this work. An optimized NW growth setting has been successfully identified for this material system growth on Si <111> substrate with a planar defect-free and pure ZB structure in both intrinsic and doped settings. Confirmation of Nitrogen incorporation and hence bandgap tuning respective to non-nitride counterparts have been achieved and confirmed using PL spectra. Successful doping of the NWs using GaTe captive source has been demonstrated for improvement of ingrown material properties via point defects compensation as suggested from Raman scattering and PL characteristics. A great promise for near-infrared region applications can be deduced from the results with the device responsivity value in the NIR region comparing well

with the literature [100, 125, 128, 135, 169-171]. Responsivity reaching 4.4×10^3 A/W and detectivity 2.6×10^{11} Jones has been reported by Liu et al. [128] on a single NW in a horizontal configuration, reaching 1100 nm emission wavelength in an InAs PD. Similar results have been shown by Zheng et al. [172] in the NIR region, achieving excellent responsivity and detectivity of 2.8×10^5 A/W and 9.1×10^{15} Jones, respectively, up to 833nm. Among a handful of vertically configured ensemble NW device reported in the NIR region [130, 173-175], Sharma et al. [151] demonstrated the highest responsivity in a GaAsSb NW, up to 1100 nm wavelength, with responsivity and detectivity reaching ~ 300 A/W and 1.9×10^{10} Jones, respectively. We surpass these previously reported device metrics in the Te-doped dilute nitride material system. However, significant room for progress and further study exists. As no intentional ex-situ annealing was carried out on NWs and device contacts, improvement in photodetector performance is possible via reduction/annihilation of NW and contact defects. Further, selective epitaxy of the NWs shall improve the NW uniformity and waveguiding effect, which can be utilized to enhance the device's performance.

This study led to the first successful demonstration of a vertically aligned Te-doped GaAsSbN NWs-based PD device with a responsivity of ~ 5 A/W (@860 nm) on SNW and ~ 3800 A/W (@1100 nm) on an ensemble NW device. Further, a detectivity of 3.2×10^{10} Jones in achieved ensemble configuration.

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A part of this work is submitted for publication in the Nanotechnology journal (Yuan, Long, and Pokharel, Rabin et.al. "Revealing charge carrier dynamics and transport in Te-doped GaAsSb and GaAsSbN Nanowires by correlating ultrafast terahertz spectroscopy and optoelectronic characterization."

Chapter 4

Selective area epitaxy (SAE) of dilute nitride GaAsSbN nanowires

4.1 Introduction

Selective area epitaxy (SAE) technique is the growth of an epitaxial layer on a patterned amorphous dielectric mask such as SiO₂ deposited on a semiconductor substrate. The patterned holes on the mask are fabricated using standard microfabrication techniques followed by selective etching of the mask layers. Precise control over the dimensions and compositions can be achieved using SAE techniques, which is crucial for achieving highly sensitive devices with a high degree of reproducibility. Further, this allows one to exploit the pattern designs for effective waveguiding that can enhance the light absorption and responsivity of the photodetectors. In NW configuration, the composition of the material is found to depend not only on the incoming fluxes but also on the type of substrate surface [176], nanowire density, adsorption, and reflection of incoming fluxes. Patterned growth thus provides a pathway to effectively control all these factors since the control over NW architecture and composition becomes much more feasible compared to ensemble growth.

In this chapter, we show a study of patterned GaAsSbN nanowires on p-type silicon <111> substrates via self-catalyzed plasma-assisted MBE. Successful demonstration of patterned NWs with decent verticality is achieved with the study of NW pitch range variation of 200-1200 nm, patterned hole diameter range of 100-350nm, and optimization of stem growth parameters. Large bandgap tuning of approximately 75 meV is achieved, as ascertained from 4K PL over the studied pitch ranges. A logistic sigmoidal growth trend is observed in the alloy system as has been detailed by S. Johnson et al. [2], different from a commonly observed trend in other III-V NWs.

The growth of patterned NWs required simultaneous optimization of various growth parameters and process parameters. The process parameters include electron beam lithography (EBL) dosage time, reactive ion (RIE) etching time, oxide layer thickness and density, and HF etching time. Growth parameters include Ga predisposition time, V/III ratio, growth seed contact angle, N-plasma RF power, and deflection plate voltage. The optimization process for obtaining optimum diameter patterned holes is discussed in our earlier works [2, 177] and thus is not included here.

4.2.1 Effect of HF etching duration

Figure 4.1 illustrates the effect of HF etching duration on the growth of nanowires on a patterned substrate with a BEP ratio of 20 and a hole diameter of 200 nm. As seen in the figure, the best growth conditions are achieved for an HF etching duration of 100 seconds. For lower etching time, there are two possibilities for preventing high-density NWs on the substrate: (i) the patterned holes are not fully exposed for correct positioning of the Ga droplets (ii) The Ga droplet does not make an appropriate contact angle for desired vertical growth. For etching duration of greater than 100 seconds leads to overexposed holes, thus making the contact angle higher than desired. Thus, the verticality of the nanowires is impaired (not shown here).

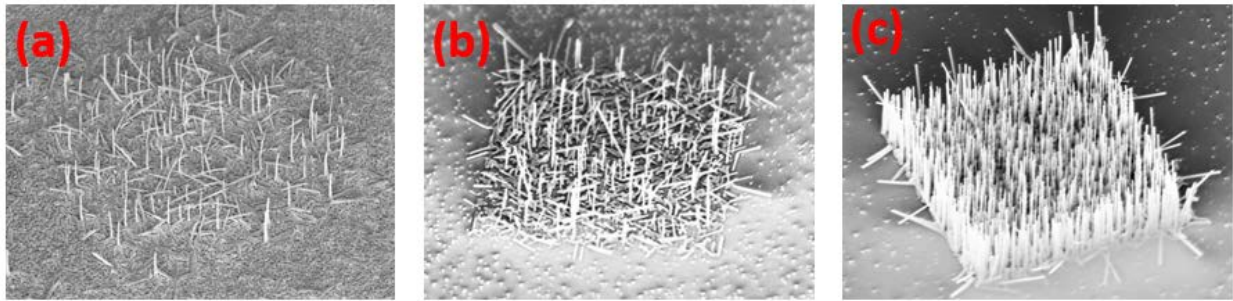


Figure 4.1: SEM image of NW growth under HF etching duration of (a) 40 secs, (b) 80 secs (c) 100 secs, for a constant Ga opening time of 20 secs, BEP ratio of 20, and a hole diameter of 200nm.

4.2.2 Effect of Ga predeposition and contact angle with Si substrate

The effect of droplet contact angle on the patterned holes can be further clarified with the variation of Ga opening duration, as shown in figure 4.2. With a lower opening duration of 10 secs, the patterned holes are not filled to an optimum level, which leads to high contact angle and thus low nucleation density and verticality. For a higher Ga opening duration of 30 secs, an increase in NW diameter and low nucleation density and fallen NWs attributable to the overfilling of the holes. Thus, a correct contact angle and hole filling are required to achieve optimum occupancy of holes for a given V/III BEP ratio.

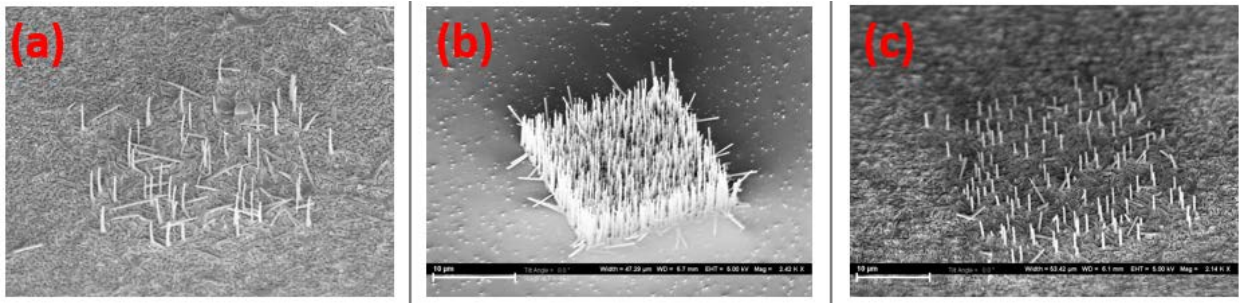


Figure 4.2: SEM image of NW growth under Ga opening duration of (a) 10 secs (b) 20 secs and (c) 30 secs for a constant HF etching duration of 100 secs, BEP ratio of 20, and hole diameter of 200nm.

4.2.3 Effect of patterned hole diameter

For similar growth conditions, the increase in patterned hole diameter resulted in a change in growth conditions drastically, as shown in figure 4.3. As shown in figure 4.3 (a, b, c), for a hole diameter of 250 nm and hole pitch of 200 nm, a large number of the holes are not filled, and the droplet contact angle is not appropriate for the vertical growth of the NWs. The result of the correct filling of holes with near-optimized growth conditions can be observed in figure 4.3 (d, e, f) for a hole diameter of 200 nm and the same pitch length of 200 nm.

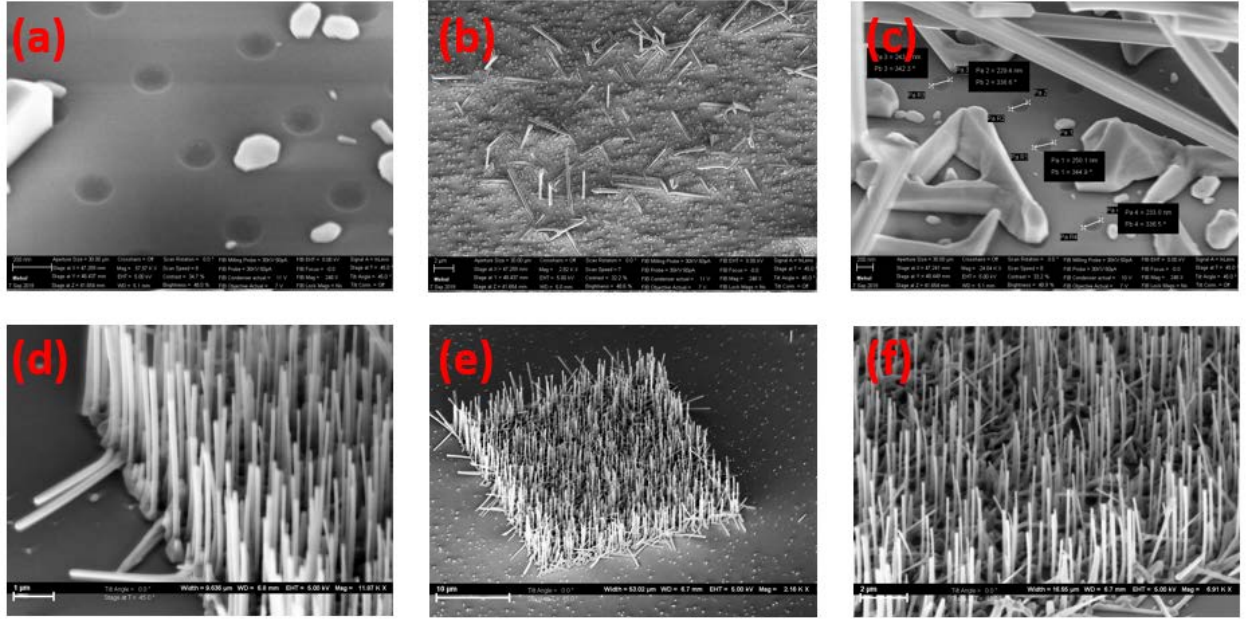


Figure 4.3: SEM images of the NWs grown under a V/III BEP ratio of 20, HF etching duration of 100 secs, Ga opening time of 20 seconds, and (a, b, c) patterned hole diameter of 250nm (d, e, f) patterned hole diameter of 200nm.

4.2.4 Growth details and optimization for best vertical yield

For all the growths variation experiments, BEP variation was fine-tuned to achieve the best occupancy of the holes and was set to 20. For a constant Ga flux, the constituent group V fluxes were varied to achieve an optimal condition for the NW growth. The NW growth consists of a GaAs and GaAsSb stem followed by axial GaAsSbN growth. The best vertical yield occurred at a patterned hole pitch length of 200 and 400 nm. As the pitch length increased, an increase in non-vertical NW density was observed, along with a concomitant decrease in nucleation density. The presence of these non-vertical NW growths is likely due to compositional gradients introduced by Sb and N in the NWs. As the incorporation of N is found to depend on the incorporation of Sb, we suppose that the higher Sb content in the NWs introduces a higher compositional gradient and hence increased non-uniformity in the growths. To verify this supposition, a second sample with lower Sb content was grown with a reduced Sb flux of 1.2×10^{-7} torr, compared to the previous

3.6×10^{-6} torr for the growth of the NW stem. The sample with high Sb content is referred to as sample A, and with low Sb, content is referred to as sample B for the rest of the discussions. A significant increase in vertical yield was achieved with sample B compared to sample A. Moreover, due to lower Sb content, reduced NW diameter was observed, which resulted in multiple nucleations of NWs from a single hole for lower pitch lengths. For higher pitch length, the diameter of NWs was high enough to obscure that phenomenon which can be attributed to higher Sb incorporation due to pitch-induced increased Sb incorporation. For both the samples, the growth of nitride NWs compared to non-nitride counterparts [10] showed a reduction in density under similar growth conditions on non-patterned substrates [151]; thus, the growth optimization parameters shall also be affected for optimum vertical yield on each pitch patterned samples. For oxide hole pitch length range of 200-1200nm, a diameter of 200 and 400 nm (figure 4.4 a-b) with a Ga opening duration of 20 s, and a GaAs/GaAsSb stem growth before dilute nitride NW growth provided the best vertical yield for sample A. Increase in pitch length of patterned holes resulted in an increase in bent and horizontal NWs attributed to the change in the distribution and composition of fluxes during the nucleation event (shown in figure 4.4 c-f).

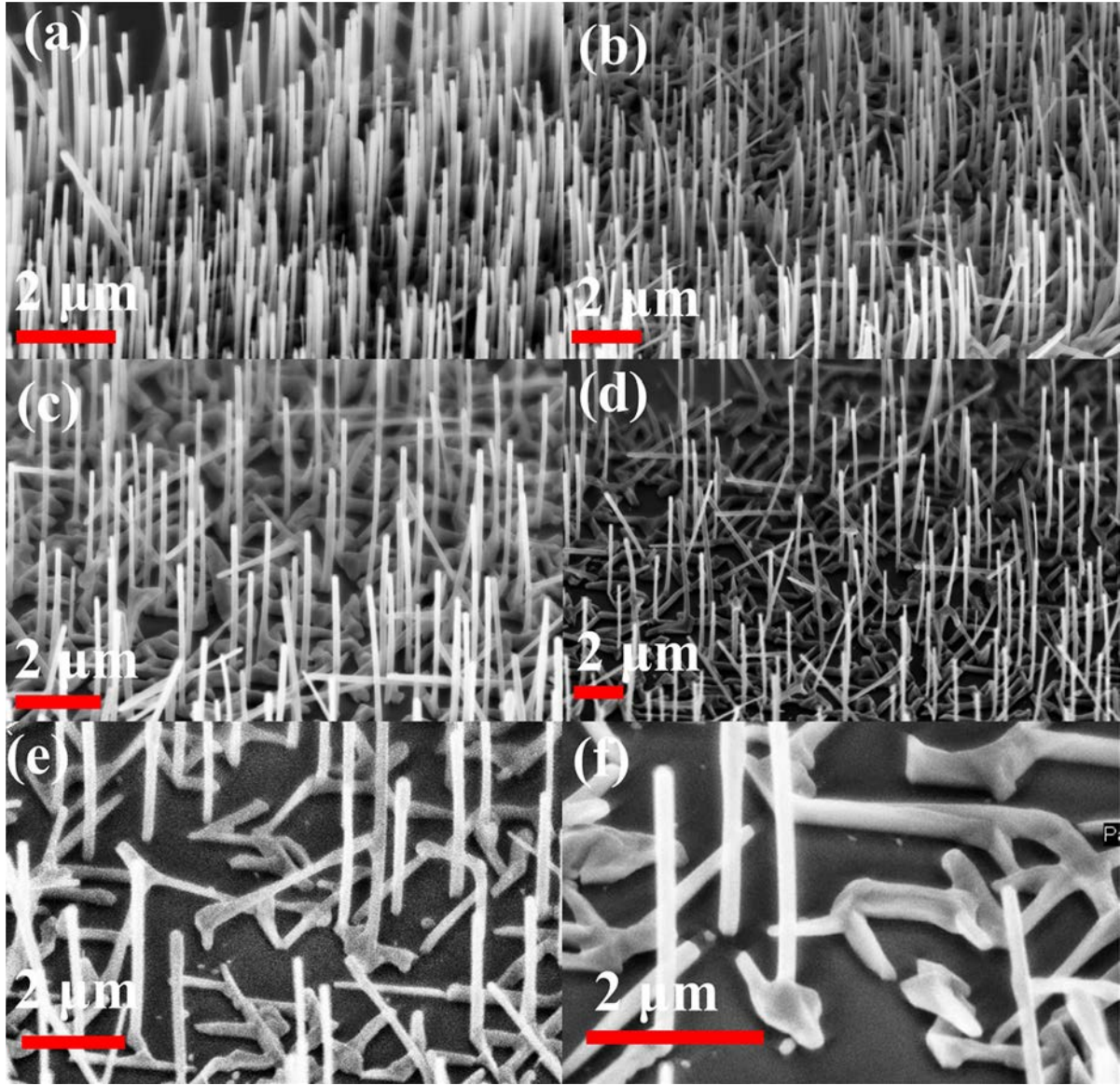


Figure 4.4: SEM images for GaAsSbN sample A for pitch lengths of (a–f) 200, 400, 600, 800, 1000, and 1200 nm [2].

The composition of Sb and N in the nucleating droplet, and hence overall composition, is likely to vary with the change in pitch. High Sb content is likely to induce strain in the NWs [80], resulting in a reduction in nucleation density. Under similar conditions, the growth of NWs with reduced Sb flux (from 8.6×10^{-7} to 1.2×10^{-7}) and growth duration (from 17 min to 10 min) yielded improved vertical yield across all the pitch lengths, as shown in figure 2a-f. The result shows that

each pitch of the patterned holes should be separately optimized for growth parameters to yield the best vertical growths.

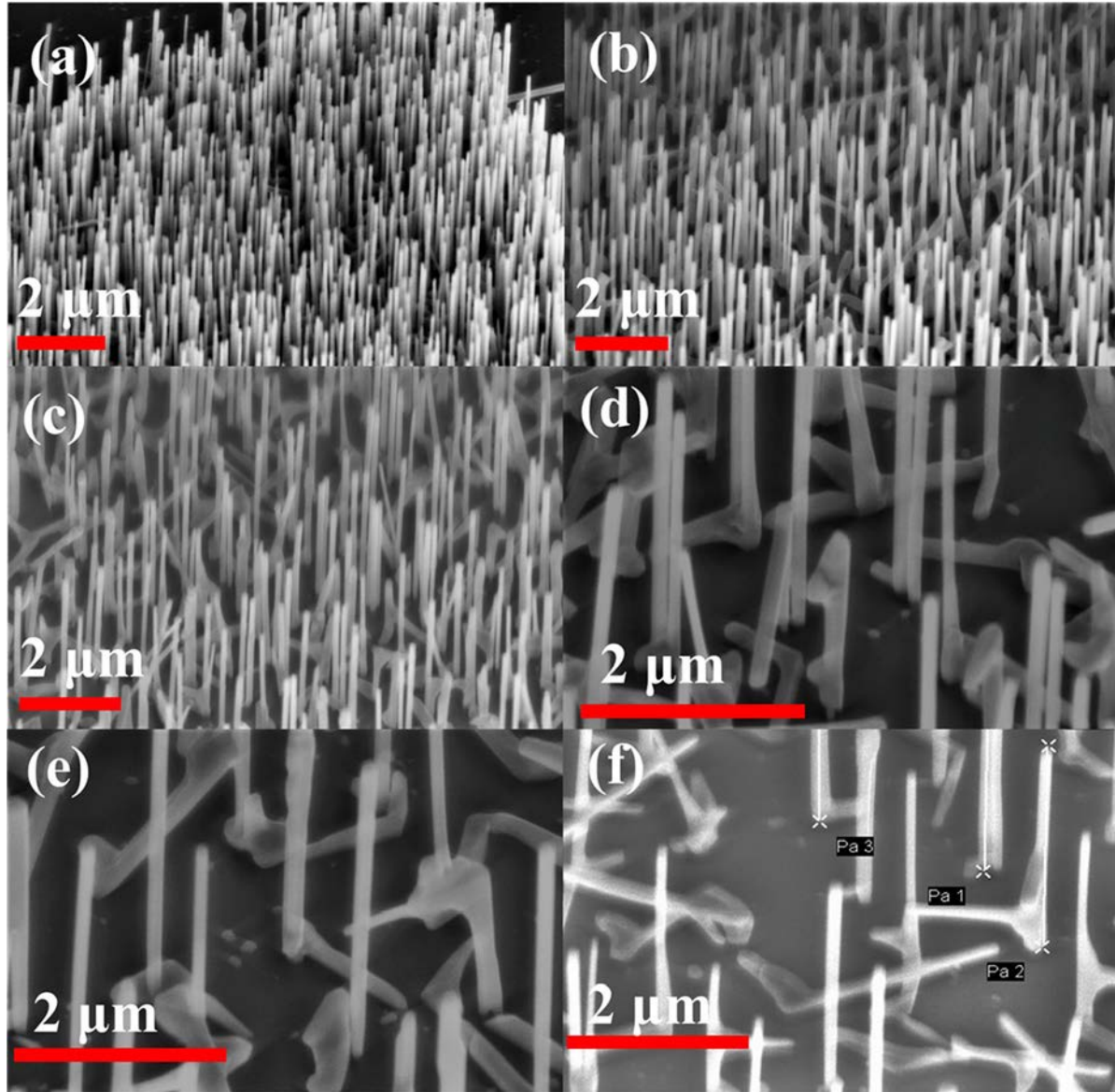


Figure 4.5: SEM images for GaAsSbN sample B with a growth time of 10 min for pitch lengths of (a–f) 200, 400, 600, 800, 1000, and 1200 nm [2].

Supporting the earlier studies [10, 178] in non-patterned GaAsSbN NW growths, a single-crystal zinc blende structure devoid of any planar defects was confirmed from HRTEM and SAED

characterization of the patterned NWs [2]. Antimony incorporation of 7% was confirmed from the EDS characterization on the bottom, middle and top segments of the NWs. The incorporation of Sb was found to exhibit inconsistent behavior towards the top segment of NWs compared to the composition on the bottom and middle segments. This is attributed to the reduced time for the N-Sb exchange mechanism at the top segment, resulting in the non-uniform incorporation of Sb and N constituents.

4.2.5 Pitch dependent bandgap tuning

Pitch-dependent PL spectral responses of the NWs were examined for two different samples, A and B, at different pitches. A redshift of 34 meV was observed in the NWs at the RT form pitch of 200nm to 1200nm (shown in figure 4.6 a). As the pitch increases, the increase in Sb incorporation should be expected and hence facilitates more N-Sb exchange mechanisms and hence higher N-incorporation.

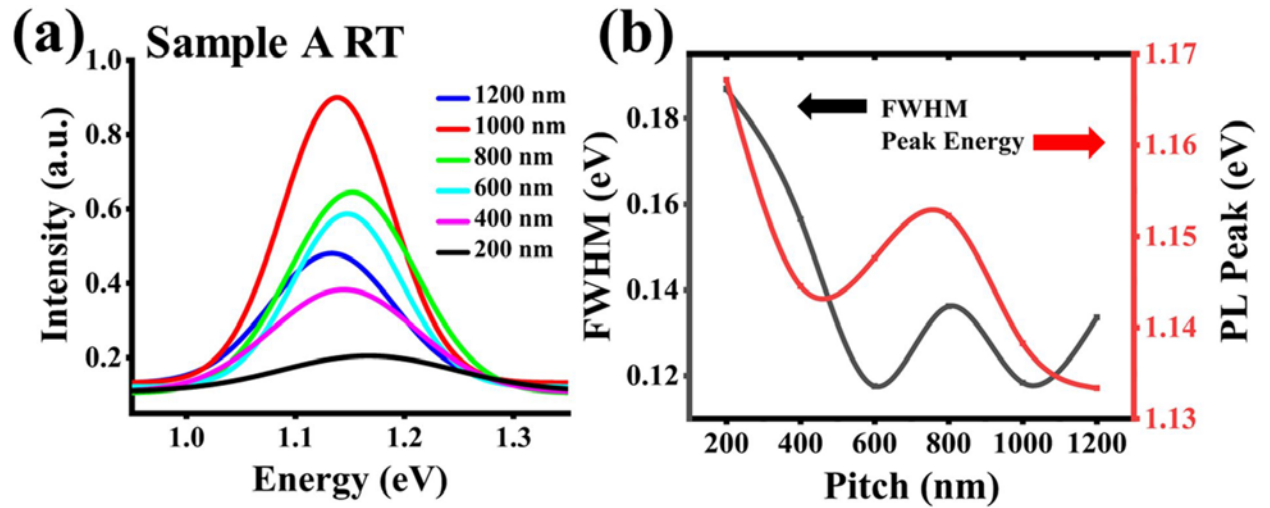


Figure 4.6: Sample A: (a) Gaussian fit for RT PL measurements, and (b) full-width-half-maxima and Gaussian energy peaks versus pitch [2].

The variation in full-width-half-maxima (FWHM) and PL peak energy for sample A is shown in figure 4.6 b, which shows a qualitative decrease in the emission characteristics of NWs as the pitch

length increases from 200 to 600nm. The overall redshift of the PL energy can be seen in the NWs with pitch, with a small blueshift between 400nm to 800nm pitch lengths.

The 4K PL results for sample A and B is shown in figure 4.7 (a) and (b). For sample A, PL peaks show asymmetric bandgap with low peak energy centered at 1.16 eV and a high energy peak of 1.23 eV for a 200nm pitch length. A pitch-dependent bandgap tuning of 73.3 meV can be observed from a pitch length of 200 to 600 nm pitches. Increased symmetry can be observed in PL response at 400 and 600 nm pitches compared to 200 nm, suggesting higher NW quality due to limited line broadening. 600 nm pitch exhibits the highest degree of symmetry compared to all the pitches. The PL response becomes more asymmetric at 800nm pitch length due to inhomogeneous line broadening. Increased incorporation of N at higher pitch length can be revealed from the low energy PL peak centered at 1.07 eV, which increases the N-related perturbations in the bandgap. The incorporation of N can be seen highest at higher pitch lengths of 1000 and 1200 nm, resulting in a more distinct low energy peak. This type of distinct low and high energy peaks is a direct result of N-incorporation in the NWs.

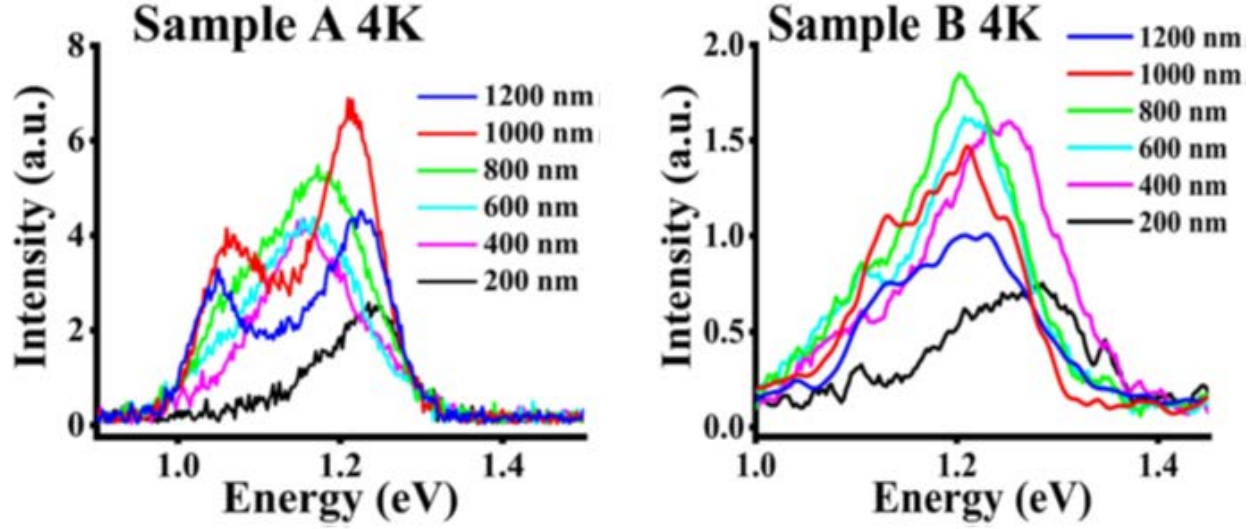


Figure 4.7: 4K PL measurements for sample A for different pitch lengths of (a) sample A and (b) sample B [2].

For sample B, clear RT peaks were not observed in the PL spectrum. The 4K PL spectrum (shown in figure 4.7 b) shows broad PL peaks, which do not have discernible N and Sb-related peaks. Rather, a broad PL spectrum can be observed across all the pitch lengths. This is true, especially for lower pitch lengths of 200 and 400 nm. Moreover, for higher pitch length, some degree of discernible N peak can be observed. This is likely due to the inhomogeneous incorporation of N in the NWs, due to lesser time of growth. Compared to sample A, NWs in sample B have less time for N-Sb exchange mechanisms through the sidewalls of the NWs. Thus, a broad PL spectrum is more likely to consist of a cluster of N and Sb-related peaks. A bandgap tuning of approximately 73 meV is achieved as pitch increases from 200 nm to 800 nm. For both samples, a higher energy peak is more dominant across all the pitch lengths, which is indicative of dominant GaAsSb composition over GaAsSbN.

4.3 Conclusion

This is the first work on selective area epitaxy of dilute nitride GaAsSbN NWs on Si, demonstrating a pitch-dependent bandgap tuning over a large wavelength range of ~75 meV for

pitch lengths ranging from 200-1200 nm. Growth parameter optimization for the best vertical yield of NWs on patterned substrates and the underlying challenges have been presented. The stem growth method has been presented to overcome the nucleation challenges for dilute nitride NWs, and the effect of Sb composition in the stem growth has been delineated concerning the vertical yield and nature of incorporation of constituent elements in the NWs. Results show that the dilute nitride GaAsSbN material system in the NW configuration is a strong contender for bandgap tuning in the NIR region spanning the telecommunication wavelength region.

A significant portion of this work is published in the Scientific Reports (Johnson, Sean, et al. "Study of patterned GaAsSbN nanowires using the sigmoidal model." *Scientific reports* 11.1 (2021): 1-14.)

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Chapter 5

GaAs/GaAsSb Separate Charge control, Absorption, and Multiplication layer (SCAM) core-shell avalanche photodetector.

1.1 5.1 Introduction

Avalanche photodetectors are a special class of photodetectors combining photodetection and high internal amplification processes within the photodetector. Due to their high gain, they are attractive for numerous applications ranging from optical interconnects, light detection and ranging (LIDAR) [179], quantum computing [180], astrology, and communication systems [181, 182], and a range of medical applications [180]. NW APDs have the advantage of improved gain and sensitivity over conventional planar devices by shrinking the impact ionization region in the nano-heterostructure. They have further benefits of strain relaxation and waveguiding effect [183]. III-V NWs grown on silicon substrates enable compatibility with mainstream silicon technology and have the opportunity of overcoming the challenge of lattice mismatch and process incompatibility resulting from differences in lattice constants and thermal expansion coefficients, offering the most direct and scalable integration route to COMS, which is a promising edge over conventional bulk devices [183]. NW APDs are also desired for low power applications due to their low breakdown voltage and hence low power consumption, reduced dark count rates (DCR), and jitter time. Core-shell configured NWs have the advantage of high sensitivity compared to axial devices due to separation of the axial light absorption and radial carrier separation [6]. Thus, CS configured NW APDs carry the potential to push the fundamental limits on higher photon counting rates to represent the state-of-the-art technology.

In this study, the growth and characterization of a separate absorption multiplication region avalanche photodetector (SAM-APD) are presented. Separate absorption and multiplication

regions in APDs enable low noise photodetector by separating the absorption and multiplication regions, thus enabling low multiplication noise. A higher bandgap GaAs is used as a multiplication layer material due to its low impact ionization noise compared to competing materials like InP and InAs in the NIR range. GaAsSb has good absorption properties in this region, encompassing a large portion of the NIR range, and has further advantages of less-stringent growth control and cost-effective alternative compared to Indium (In) containing alloys. Thus, a tunable bandgap GaAsSb is used as an absorber layer in our NWs.

This chapter provides the details of the growth optimization of ensemble NW SAM-APDs and the successful fabrication of the device on Si <111> n-doped substrates. The growth of NWs is accomplished by using MBE, and a variety of fabrication and characterization tools have been used to successfully demonstrate APD devices. A simulation approach has been used to calculate and optimize the E-field in the proposed NW heterostructure.

1.2 5.2 Proposed NW heterostructure and band diagram

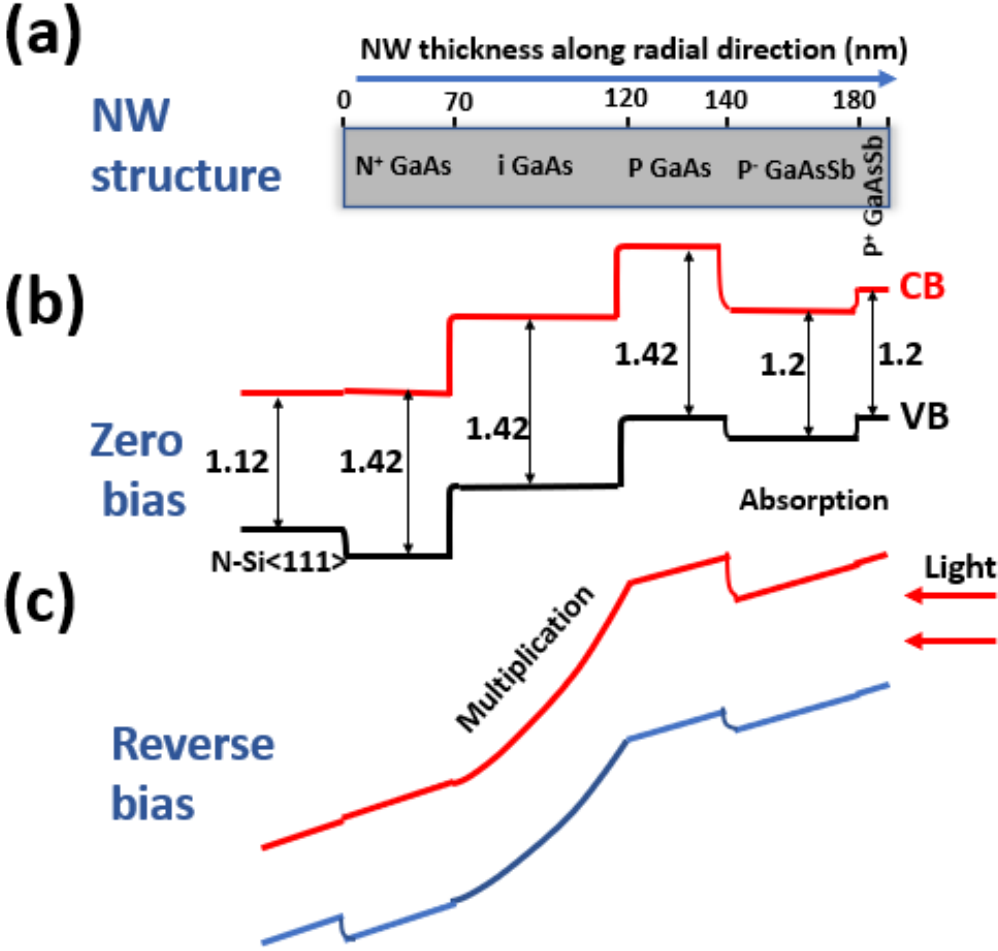


Figure 5.1: (a) NW structure along the radial direction with lengths (b) and (c) band diagram at zero bias and reverse bias conditions, respectively, along with the nanowire structure in a radial direction.

A schematic of band profile along the radial direction (as shown in figure 5.1 a) of designed SAM-APD NWs at zero bias and reverse bias conditions are shown in figures 5.1 (b) and 5.1 (c). Under reverse bias, there is a small barrier for both the holes and electrons, responsible for higher observed breakdown voltage. The incoming light is absorbed onto a non-intentionally p-doped GaAsSb absorption layer of radial thickness ~20-30 nm. The absorbed carriers (holes and electrons) are accelerated towards the high-field NIP region of GaAs, where it gets multiplied into multiple carriers in the i-GaAs region to initiate an avalanche mechanism under high reverse bias.

5.3 E-field simulation using COMSOL Multiphysics

Numerical simulation provides insights into the underlying fundamental physical phenomenon that governs the device's performance. Optimization of the device structure and performance evaluation before the device fabrication process using simulation approaches curtails the experimental time and resources. Here, we use a Finite Element Method (FEM) based numerical solution to analyze the influences of NW dimensions and configurations and doping on the E-field characteristics of the device. A brief description of the equations used to model the NWs is discussed in the following paragraphs.

The electric potentials and charge carrier concentration at each point of the meshed structure have been solved using continuity equations for electrons and holes and Poisson's equation.

$$\nabla \cdot \mathbf{J}_n = -e(G_n - R_n) \quad \text{-----5.2.1}$$

$$\nabla \cdot \mathbf{J}_p = e(G_p - R_p) \quad \text{-----5.2.2}$$

$$\nabla \cdot (\epsilon \mathbf{E}) = \nabla \cdot \epsilon (-\nabla \phi) = \rho = e(p - n + N_d^+ - N_a^-) \quad \text{-----5.2.3}$$

Equations 5.2.1 and 5.2.2 represent the current density continuity equations for electrons and holes, respectively. Here, J_n is the electron current density, J_p is the hole current density, e is the electronic charge, and G_n , R_n , and G_p , R_p is the respective generation and recombination rates of electrons and holes.

Equation 5.2.3 represents Poisson's equation relating the Laplacian of the electric potential ϕ to the total charge density. Here, n , p , N_d^+ , and N_a^- are the electron, hole, ionized donor, and ionized acceptor concentrations, respectively, for a material with a relative permittivity of ϵ . Current densities at steady-state conditions are described by the following equations.

$$\mathbf{J}_n = en\mu_n \nabla E_c + \mu_n k_B T \Omega \left(\frac{n}{N_c} \right) \nabla n \quad \text{-----5.2.4}$$

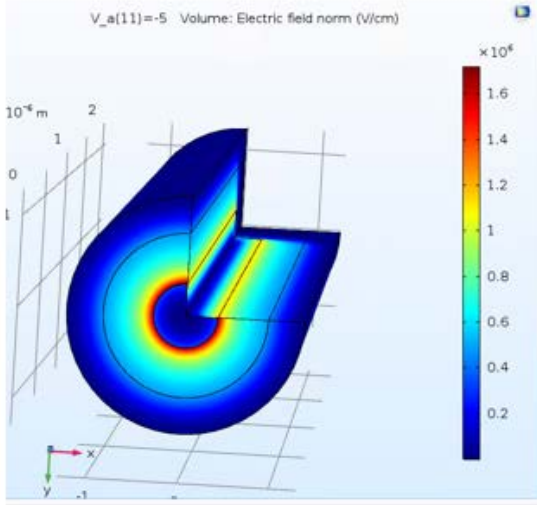
$$\mathbf{J}_p = ep\mu_p \nabla E_v + \mu_p k_B T \Omega \left(\frac{p}{N_v} \right) \nabla p \quad \text{-----5.2.5}$$

Here, E_c and E_v are the conduction band, and valance band energy levels, μ_n , and μ_p are the mobility of electrons and holes, k_B is the Boltzmann constant, and T is the absolute temperature.

A range of physical phenomena has also been employed to effectively replicate NW characteristics, namely doping of each segment, recombination mechanisms, Fermi-Dirac statistics (which takes into account the degeneracy factors), and bandgap narrowing, surface states, and NW contacts. Since the contacts have been optimized to achieve ohmic contact, an ohmic metallic contact has been used in the simulation.

Numerical modeling using COMSOL, as described above, has been employed to optimize the device structure of the proposed NW device. A realistic device characteristics simulation in three-dimensional (3D) geometry along with the number of physical phenomena and boundary conditions is realized using finite element method (FEM) simulation using COMSOL Multiphysics. The NWs have been modeled using a 2-D rectangle with cylindrical symmetry, mimicking a 3D NW, thus reducing the computational cost. The simulated NW geometry is based on the experimental dimensions of NW obtained through SEM measurements, and later the NW growth is optimized based on the simulation results. Figure 5.2 shows a schematic of NW CS configured 3D simulation using a 2D rectangular model. The E-field inside the NW structure can be easily visualized inside the geometry for a given doping and segment thicknesses. An illustration of E-field simulation and plotting for a GaAs NW PIN structure is shown in figure 5.2.

(a)



(b)

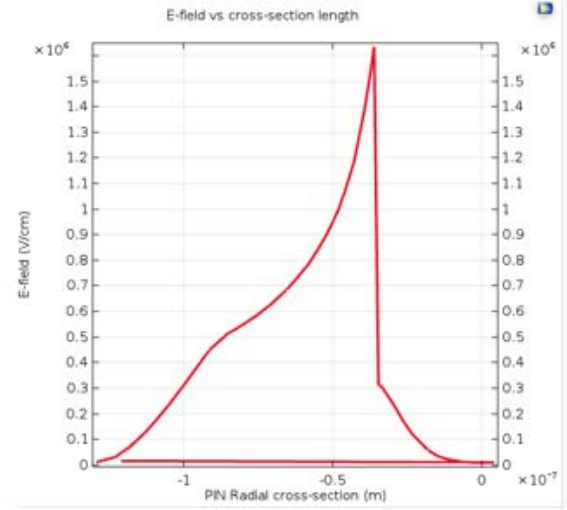
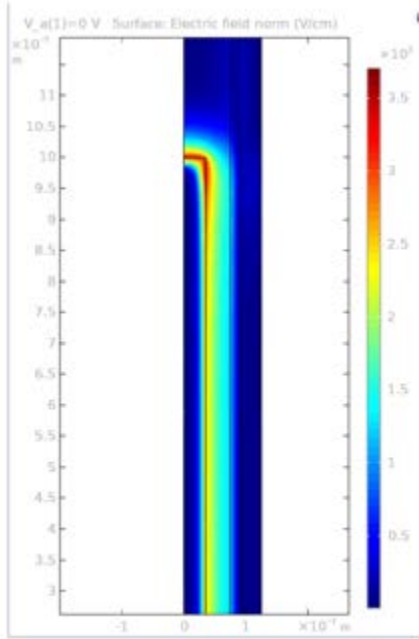


Figure 5.2: (a) A E-field simulation using 2D axisymmetric cylindrical model using COMSOL Multiphysics mimicking a GaAs core-shell NW and doping profiles (b) E-field plot across the NW radial cut section.

(a)



(b)

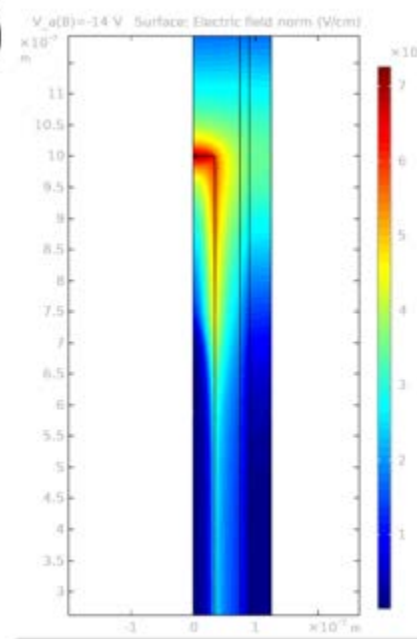


Figure 5.3: E-field profile for proposed NW structure in figure 5.1 for a reverse bias voltage of (a) 0V and (b) 14V. An NW doping density of $2.0 \times 10^{18} / \text{cm}^3$ for N-GaAs core and $5.0 \times 10^{17} / \text{cm}^3$ for N-GaAs charge control layer was used with an intrinsic GaAs section doping density of $5 \times 10^{15} / \text{cm}^3$ and intrinsic GaAsSb segment doping of $1.0 \times 10^{16} / \text{cm}^3$.

The variation of E-field across the NW structure for variation in multiplication region thickness and doping of N and P segments are shown in figure 5.4 below.

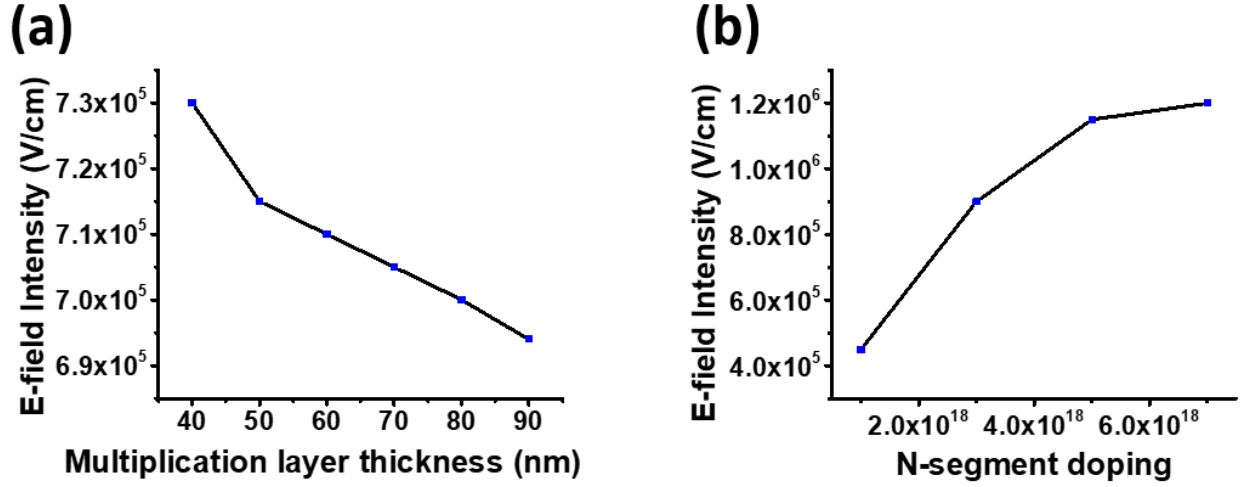


Figure 5.4: Variation in maximum E-field in the multiplication region with change in (a) multiplication region thicknesses and (b) N-segment doping.

For the proposed NW structure, simulations have been performed for a range of doping and NW segment thicknesses. A radial thickness of GaAs N-core of 35 nm has been selected based on the optimized growth conditions of N-core on N-Si <111> substrate. A doping density of $2.0 \times 10^{18}/\text{cm}^3$ for N-GaAs core has been selected based on the optimized Te-doping conditions yielding the best NW optical properties and verticality. The thicknesses and doping of GaAs i-region, GaAs p-region, and GaAsSb absorber region has been tuned to minimize the breakdown voltage in the NW device within the possible growth limits using MBE. A summary of optimized doping and thicknesses of segments used in the simulation and hence NW growth is shown in table 5.1.

Table 5.1: Summary of the NW segments doping profile and radial segment thicknesses.

--

GaAs	2.0×10^{18} (n+ type)	35 nm (core)
GaAs	Undoped	25 nm
GaAs	5.0×10^{17} (p type)	10 nm
GaAsSb	5.0×10^{16} (p type)	20 nm
GaAsSb	5.0×10^{17} (p+ type)	5nm
AlGaAs	7.0×10^{17} (p type)	5nm
GaAs	Undoped	5nm

5.4 NW growth optimization on n-Si <111> and PL emission characteristics

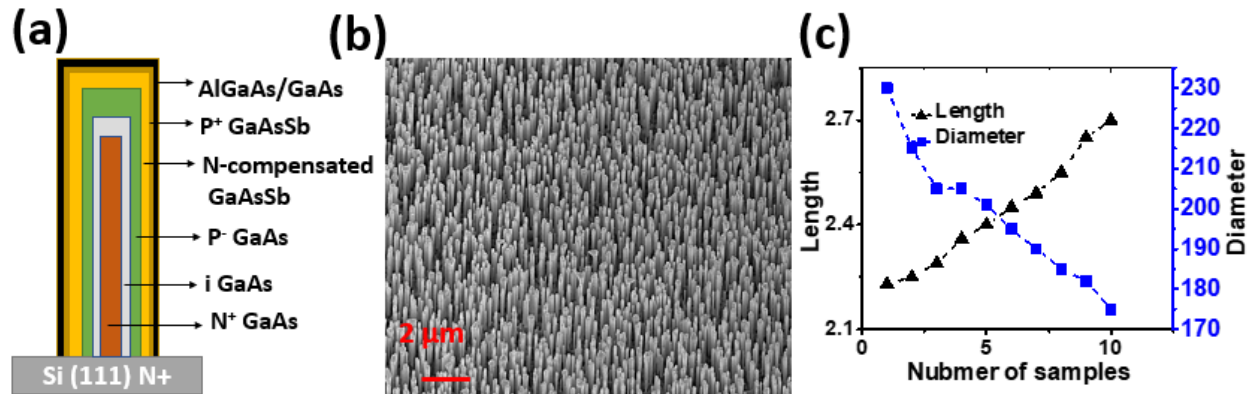


Figure 5.4: (a) Core-shell NW structure schematic, (b) SEM image of ensemble NWs grown on Si<111> substrate (15 % Sb incorporation), and (c) Variation of NW length and diameter for the ensemble NW samples.

A schematic of the NW growth structure is shown in figure 5.4 (a). An N⁺ GaAs core was grown using Tellurium (Te) as a dopant source at 540 °C. Optimization of dopant temperature was

performed first to yield the best NW PL emission intensity, and the details of the optimization process can be found elsewhere [161]. To achieve the best vertical yield, the NW core was grown at a low step substrate temperature of 615/600 °C at a V/III BEP ratio of 10 for 20 minutes. The details of the NW dimension optimization process are shown in appendix figure A1. This can be viewed as an evidence of shell growth in our NW structure following the termination of axial core growth. A detailed investigation of the core-shell configuration growth and TEM verification is done on our earlier works by Kasanabonia et al. [144] and the growth methodology is adopted largely in the growth optimization of this work. The growth of the core was terminated by keeping the same BEP ratio for 6 minutes. For the i-GaAs segment growth, the BEP ratio was increased to 12 at a substrate temperature of 550 °C under As-rich conditions to facilitate VS growth. A low Beryllium (Be) doped GaAs segment at a Be cell temperature of 900 °C was grown, followed by an intrinsic GaAs region. This was followed by the absorption layer of GaAsSb with Te-compensation to achieve low doping in the GaAsSb segment. An Sb flux range of 7×10^{-7} torr to 3.2×10^{-6} torr and an Arsenic flux range of 4.0×10^{-6} torr to 6.5×10^{-6} torr was used to maintain a BEP ratio of 12 for this segment at a substrate temperature of 580 °C. Finally, a p^+ segment of GaAsSb followed by a passivation layer of GaAs/AlGaAs was grown to effectively passivate the NW surface at a substrate temperature of 465 °C. SEM image of optimized NW growth is shown in figure 5.4(b) for ~12% Sb incorporation. The NW samples grown were typically $2.4 \pm 0.3 \mu\text{m}$ long of $205 \pm 25 \text{ nm}$ diameter (shown in figure 5.4 c). This sample representing 12% Sb incorporation in the absorption region shall be referred to as NIPSb12 hereafter.

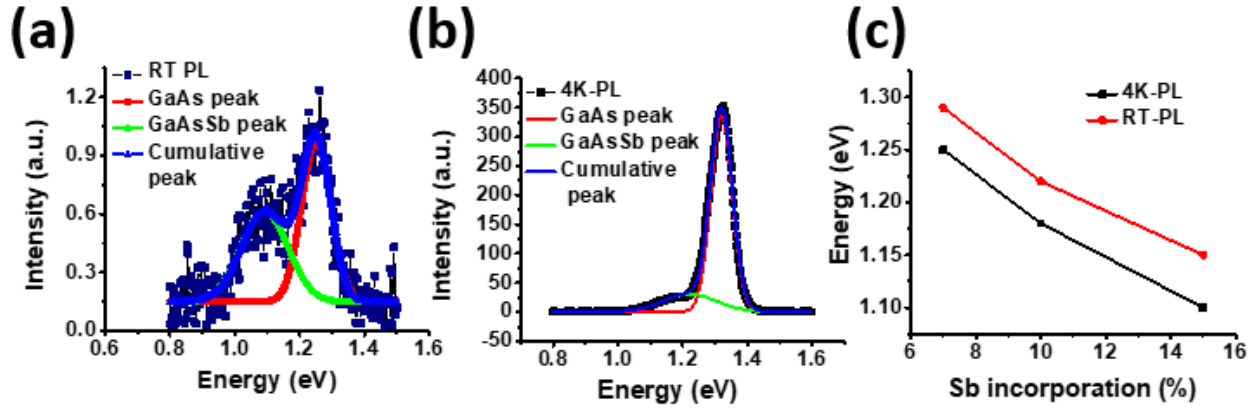


Figure 5.5: (a) and (b) represent respective RT and 4K PL-spectra for antimony incorporation of 15%, (c) GaAsSb PL peak positions at different Sb incorporation (up to 15%) at RT and 4K.

Figures 5.5 (a) and 5.5 (b) show the room temperature (RT) and 4K PL spectra, respectively, of the NW APD structure corresponding to an Sb incorporation of ~15%. This is estimated based on our earlier works [144, 184], which matches closely with the energy gap calculation for thin-film GaAsSb material as shown in equation 5.4.1. The Distinct peak positions at 1.1 eV and 1.30 eV at RT and 1.15 and 1.34 at 4K are observed, corresponding to GaAsSb and GaAs bandgap emissions. Sb incorporation of up to 15 % was achieved in the NWs without adversely affecting the NW growth conditions, and the corresponding RT and 4K PL emissions are depicted in figure 5.5 (c). The Sb composition for the obtained energy peaks is calculated as follows:

$$\text{Energy gap} = 1.42 \text{ (GaAs bandgap)} - 1.9x + 1.2x^2 \text{ (for } 0 < x < 0.3 \text{)} \text{ (At room temperature)} \text{ ----- 5.4.1}$$

5.5 Device demonstration and electrical, and optical characterizations.

The details of the device fabrication process using Au/Ti front contact and Au/Ni back contact are explained previously in chapter 3. NW devices were also fabricated using silver contacts on both NWs and silicon surfaces in order to increase the transparency of contacts to the light.

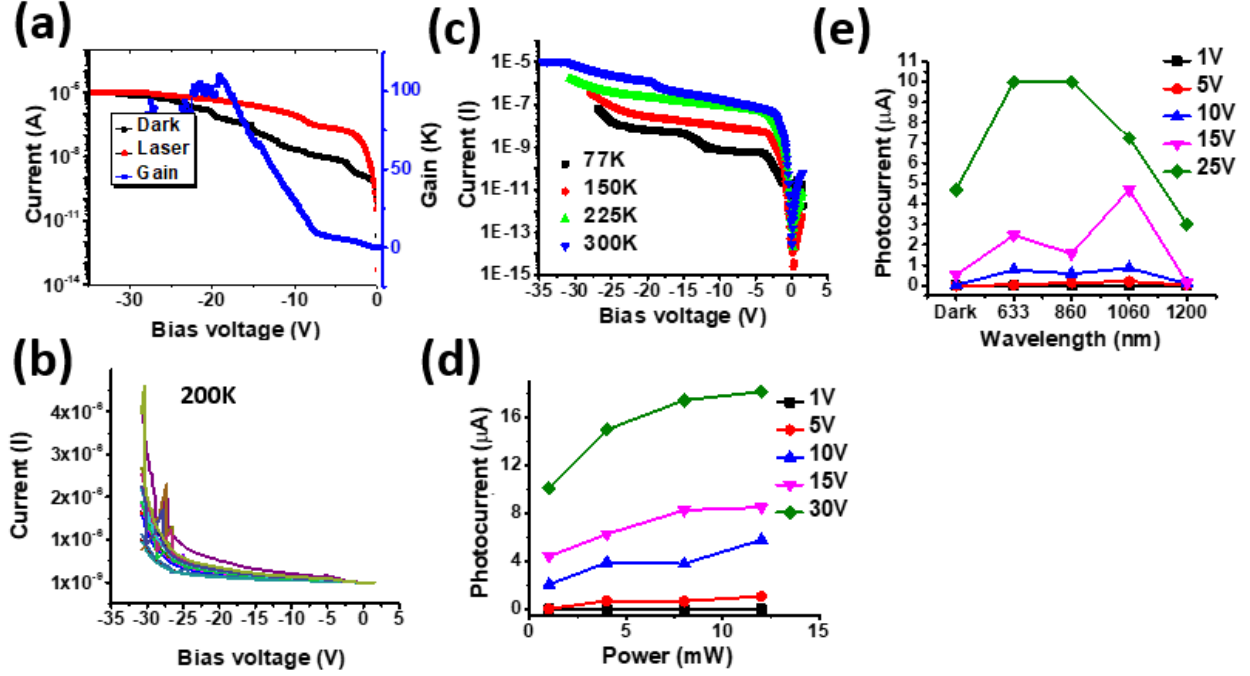


Figure 5.6: (a) Dark current, photocurrent, and gain of the device under technologically relevant illumination wavelength of 1060 nm at 200 K, (b) multiple dark I-V sweeps at 200 K temperature showing the range of hysteresis, (c) temperature dependence of dark current from 77K to 300K, (d) power dependence of the device for a range of illumination power and bias voltage under 633 nm illumination wavelength at 200K, and (e) spectral response of the device at 200K for a range of voltage from 1 V to 25 V.

Temperature dependence I-V breakdown characteristics from 150 K to 250 K under dark conditions (Fig. 5.6 c) reveal a positive temperature coefficient, which is characteristic of an avalanche breakdown mechanism in our NWs. At 200 K We measure a dark current of 10 μ A or lower at the breakdown temperature. A temperature coefficient of ~ 9.2 mV/K is observed up to 150 K, which increased to ~ 10 mV/K with a further increase in temperature. The difference in temperature coefficient is likely due to the activation of traps at higher temperatures, increasing the probability of trap-assisted tunneling. Also, APD breakdown characteristics are less sharp at higher temperatures, attributed to increased zener tunneling leakage current. At higher temperatures, the trap levels near the band edge are activated along with an increase in thermal carrier concentration, which gives rise to increased current density in the device, increasing the probability of tunneling. A negative dependence on breakdown was seen at room temperature, indicating the dominance of thermal carriers ultimately resulting in Zener or a combination of

Zener and avalanche breakdowns. We observed a shift of ~ 10 V in V_{BR} towards higher voltage after initial sweeps and minimal change following a large number of sweeps. The large shift in V_{BR} after the initial sweeps is possibly due to annealing of the NW and NW/contact interface with DC I-V sweeps resulting in a decrease in the overall device dark current, and/or the breakdown of smaller diameter NWs. The variation in breakdown characteristics was found to be in the range of 30 ± 3 V for 250 K temperature. Similar behavior was found across all temperatures, with the extent of variation being slightly greater at a lower temperature. At 77 K, the V_{BR} variation was found to be in the range of 25 ± 4 V. We attribute this V_{BR} variation to two possibilities: (i) the non-uniformity in the thickness of the grown NW samples (as shown in figure 5.4 c) and (ii) doping variation amongst the segments in each of the ensemble NWs contributing to breakdown characteristics. One or both of these possibilities can have a profound effect on the threshold E-field required for the onset of punch-through and the V_{BR} of the device. It is to be noted that a single or only a few NWs among several NWs in contact is likely to show breakdown characteristics of the device. Thus, the breakdown of a nanowire after subsequent sweeps can contribute to the change in V_{BR} under a specified contact. Further, the trap filling after the initial sweep is an additional factor cause that can contribute to the observed variation in V_{BR} . The presence of traps in the NW device is also supported by the power dependence photocurrent characteristics in figure 5.6 (f), which shows a saturation of the photocurrent with illumination >10 mW power. Low-intensity illumination showed a linear increase in photocurrent until saturation near or after five mW of illumination. Further increase in illumination showed a sub-linear characteristic at higher bias voltage, indicating the saturation of absorption in nanowires. For lower biases, the absorption was found to increase with illumination power exceeding five mW. Lower variation of breakdown voltage at higher temperatures can be attributed to the generation-current being higher with increased temperatures, and a similar observation has been made in literature by Farrell et al. [179].

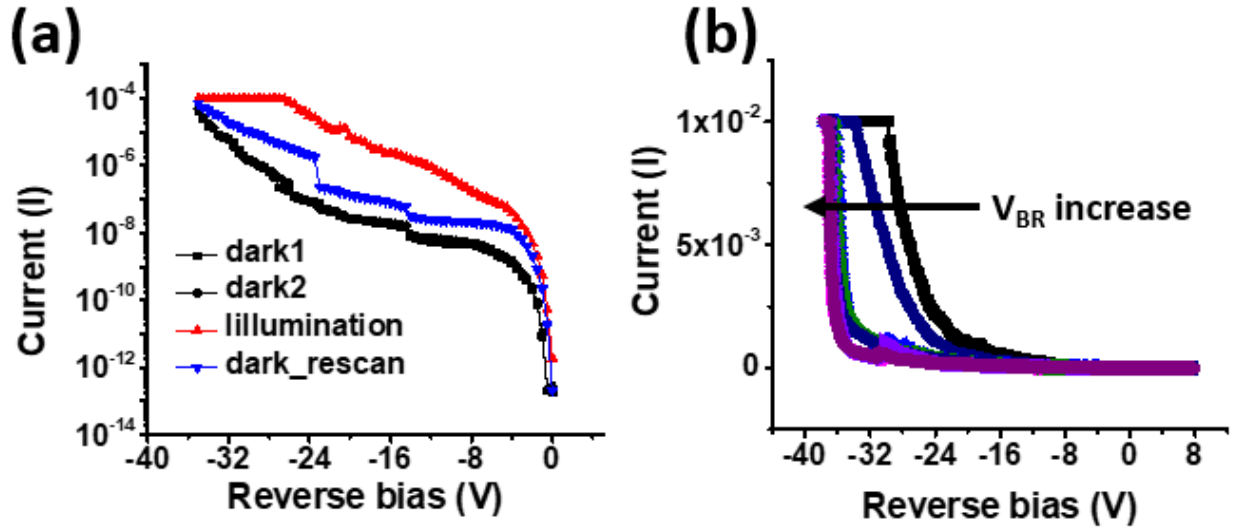


Figure 5.7: DC I-V sweeps before and after 633nm laser illumination at 200K, (b) Change in V_{BR} of the device with subsequent DC I-V sweeps at 200K.

The data points were taken after many sweeps, which resulted in the burning of very low diameter NWs present under an NW contact resulting in a near-consistent I-V characteristic for the NW contact under consideration (refer to figure 5.7 (b) for the observed hysteresis at the beginning compared to the stable operation of the device). An increase in dark current following the illumination is observed (with sufficiently high illumination of 30mW), which indicates the presence of traps in these nanowires, as shown in figure 5.7 (a). The presence of multiple nanowires under contact and breakdown of lower diameter NWs resulted in an increase in V_{BR} with subsequent sweeps, as shown in figure 5.7 (b). The breakdown voltages were consistent after multiple sweeps with only a marginal fluctuation.

Wavelength dependence of photocurrent in comparison to dark current is shown in figure 5.6 (e) shown at different reverse bias voltages. APD devices exhibited good photo absorption up to 1064 nm wavelength and were finally cut off after 1100 nm.

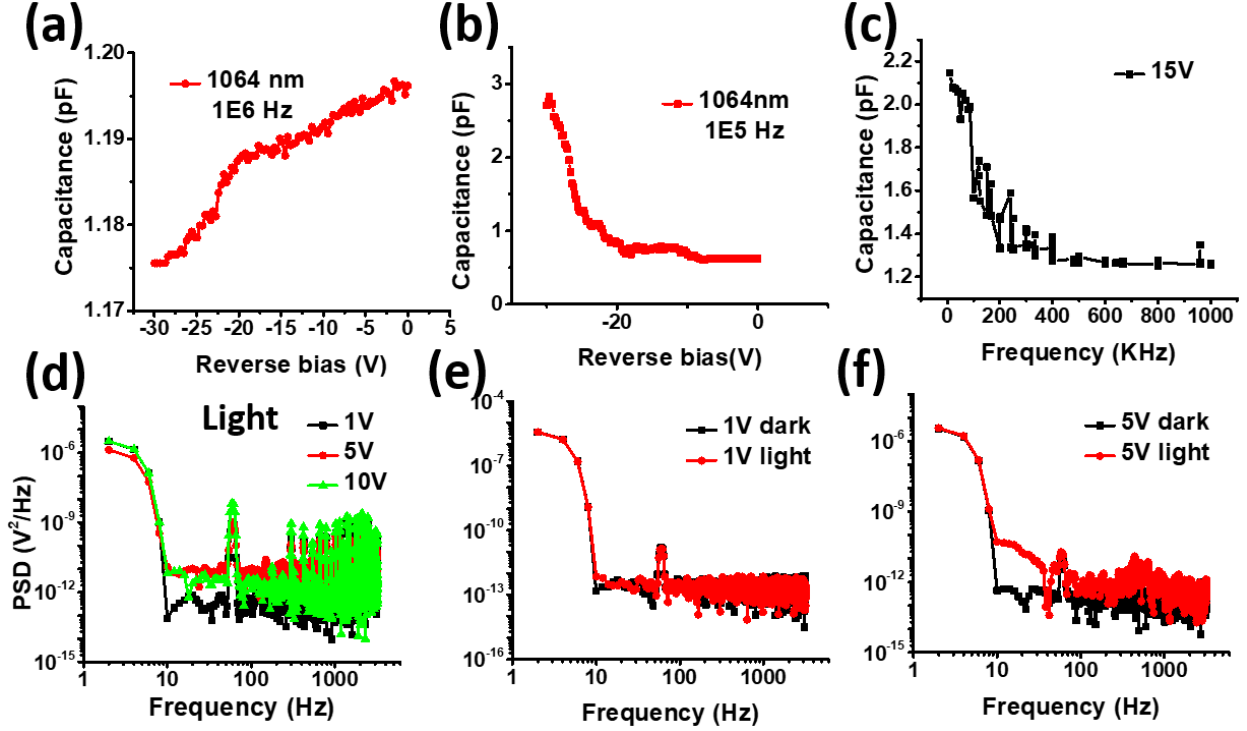


Figure 5.8: (a) Capacitance voltage measurement of the device under 1060 nm illumination and 10^6 Hz, 30 mV AC power at 200K, (b) Capacitance comparison at 1060nm illumination and 10^5 Hz ac signal frequency, 30 mV AC power at 200K, (c) Frequency dependence of capacitance at a reverse bias of 15V (d) Comparison of device noise under 1064 nm illumination conditions, (e) and (f) dark and illumination noise at 1V and 5V reverse bias respectively.

The corresponding CV characteristics at 200 K (fig. 5.8a) indicate a gradual depletion of the charge layers and a start of avalanche breakdown. At 200 K, a breakdown is observed after 25 V reverse bias corresponding to the rapid change of device capacitance with increased bias voltage. A distinct punch-through region cannot be identified from the dark C-V curve corresponding to I-V characteristics, which indicated punch-through at significantly lower voltages (~ 5 V). The device showed a decrease in breakdown voltage with illumination, after which the capacitance values are equivalent for dark and illuminated conditions. At a frequency lower than 400 KHz, inverse characteristics were seen, i.e., an increase in capacitance was observed with an increase in reverse voltage (fig 5.8 b). The localized interface trap states at the Schottky junctions located at the top and bottom NW contacts are likely to follow the AC signal at lower frequencies, yielding an excess capacitance [185]. Figure 5.8 (c) shows the inversion characteristics at a lower AC signal frequency of 10^6 Hz. A steady capacitance value was observed after 400 kHz (fig.

5.8(c)), after which the traps are unable to follow the applied AC signal frequency. Low-frequency noise (LFN) characteristics were invariant under both dark and illuminations for a reverse bias up to 3 V (see fig. 5.8(d)). A change in noise level is observed only after punch-through (see figs. 5.8(e) and 5.8(f)) due to an increase in current flow and hence randomness of the carriers flowing through the device.

To extend APD characteristics of the NWs to RT, segment-wise in-situ annealing of the heterostructures for 120 sec was explored along with post-growth in-situ annealing of the NW samples for 5 minutes in an ultra-high vacuum of 1.5×10^{-10} Torr at 465 °C (also performed for NIPSb12 samples). The characteristics of the APD devices thus obtained are shown in figure 5.9. This sample representing 12% Sb incorporation in the absorption region along with segment-wise annealing shall be referred to as A-NIPSb12 hereafter.

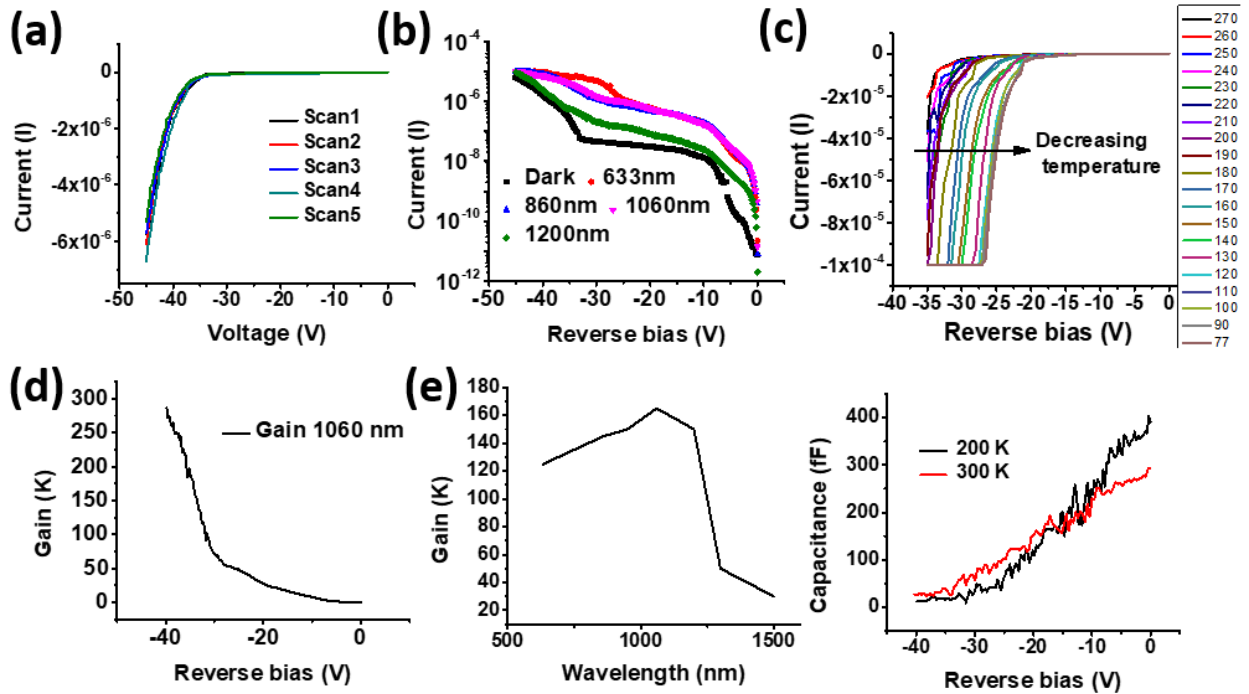


Figure 5.9: (a) Five repeated dark I-V measurements of the device at 300K temperature, (b) spectral response of the devices up to 1500 nm wavelength, (c) Temperature dependence of the NW device with multiplication region thickness of ~ 35 nm, (d) gain of the device with reverse bias at 1060 nm wavelength, and (e) capacitance-voltage measurements of the device at 200 and 300 K temperature.

Increased consistency in I-V features under dark conditions of the APD NW devices was obtained after the segment-wise annealing and continued in-situ annealing step in the UHV environment as shown in figure 5.9 (a). Contrary to the previous observation change in the breakdown characteristics of the devices (fig 5.8(b)) were minimal, we hypothesize a decrease in the trap states in the heterostructure interfaces with segment-wise growth annealing. The device showed good spectral sensitivity up to a wavelength of 1100 nm, (shown in figure e 5.9 (b), (e)). Positive temperature dependence of I-V was observed across a large temperature range of 77 K-300 K as shown in figure 5.9 (c), which is a clear indication of avalanche characteristics. A device gain exceeding 150 at 1060 nm wavelength at RT is achieved. To confirm avalanche characteristics, C-V measurements were taken at two temperatures of 200 K and 300 K, which showed an increase in the breakdown of the device indicated by slower depletion of the NW channel with an increase in the temperature.

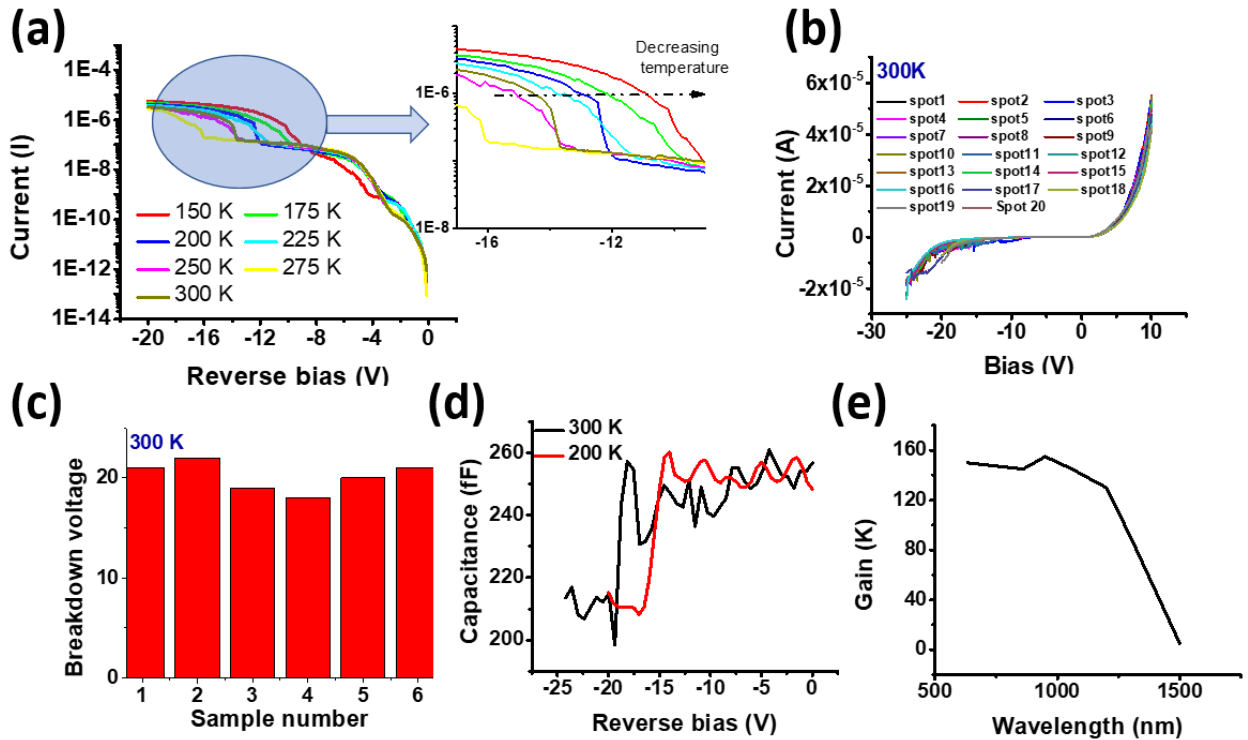


Figure 5.10: (a) Temperature dependence of the NW device with multiplication region thickness of ~25 nm, inset shows the enlarged breakdown region at different temperatures, (b) twenty cycles of dark I-V measurements of the device at 300 K temperature, (c) fluctuation in breakdown voltage across the samples, (d) capacitance-voltage measurements of the device at 200 K and 300 K temperature, (e) spectral response measurement (in terms of gain) of the devices up to 1500 nm wavelength for a reverse bias of 18 V.

To further tune down the breakdown voltage of the NW APDs, a thinner multiplication layer of GaAs (20 nm) is employed resulting in lowering the breakdown voltage to 20 ± 3 V at RT. E-field intensity varies inversely with the multiplication region thickness (figure 5.4 (a)). Thus, a lower reverse bias voltage is necessary to cause the avalanche initiation. Moreover, a thinner multiplication region increases the tunneling probability and results in increased overall device dark current and hence the decrease in the observed gain and signal to noise ratio. Decreasing the multiplication thickness below 20 nm resulted in a large device dark current, and the disappearance of avalanche characteristics at room temperature (not discussed here). For 20 nm multiplication thickness, the Sb composition in the absorption layer was further increased to extend the spectral sensitivity to 1300 nm wavelength. This sample representing 30% Sb incorporation in the absorption region and thinner multiplication region along with segment-wise annealing shall be referred to as A-NIPSb30 hereafter. SEM image and corresponding band emissions observed from photoluminescence are shown in figure 5.11 for a high Sb incorporation of ~30% in the absorption region. An increase in 2D growths and NW diameter increase of 15 ± 3 nm for the same growth duration is assigned to increased Sb incorporation, in the absorption region. Multiple GaAsSb related peak from 0.85 to 1.05 eV is observed, in photoluminescence spectroscopy (fig. 5.11 (b)). The observance of multiple GaAsSb-related peaks is attributed to the segregation effect that results in a compositional grading in the grown structure [186]. A very weak GaAs-related peak was observed at ~1.38 eV. This observation compared to the lower Sb present sample is potentially

due to a thicker and more defective absorption region, thus limiting the light absorption in GaAs regions towards the core.

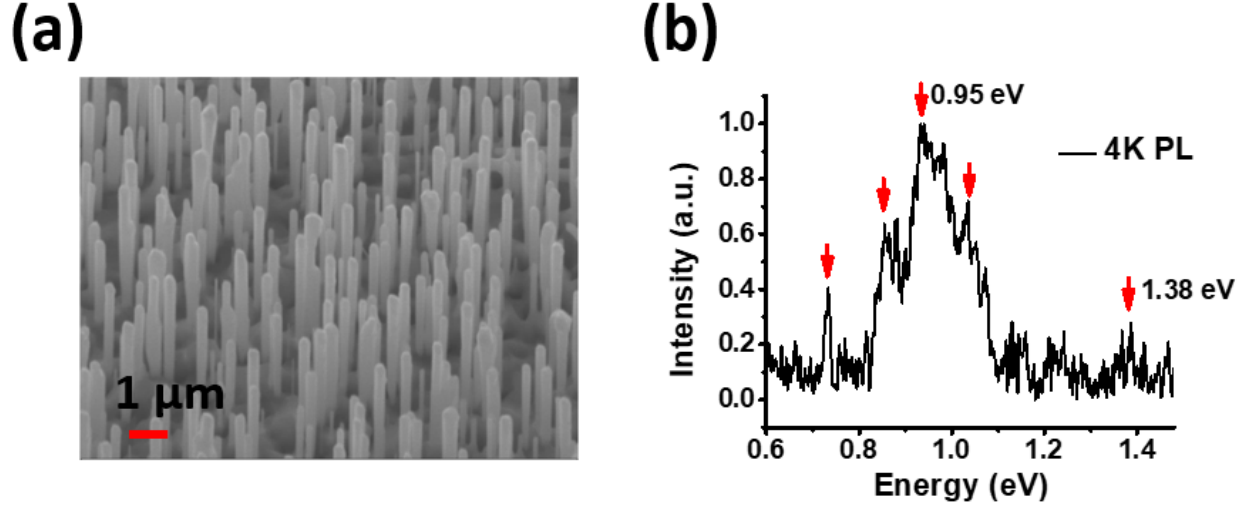


Figure 5.11: (a) SEM image of SAM-APD for Sb incorporation of $\sim 30\%$ in the absorption region, (b) corresponding photoluminescence at 4K temperature showing multiple GaAsSb related peaks centered around 0.95 eV.

The temperature dependence of the device ranging from 150 K to 300 K shows a positive temperature coefficient of the device measuring approximately 50 mV/K. Figure 5.10 (b) shows the result of 20 dark current measurements of an NW sample at different spots, giving a breakdown voltage fluctuation by ~ 3 V from 20 V (shown in figure 5.10 (c)). The spectral I-V measurements of the device are shown in figure 5.10 (e). Devices showed excellent gain up to an illumination wavelength of 1200 nm and decent gain at 1300 nm wavelength after which the absorption was cut off rapidly, and the gain of the device rapidly decreased at 1500 nm illumination. Corresponding C-V characteristics (figure 5.10 (d)) at 1200 nm illumination shows a breakdown following 20 V reverse bias at 300 K, after which the device capacitance assumes a near-constant

value with increasing bias. The C-V characteristics of the device support the positive temperature coefficient observed in the I-V characteristics.

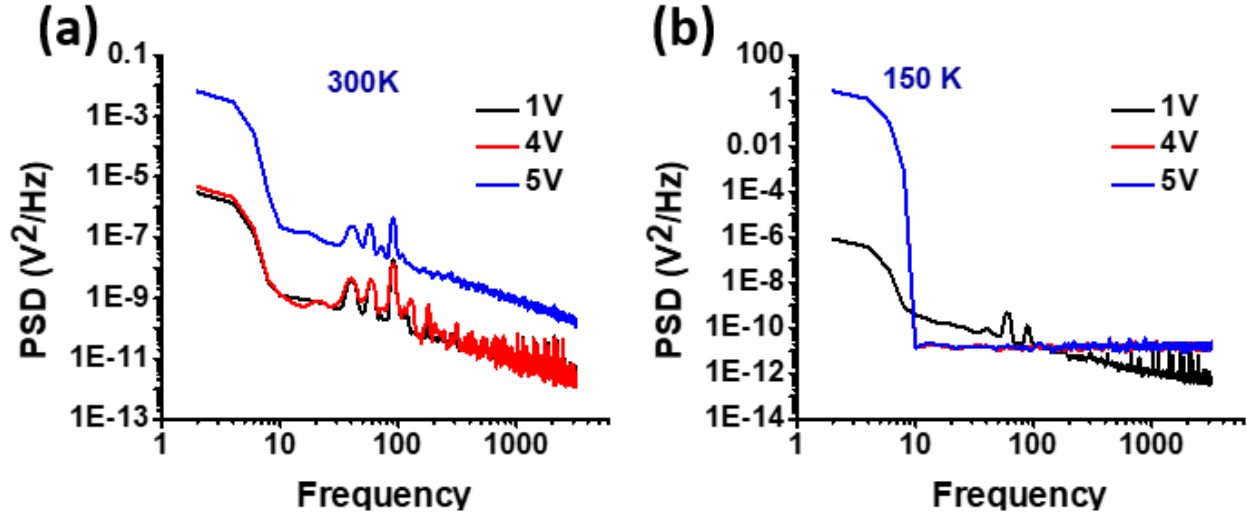


Figure 5.12: Low-frequency noise of the 25 nm multiplication layer APD for different reverse bias voltage at (a) 300 K and (b) 150 K.

A study of low-frequency noise was done to study the avalanche characteristics further. At 300K, a significant increase in noise was seen at 5 V reverse bias, and the characteristics of the device showed a Lorentzian characteristic for low frequency attributed to G-R noise and a $1/f$ dependence for higher frequencies which is attributed to the trap dominance in the device (fig. 5.12 (a)). The noise characteristics changed to a less-trap dominance feature at 150 K temperature, due to the freeze-out of deep level traps at lower temperatures. Unlike 300 K, an increase in noise was seen at 4 V reverse bias instead 5 V. This is attributed to the change in punch-through voltage with a decrease in temperature. Due to the freeze-out of the trap states, a lower E-field is sufficient to cause the multiplication layer fully depleted of charge carriers and thus a decrease in the punch-through voltage as shown in figure 5.12 (b). A summary of the samples studied is listed in table 6.1.

Table 5.2: A summary of performance metrics for the APD samples under study.

Sample	Sb incorporation (%)	V_{BR}	Gain	Maximum operation wavelength	Detectivity
PINSb12	12%	~30 V @ 200K	>100 at -20V and 1060 nm	1.1 μm	$5.0 \cdot 10^{10}$ Hz ^{0.5} /W at -25V
A-PINSb12	12%	~35 V @ RT	>250 at -35V and 1060 nm	1.1 μm	$7.0 \cdot 10^{11}$ Hz ^{0.5} /W at -25V
A-PINSb30	30%	~20 V @RT	>150 at 18V and 1060 nm	1.3 μm	$2.0 \cdot 10^{10}$ Hz ^{0.5} /W at -15V

Our as-grown ensemble SACM core-shell APDs were demonstrated up to an illumination wavelength of 1.3 μm at RT with a responsivity of ~ 0.2 A/W at a punch through the value of ~ 5 V. With the experimental optimization, a breakdown voltage as low as ~ 20 V is demonstrated at RT with a positive temperature coefficient of 50 mV/K. A gain value of 20-30 is observed before a breakdown in linear mode, while RT avalanche gain in Geiger mode reaches up to 160 at 18 V reverse bias at an illumination wavelength of 1.1 μm . The C-V measurements yielded a maximum capacitance of a few hundred femto-farad, which is an important result for high-speed device operation applications. A comparison of this work with works in nanowire APDs in literature is shown in table 6.2.

Table 5.3: Figure of merits of NW APDs in literature.

NW Material	Device structure	Growth substrate	Operation wavelength (nm)	Dark current, breakdown voltage (V_{br})	Gain (k)	Responsivity (A/W)	Ref
GaAs	p-n shell/core	GaAs	730	216 at -12V	-	-	[187]
Si	p-i-n	-	488	-38V	100	1.16×10^{-3} at -22V	[188]
CdS/Si	Crossed n/p	-	488	~ 100 pA for $< V_{br}$, -9V	5×10^4 at -9V		[189]
Si	p-i-n	-	600	-14V for 500nm thickness	2300 at -35V	-	[190]
InP & InP/InAsP (**QD)	p-n & p-QD-n	Si	532	~ 1 pA for $V_{br} < -15$ V	2.3×10^4 & 1.3×10^4 at -8V	-	[191]
GaAs	p-n shell/core	GaAs	730	10 μ A at -3V, $V_{br} \sim -9.5$ V	216 at -12V	0.27 at -3V	[187]
Si	p-i-n	Si	633	~ -10 V at 500nm	5.9×10^4 at -10V	1.4×10^{-5} (Voltage NA)	[192]
InGaAs/GaAs	p-n	GaAs	1064	-	96 at -6.8V	-	[193]
InP & InP/InAsP	p ⁺ /n/n ⁺ & SAM	Si	532	~ 10 pA at -33V, $V_{br} \sim -31 \pm 6$ V $V_{br} \sim -28$ V for p ⁺ /n/n ⁺ at 77K	12 at -28V for SAM	5 for p ⁺ /n/n ⁺ & 0.15 for SAM	[194]
InGaAs/GaAs (Single photon PD)	p-i-n SAM	GaAs	1064	-17V	-	-	[195]
This work GaAs/GaAsSb	n-i-p-abs SCAM	Si <111> N⁺	Upto 1300 nm	~ 10 nA at -5V (at RT) $V_{BR} 20V \pm 3V$	20-30 at 10V, 160 at 18V (at RT and 1060 nm)	0.2 A/W at unity gain (5V).	

It is to be noted that the wavelength of operation of our NW device extends up to 1.3 μm with the highest gain observed at 1.1 μm wavelength. Most of the reported works in NWs operate in visible and near-infrared regimes up to 1.1 μm . Among the reported NW APDs, the work by Farrell et Al. [179, 196] and Senanayake et Al. [197] showcases a low breakdown APD with high internal gain. Avalanche gain of 96 is reported by Farrell et al. at a very low V_{BR} of 6.8 V and a wavelength of 1064 nm. Avalanche gain exceeding 200 at a very small bias voltage of 12 V is demonstrated utilizing surface plasmons in the nanostructures in C-S GaAs configured NPs [197]. We have demonstrated a similar performance device in C-S configured NWs in terms of gain characteristics at RT, while the device operation has been extended to a longer wavelength of 1.3 μm . It is to be noted that the major difference between all the reported NWs and ours is that our work is on the non-patterned substrate while the literature reports are on a patterned substrate.

5.6 Towards high-performance SAM-APDs

This work is intended to show the potential of NWs in achieving selective performance improvements for high-gain and low-power photon counting devices. Despite the challenges in the non-uniformity associated with the free-standing ensemble NW growth, we were able to demonstrate an excellent device performance with a temperature of operation up to 300 K. Demonstration of high-quality APD with consistent punch through and breakdown characteristics is impaired by the limitations of the epitaxial growth technique used. First, the control of NW diameters corresponding to VS growth of shell cannot be precisely controlled in ensemble growth. One possible solution to this issue is the use of patterned APD growth with controlled pitch length, which can improve the non-uniformity in these values substantially. Another important factor is the optimization of ohmic contact on nanowires, facilitating light absorption below the contact surfaces. Various methods of contact have been practiced in literature, including angle metalized contact, transparent contacts, and dispersed NW contacts (our current practice). Annealing has been a common technique to improve the characteristics of most of the methods used. Yet, the reliability of contacts at the nanoscale is

often in question due to the difficulty of obtaining trap-free ohmic contacts with nanowires. Single NW devices serve a better purpose in terms of consistency in the device metrics, however, lack the advantage of NW forest in obtaining significantly higher quantum efficiency and hence can be used only as

1.3 5.7 Conclusion

A GaAsSb/GaAs based SAM-APD NW device in CS configuration is successfully demonstrated in ensemble configuration on unpatterned n-Si<111> substrate for the first time. NW growth was successfully optimized with doping optimal doping and structural thicknesses. A simulation approach has been used as an initial guide to study the E-field distribution in the NW segments in the proposed NW heterostructure. A breakdown voltage of ~20 V reverse bias and a gain over 150 at room temperature has been demonstrated at 1100 nm wavelength and we report a significant gain of ~80 at longer 1300 nm wavelength at V_{BR} . The Avalanche breakdown mechanism in the NWs was confirmed using the temperature-dependent I-V characteristics and C-V characteristics. Furthermore, silver NW contacts were used to maximize the light absorption in the NW APDs. Despite some challenges and limitations, results show great promise towards achieving high sensitivity avalanche photodetector in the NIR region.

The manuscript for this work is under preparation for submission to a suitable scientific journal.

Chapter 6

Conclusions and Closing Remarks

This dissertation work focused on two different material growth (GaAsSbN (Te) in axial configuration and GaAs/GaAsSb multi core-shell) and accessing their properties and translation into device performance. Along with the exploration of material growth from numerous perspectives along with their physical, electrical, and optical characterization and analysis, we presented a variety of insights into understanding the unexplored properties of these alloys. In addition, we have demonstrated the NW device with both material systems and highlighted important performance metrics along with the challenges we faced and solved.

In dilute nitride GaAsSbN (Te) axial growth, we studied the nanowire stem growth, substrate temperature, cell temperatures, and the RF plasma exposure in the background. These vital parameters were studied concerning the change in material properties and were crucial in achieving structurally defect-free nanowires. By improving the quality of GaAsSbN NWs, we showcase the NW Schottky device with uniform NW density, morphology, and improved optical properties for demonstrating the Schottky device with high responsivity.

In GaAs/GaAsSb-based material system, we demonstrated sensitive SCAM APDs by studying and optimizing the complex material growth structure, device geometry, and doping profiles. We have attempted to solve several issues encountered in traditional planar devices and have been successful in decreasing the voltage of operation, suppressing the noise to increase the signal-to-noise ratio, and extending the device's room temperature operation beyond 1.1 μm wavelength

up to 1.3 μm , important telecommunication wavelength. We also demonstrate a very low device capacitance required for high-speed operation applications.

A summary of the achievements of each work and the underlying future outlooks are discussed below.

6.1 Ensemble growth of GaAsSbN (Te) NWs and photodetector demonstration

We presented a unique approach for the growth optimization of GaAsSbN NWs in undoped and doped configuration via optimization of NW stem growth and the nature of N-incorporation in the NWs. High-quality NWs were demonstrated with room temperature photoluminescence with compositional uniformity devoid of planar defects in axial configuration. An insight into the nature of n-type dopant incorporation using GaTe captive source was presented, which provided a pathway to improve the defect concentration inherent with dilute nitride NWs in this material system. Exciting device performance was achieved with a very high responsivity of ~ 3800 A/W in ensemble configuration (at a wavelength of 1100 nm) and ~ 5 A/W in single NW configuration (at a wavelength of 860 nm). Findings presented in this work showcase rich prospects for bandgap engineering in the NIR region using doped GaAsSbN NWs. This work can pave a path toward the development of an alternative material system with unique features such as ultrafast signal detection and high-performance defect engineered devices operating in the NIR region up to 1.7 μm . **This is the first successful realization of NW dilute nitride GaAsSbN photodetector device in axial configuration, and this work is published in Applied Electronic Materials. (Pokharel et al., pubs.acs.org/acsaelm, DOI: 10.1021/acsaelm.0c00450).**

A provisional patent is filed for this work • **“MBE growth of high-quality dilute nitride GaAsSbN for room temperature near-infrared photodetection application”, Invention disclosure completed. Disclosure no: JSNN0034 0821**

6.2 Patterned growth of GaAsSbN (Te) NWs

After the successful realization of ensemble dilute nitride NWs, the study was extended to the successful realization of these NWs in patterned configuration. A study of NW growth over a large pitch length range of 200-1200 nm was presented for an oxide hole diameter of 200 nm. The optimization of NW stem composition for best vertical yield is presented, and a pitch-dependent bandgap tuning of ~ 75 meV was achieved, compared to the bandgap tuning of 40-50 meV in non-nitride counterparts. Pitch-dependent bandgap tuning can be exploited to achieve photodetectors with wide wavelength operations as well as multispectral sensing spanning the telecommunication wavelength region. This work shall be a foundation for the realization of dilute nitride photodetectors with enhanced performance metrics compared to ensemble configuration. **This is the first report on the growth of patterned arrays of dilute nitride GaAsSbN NWs and is published in scientific reports (Johnson et al., Scientific Reports, DOI: 10.1038/s41598-021-83973-9)**

6.3 GaAs/GaAsSb separate absorption multiplication core-shell avalanche photodetectors

A GaAs/GaAsSb-based avalanche photodetector with a separate absorption and multiplication region was successfully designed and grown using the epitaxial method for the first time on a non-patterned Si substrate. These are the first results of successful APD both from the material aspect as well as ensemble NW configuration on the non-patterned substrate. We presented a simulation approach and experimental approach to best optimize the heterostructure thicknesses and doping profiles in the NWs. Optimization approaches have been presented to extend the

device operation to room temperature. First, we demonstrated performance parameters with gain exceeding 100 at 200 K at a wavelength of 1064 nm. A breakdown voltage of 30 V at 200 K was achieved. With the optimization of material growth and annealing, we successfully extended the operation temperature to RT with a breakdown voltage of 35 V. Subsequently, we successfully incorporated 8-30% Sb at. % in the absorption region to extend the wavelength of operation up to 1.3 μm and successfully decreased the breakdown voltage to 20 V at RT.

In summary, we demonstrate a room-temperature operation of a highly sensitive SCAM structure avalanche photodetector which operates up to 1.3 μm wavelength. Further, we offer flexibility in bandgap tuning by simply varying Sb composition in the absorption region without considerable impact on the multiplication noise of the photodetector. These features are attractive for beyond 1 μm applications in the industry. While most of the NW APDs reported do not have a separate absorption layer and use other forms of enhancement for maximizing light absorption; we use a separate absorption layer in our APDs to facilitate wavelength-tunable light absorption and lowering multiplication noise, which is crucial for higher wavelength applications.

This work has shown a potential for achieving a low-cost alternative material system to achieve high sensitivity nanoscale devices aimed toward single photon counting using GaAs/GaAsSb material system. **The manuscript for this work is under preparation for submission to a scientific journal.**

6.4 Future work

We have delineated important material properties and growth aspects of dilute nitride NWs via epitaxial growth which can open numerous avenues in bandgap tuning as well as introduce exciting features in nanoscale devices using this material system. There is an excellent opportunity for extending the work on dilute nitride to achieve highly sensitive photodetectors in

the advanced configuration as well as exploring the defect engineering possibilities. For instance, the work on bandgap tuning of the GaAsSbN NWs can be translated into achieving telecommunication wavelength photodetection by incorporating the Nitrogen in the absorption layer of SCAM APDs, thus overcoming the difficulty of bandgap tuning using high Sb composition. The work on selective area epitaxy of these dilute nitride NWs can be successfully translated into understanding the nature of nitrogen incorporation and overcoming the growth difficulties, in achieving future high-performance patterned NW photodetectors with dilute nitride alloy segments.

The work on SCAM APDs using GaAs/GaAsSb material systems can have far-reaching implications. There is room for various inclusions and improvements in achieving a single photon detector using this CS configuration. The use of surface plasmons on selectively grown nanostructures as demonstrated by Farrell et. Al [193] can be applied to our NW APDs in achieving increased sensitivity. The use of tapered nanowire arrays has the advantages of minimizing reflection of incoming light, availability of a large diameter range for resonant coupling of guided modes over a large wavelength range, and maximization of absorption efficiency via pitch length tuning [198]. The latter provides another possibility we can easily explore to maximize the absorption of light across different wavelengths. Investigation on the further optimization of trap-free ohmic contacts, nature, and mitigation of core-shell interface traps, and simulation study of the dead-space effect in our heterostructure is crucial to achieving single-photon detection at 1.1 μm and beyond.

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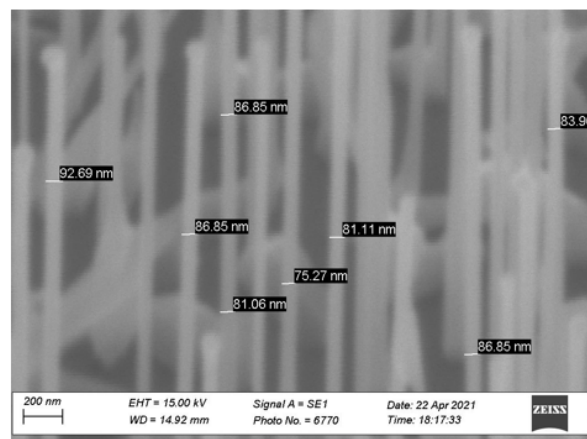
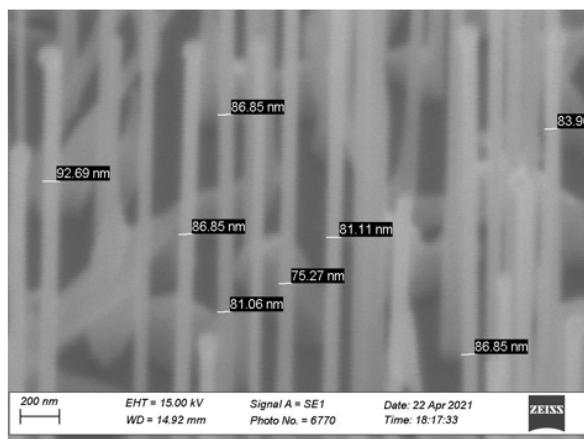
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Appendix

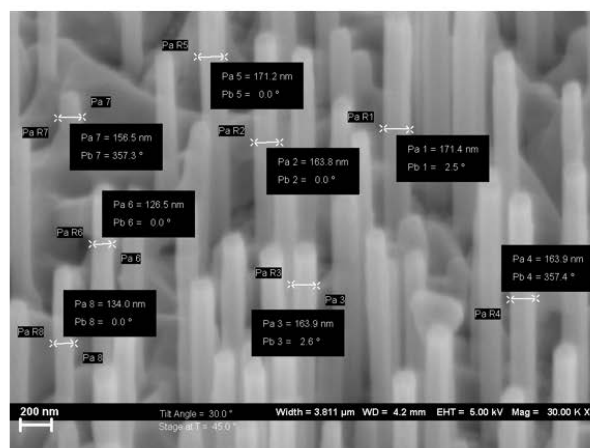
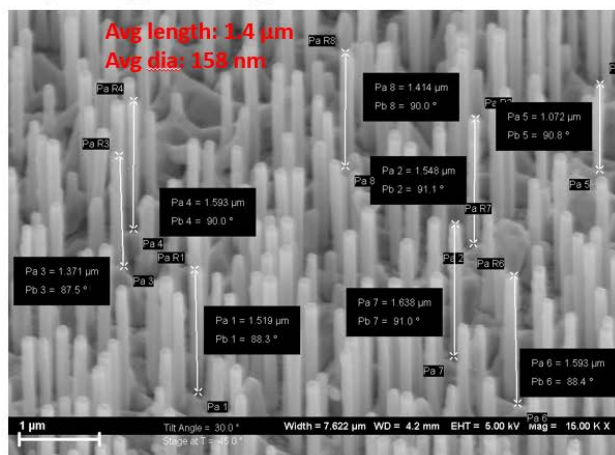
Figure A1: SCAM APD Growth: segment-wise SEM images (Demonstration of core-shell configuration growth procedure in segment optimization process).

N-core growth: 30 mins



Diameter range	85±10 nm
Length range	2.7±0.3 μm
Radial growth rate	~2.8 nm/min
Axial growth rate	90 nm/min

N, I segment growth

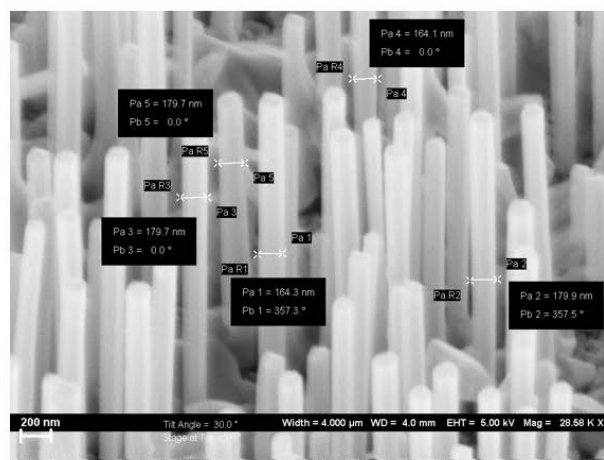
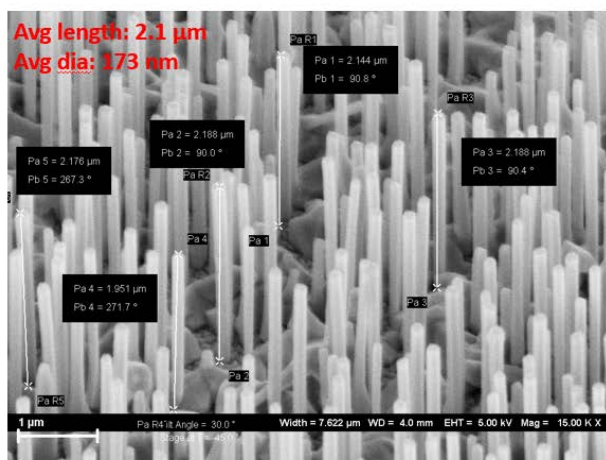


Core growth duration: 10 mins, I-segment growth duration: 25 mins.

Diameter range	145±20 nm
Length range	1.4±0.2 μm
Radial growth rate (I-GaAs)	2.2 nm/min

Axial growth rate	NA
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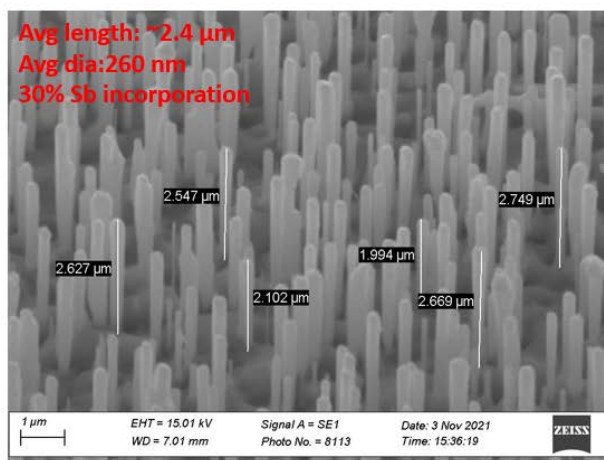
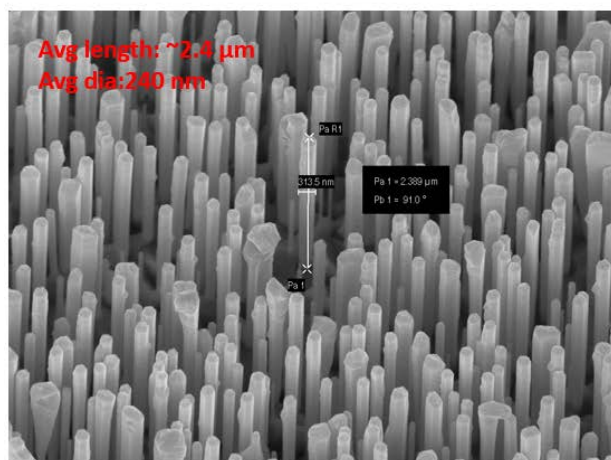
N, I, P segment growth



Core growth duration: 15 mins, I-segment growth duration: 25 mins, P-segment growth duration: 10 mins.

Diameter range	170 $\pm$ 20 nm
Length range	2.1 $\pm$ 0.2 μm
Radial growth rate (P-GaAs)	2.0 nm/min
Axial growth rate	NA

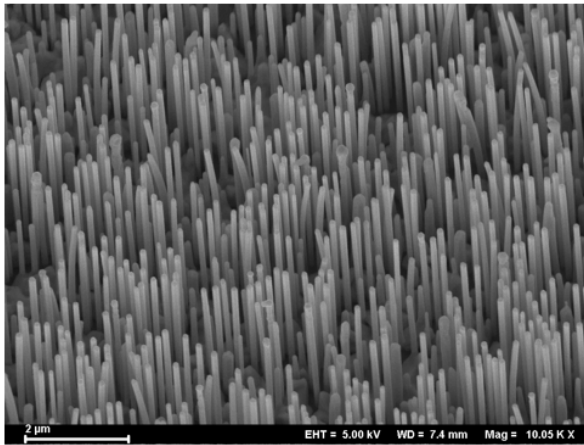
NIP-Abs layer, contact and passivation layer segments growth



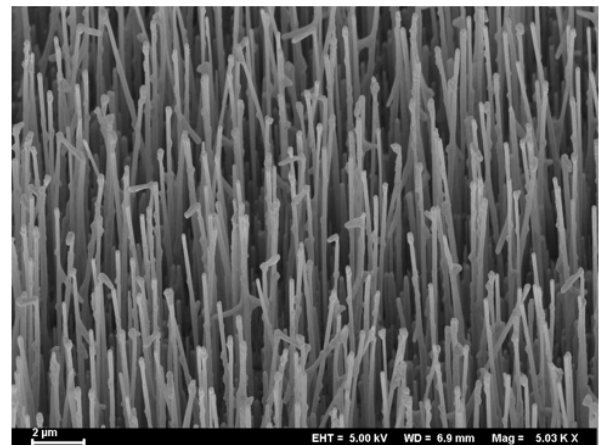
Core growth duration: 15 mins, I-segment growth duration: 25 mins, P-segment growth duration: 10 mins, Absorption layer growth duration: 15 mins, contact layer growth duration: 3 mins, Passivation layer growth duration: 5 minutes.

Diameter range	240±30 nm
Length range	2.4±0.3 μm
Radial growth rate (i-GaAsSb)	2.25 nm/min (12% Sb), 2.7 nm/min (30%)
Axial growth rate	NA

Properly droplet terminated sample



Improperly droplet terminated sample



Improperly terminated axial growth/regrowth of NW in top of axially terminated NWs result in a very long, and bent NWs because of axial strain accumulation.