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**A Study of GaAs_{1-x}Sb_x Axial Configured Nanowires Based Schottky and p-i-n
Ensemble Near-Infrared Photodetectors**

Shisir Devkota

North Carolina A&T State University

A dissertation submitted to the graduate faculty
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Biographical Sketch

Shisir Devkota was born in Nepal in 1992. He earned his bachelor's degree in Electronics and Communication Engineering from the Western Region Campus (WRC) in 2016. In the final year of his undergraduate study, he worked on a group project entitled "GPS and GSM based accident detection system." In addition, he completed an internship in Nepal Telecom Bharatpur as per the partial fulfillment of his undergraduate studies. After graduating from WRC, he joined the Nepal Academy of Science and Technology (NAST) as a research assistant. In 2017, he joined as a Ph.D. student in the Nanoengineering department in the Joint School of Nanoscience and Nanoengineering (JSNN) at North Carolina A&T State University, Greensboro, NC, USA. In his Ph.D., he worked under the supervision of Prof. Dr. Shanthi Iyer in the Molecular Beam Epitaxy (MBE) system. His research primarily focused on the growth, characterization, and optimization of group III-V (i.e., GaAsSb) semiconductor p-i-n NWs to realize near-infrared (NIR) photodetectors. As the MBE lab manager, he actively participated in troubleshooting, installation, preventive maintenance, and MBE system maintenance. His five years of experience designing, executing, and analyzing experimental research resulted in 4 peer-reviewed journal publications, including a provisional patent application.

Dedication

Dedicated to my parents and my late grandmother Hari Maya Adhikari

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I want to thank my advisor, Prof. Shanthi Iyer, for providing me with an opportunity to work in her inclusive and dynamic research group to polish my research skills. Working closely with her, I was able to identify the existing challenges in the current field of study and develop an approach to address those challenges.

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List of Publications

1. **S. Devkota**, et al. "A study of n-doping in self-catalyzed GaAsSb nanowires using GaTe dopant source and ensemble nanowire near-infrared photodetector" *Nanotechnology*, 2020, DOI: 0.1088/1361-6528/abb506
2. **S. Devkota** et al. "A Study on the Effects of Gallium Droplet Consumption and Post Growth Annealing on Te- Doped GaAs Nanowire Properties grown by Self-Catalyzed Molecular Beam Epitaxy" **submitted to Catalyst, under review**

Manuscript under preparation

1. **S. Devkota**, et al. "High detectivity heterojunction PIN GaAsSb nanowire photodetector for near-infrared photodetection application"

Related NW publications

1. S. Nalamati, **S. Devkota**, et al. "Hybrid GaAsSb/GaAs Heterostructure Core-Shell Nanowire/Graphene and Photodetector Applications" *ACS Applied Electronic Materials*, 2020, DOI: 10.1021/acsaelm.0c00433
2. P. Ramaswamy, **S. Devkota**, et al. " A study of dopant incorporation in Te-doped GaAsSb nanowires using a combination of XPS/UPS, and C-AFM/SKPM." *Scientific reports* 11.1 (2021): 1-14.
3. R. Pokharel, P. Ramaswamy, **S. Devkota**, et al. "Epitaxial High Yield Intrinsic and Te-Doped Dilute Nitride GaAsSbN Nanowire Heterostructure and Ensemble Photodetector Application" *ACS Applied Electronic Materials*, 2020 DOI: 10.1021/acsaelm.0c00450

4. L. Yuan, R. Pokharel, **S. Devkota**, et al. “Revealing charge carrier dynamics and transport in N-doped GaAsSb nanowires by ultrafast optical pump and terahertz probe spectroscopy”
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5. M. Parakh, P. Ramaswamy, **S. Devkota**, et al. “Investigation of the electrical and optical properties of Al₂O₃ passivated GaAsSb nanowires” **(Accepted conditionally Nanotechnology)**

Conference Presentations

1. **S. Devkota**, et al. “A n-GaAsSb ensemble nanowire photodetector for near-infrared application” ICTN-KLA, August 24-26, 2021, India. **(Contributory oral presentation)**
2. **S. Devkota**, et al. “A study of n-doping in MBE grown GaAsSb nanowires using GaTe dopant source and ensemble nanowire near-infrared photodetector” CSS November 12 & 13, 2020, North Carolina. **(Oral presentation)**
3. **S. Devkota**, et al. “A Te doped GaAsSb ensemble nanowire photodetector for near-infrared application” EMC, June 23-25 **(Oral presentation)**
4. **S. Devkota**, et al. “A Near-Infrared Te-Doped GaAsSb Ensemble Nanowire Schottky Barrier Photodetector” Material Research Society (Spring/Fall), Nov 28- Dec 4, 2020, Boston, Massachusetts **(Oral presentation)**
5. **S. Devkota**, et al. “N-type Doping of GaAs Nanowires Using GaTe Source Grown by Ga-Assisted Molecular Beam Epitaxy” 35th NAMBE September 22-25, 2019, Ketchum, Idaho **(Poster presentation)**

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Invention disclosure: GaAsSb axial p-i-n NWs operating in the NIR region **(under preparation)**

Abstract

GaAsSb is a material of choice for implementing p-i-n junction in nanowire (NW) configuration due to their high intrinsic carrier mobility, direct bandgap, and bandgap tunability encompassing the low loss telecommunication near-infrared wavelength region. Further, presence of only a single group III element in this material system offers several advantages for the growth in a nanowire geometry. Devices in one-dimensional architecture are preferred over their thin-film counterparts due to their ability to heterogeneously integrate with silicon technology, improved photo absorption, material quality, and device performance. Moreover, advantages of the NW configuration and the p-i-n junction blend perfectly in the axial p-i-n NWs, broadening their scope of applications in light detection and ranging (LIDAR) technology used in autonomous vehicles, optical interconnects, and 5G communication. However, the fabrication of ensemble NW photodetector (PD) utilizing the axial p-i-n NWs has been limited, as they suffer from severe growth challenges.

This dissertation addresses the material quality, doping, and interface challenges encountered during the axial NW growth of GaAsSb by molecular beam epitaxy using unique growth approaches. A detailed and systematic study of the doped NWs, Schottky barrier devices, and p-i-n devices were carried out and correlated to the growth issues. Detailed device characterization gave greater insight into the device physics and successful realization of Schottky junction and p-i-n junction-based PD devices in the ensemble NW configuration. Te-doped Schottky PD devices with a responsivity of ~ 620 A/W and a detectivity of $1.2 - 3.8 \times 10^{12}$ Jones and high-quality axial p-i-n based PD devices with the responsivity of ~ 120 A/W and the detectivity of $\sim 1.3 \times 10^{13}$ Jones operating up to $\sim 1.1 \mu\text{m}$ have been successfully demonstrated. The findings of this dissertation can be extended to the patterned NWs growth to improve further

the device performance and broaden the wavelength range of operation encompassing the low loss telecommunication wavelength range.

CHAPTER 1

Introduction

1.1 Overview

Among the variety of ternary III-V compound semiconductor material systems, GaAsSb demonstrates an intriguing trait to be used in near-infrared (NIR) photodetector (PDs) because of its higher phase purity, enhanced carrier mobility, and the ease of bandgap engineering [1]. In addition, the GaAsSb covers the low loss telecommunication wavelength of 1300 nm and 1500 nm triggering extensive research. In addition, significant attention is gained by inorganic III-V compound semiconductor NWs due to their direct bandgap (i.e., minima of the conduction band are precisely in the same place as the maxima of the valence band in k-space), higher photocarrier mobility and lifetime, enhanced photoabsorption, and the flexibility for bandgap engineering [2]. Furthermore, inorganic PDs are preferred over organic, as organic PDs are characterized by lower charge carrier mobility and suffer from stability issues in the ambience [3], [4]. III-V materials in nanowire (NW) configuration have a strong potential to be utilized as a building block for the next generation of nanostructured devices. The ease of growing high-quality epitaxial layers in NW configuration with minimal residual carrier concentration enables the fabrication of high-performance nanostructured optoelectronic devices with low leakage current, high speed, reduced capacitance, and higher quantum efficiency [5]. Furthermore, the elastic strain relaxation stemming from a smaller NW footprint offers the flexibility to incorporate homojunction and heterojunction with minimized interface roughness and defect density [6]-[8]. Generally, NWs are grown utilizing the widely accepted vapor-liquid-solid (VLS) mechanism developed by Wagner and Ellis in 1964 [9]-[12].

Antimony-based ternary III-V semiconductor p-i-n NWs are studied extensively in various configurations, namely, homojunction and heterojunction for PD applications. A proliferation of research interest in heterojunction p-i-n NWs over the homojunction is ascribed to increased absorption and suppressed dark current, a prerequisite for PD application. Similarly, based on the presence of p-i-n junction, NWs can be categorized into axial and radial (often referred to as core-shell (C-S)) configurations. In the axial configuration, the junction lies in the longitudinal direction as opposed to the presence of a junction in the lateral direction in the radial configuration. The axial configuration has triggered significant research due to the better crystalline quality, minimal shadowing effect, higher degree of tolerance to doping variation, ease of device fabrication, and characterization [13]. On the other hand, the dominant vapor-solid (VS) growth mechanism in radial configuration results in an uneven doping profile due to the facet-dependent dopant incorporation. In addition, VS-grown interfaces are highly defective and rough, exhibiting poor electrical and optical properties. Thus, Attaining a clean interface without defects is a challenge in a radial configuration, which is critical to high-performance devices.

In contrast, the factors mentioned above have minimal influence on the p-i-n NWs grown in the axial configuration, making them a promising candidate for the NIR PD applications. However, the successful realization of high-quality axial heterostructure p-i-n NWs is limited by the infamous reservoir effect, stemming from the solubility difference of the growth species, compromising the interface quality and sharpness [14], [15]. Generally, group III species' solubility is higher than group V in gallium (Ga) catalyst droplet, implying the reservoir effect will be pronounced with an increased number of group III species. Thus, to minimize the potential reservoir effect, III-V-V is preferred over the III-III-V material system to grow the axial ternary III-V heterostructured p-i-n NWs [16].

1.2 Advantages of NW

III-V materials at an industrial scale are limited by the higher cost of substrate materials and a dedicated and optimized process technology requirement. However, III-V materials in the NW configuration, due to their one-dimensional (1-D) structure and small cross-sectional area, demonstrate several attributes that are almost inconceivable in their two-dimensional (2D) thin-film counterparts, thus making them attractive for their utilization in the next generation nanostructured devices. The following section has delineated the advantages of various NW characteristics over thin films.

1.2.1 Heterogenous integration with Si technology. The evolution of the semiconductor manufacturing processes over the past few decades has reached the limit of Moore's law such that the device scaling will no longer follow the previous path. As the bottleneck has been hit in the monolithic integration, design complexities and increased cost at each process node are introduced. So, to address this issue, semiconductor companies are working tirelessly for a cost-effective design while at the same time increasing the system functionality, for which heterogenous integration might be an appropriate technology.

A small NW footprint enables the pseudomorphic growth of high-quality single-crystalline materials irrespective of the lattice mismatch with the substrate. The flexibility offered by NWs in the choice of substrate enables heterogeneous integration on the Si platform for Si photonic devices, as it can reduce the device footprint with increased device density and for the cost-effective device design using the complementary metal-oxide-semiconductor (CMOS) fabrication techniques [17], [18].

1.2.2 Improved photo absorption. The prime advantage of NWs in comparison to thin films lies in the extent of incident light absorption. In NWs, the photoabsorption is significantly

enhanced as the ensemble of NWs has a higher tendency to concentrate the incident light to the NW core due to the pronounced antenna effect [19], [20] when compared to thin films for an equivalent amount of material [21], [22]. Similarly, the refractive index mismatch between the NW ensemble and the surrounding air forms the graded refractive index layer [20] engendering the anti-reflection properties [23], [24]. Moreover, the random growth of vertical ensemble NWs with optimum fill factor increases the optical path length due to multiple scattering [20], [25] and suppressed specular reflection. Further, the alignment of incident light propagation direction along the NWs axis [20], [26] contributes to enhanced photo absorption. Thus, all these phenomena prevailing primarily in NWs act in unison, enhancing the light coupling to the NWs compared to thin films.

1.2.3 Improved material quality and device performance. Reduced interface area between the NWs and the substrate and large surface area of the 1-D architecture allows the elastic relaxation of strain and minimizes crystalline defects' density due to the proximity of the surface, respectively [27]. These can be suitably exploited to realize high crystal quality heterojunctions in a 1-D configuration easily.

The NW devices exhibit a capacitance in the sub- fF range [28], essential for low-power and high-speed applications. A reduced RC delay attributed to a lower capacitance value stemming from the lower electrical cross-section [21], [22], [29] promotes high-speed applications. In addition, significantly lower dark current density (I_D) due to the minimized density of crystallographic defects aids in suppressing the noise level, improving the overall NW device performance. It is noted that the NW advantages over their thin-film counterparts cited above are some of the few ones amongst many, and we have chosen only those that are pertinent to this dissertation work. These advantages establish them as a potential building block for next-

generation nanostructured optoelectronic device applications. Among the various applications, namely waveguides, logic circuits, thermoelectrical devices, gas sensors, light-emitting devices, photodetectors, and piezo electronics, the following section will focus on the PD application NWs, which is the primary goal of this dissertation work.

1.3 Nanowire photodetectors (PD)

A PD is an optoelectronic p-n junction device operating in a reverse-biased condition to convert the incoming optical signal into an electrical signal. The dynamics of photogenerated carriers, i.e., drift or diffusion, in an electric field (E-field) substantially influence the PD performance [30]. The junction is a key in a PD device, as it enables effective photocarrier separation due to the generation of an internal E-field. Photodetectors utilizing the photovoltaic effect are used at zero bias, referred to as a photovoltaic mode or under the reverse biased condition, known as a photoconductive mode [31]. The magnitude of dark current in photovoltaic mode is less than that of photoconductive mode, emanating the sizable detectivity. However, the responsivity is compromised as there is no internal gain. Similarly, in the photoconductive mode, the junction capacitance is suppressed due to increased junction width, improving the device response speed. Therefore, NW photodetectors are suited for an application that calls for enhanced sensitivity, fast response, reduced cost, and durability. Photodetectors generally operate under reverse biased conditions due to the lower dark current, minimized device noise level, and reduced RC delay improving the device performance and the detection limit. The other reason for the PD operating in reverse bias is the device photoresponse is masked in the forward bias. In the recent field of study, avalanche photodiodes (APD) and p-i-n photodetectors are gaining tremendous attention. Still, p-i-n NW PD are preferred over APD due to the suppressed noise level and higher bandwidth, enabling faster data transfer [32]. In addition, the p-i-n PD can detect photons in the

absence of external bias, giving rise to the self-powered application [33], [34] and making them a suitable candidate for low power and high-speed devices. P-i-n PDs are preferred over the Schottky diode PD in telecommunication applications because their performance is compromised at a higher wavelength due to the reflection and absorption of the light in the metal layer. In addition, the magnitude of dark current is significantly higher in the Schottky diode PDs degrading the overall detection limit of the detector. However, the Schottky diode PDs are extensively used in the switching application [35].

1.4 Photodetector figures of merit:

The performance of a PD is characterized by four performance metrics, responsivity, dark current, external quantum efficiency (EQE), and noise equivalent power (NEP), often referred to as the PD figure of merit.

1.4.1 Responsivity ($R(\lambda)$). The responsivity, $R(\lambda)$, is defined as the magnitude of photocurrent (I_{photo}) induced per unit incident power (P_{in}) and has the unit of A/W. It gives an estimate of the achievable electrical signal at given excitation power. A PD with higher responsivity suggests its ability of higher electrical power generation, keeping the optical power constant. The PD responsivity can be calculated employing the following formulae [36], [37]:

$$R_{\lambda} = \frac{I_{photo}}{P_{in}} \quad (1)$$

1.4.2 Dark current (I_D). Ideally, diffusion of thermal carriers under the influence of external bias results in the dark current (I_D) in a photodetector. But, in a practical photodetector, diffusion current is accompanied by a few more currents, increasing the overall dark current. Thus, the magnitude of the total dark current flowing through a PD is expressed as [5]:

$$I_D = I_{dif} + I_{g-r} + I_t \quad (2)$$

Here, I_{dif} is the diffusion component, I_{g-r} is the generation-recombination component, and I_t is the tunneling induced dark current of the dark current. The origin of I_{dif} is the carrier concentration gradient and is dependent on the bandgap of semiconductor material and is independent of the applied bias but increases exponentially with temperature [31]. In contrast, the I_{g-r} and I_t are related to the quality of the materials, and the applied bias strongly influences any defects related currents. Under forward bias, I_{g-r} is due to the recombination of the injected carriers, whereas, in reverse biased conditions, the generation process is predominantly responsible for I_{g-r} . In a photodetector, I_{dif} and I_{g-r} are the two prime sources of dark current and define the temperature dependence of dark current. Thus, the temperature dependence of the dark current depends on the material bandgap, material quality, the device structure, and so forth. Moreover, the magnitude of dark current greatly determines the noise level and the power loss due to inevitable joule heating; thus, a lower dark current is desirable for realizing high sensitivity photodetectors. In addition, a device with a higher dark current needs an additional cooling system, which increases the overall device cost.

1.4.3 External quantum efficiency (EQE). EQE is the total number of photogenerated carriers to the total number of excitation photons. For a particular PD, EQE greater than 1 suggests the existence of internal gain, i.e., a single photon capable of generating multiple e-h pairs. EQE of a PD can be expressed numerically as [38]:

$$EQE = R_\lambda \frac{hc}{e\lambda} \quad (3)$$

Where h is Planck's constant, c is the velocity of light, and λ is the wavelength of the incident light.

1.4.4 Noise equivalent power (NEP). The minimum input power required for a PD to achieve the signal-to-noise ratio (SNR) equal to 1 is called NEP. It measures the minimum

detectable signal intensity from the noise of the PD and is directly related to dark current. The NEP of a PD can be computed employing the following relation [39]:

$$NEP = \frac{\sqrt{\langle i_n \rangle^2}}{R_\lambda} = \frac{\sqrt{S_0[\ln(B) + 1]}}{R_\lambda} \quad (4)$$

Here, i_n is the noise current, basically determined by the dark current. Similarly, B is bandwidth, S_0 is an independent constant. Let us assume two photodetectors, A and B, with dark current $I_A = 10 \mu A$ and $I_B = 100 \mu A$ with the responsivity $R_A = R_B = 10 A/W$. Then using the relation mentioned above, $NEP_A = 1 \mu W$ and $NEP_B = 10 \mu W$ was calculated. From the calculation, the minimum detectable power of detector B is $10 \mu W$ suggesting that it cannot detect an incoming signal with a power less than $10 \mu W$. But in the case of detector A, it can detect an incoming signal with the power of $1 \mu W$, suggesting device A is more sensitive than B. Thus, NEP gives a measure of device sensitivity.

1.4.5 Specific detectivity (D^*). The detectivity is a PD figure of merit extracted from NEP, area, and bandwidth (B), enabling the comparison between the PDs of different geometry. In addition, it gives a measure of minimal optical signal intensity that a PD can detect. The quantity derived after the normalization of detectivity with the area is called the specific detectivity. Thus, the specific detectivity measures the PD performance independent of the device geometry. The specific detectivity of a PD can be calculated as:

$$D^* = \frac{\sqrt{B}}{NEP} \quad (5)$$

1.4.6 Response time (τ_r). The time taken by the generated signal of a PD to transition from 10 % to 90 % of the peak intensity if considered the rising edge and converse in the falling edge

of the signal [40]. There are two response times of a PD, rise time and fall time. A PD with a shorter response time is desired for the high-speed application. Generally, the commercial PDs have the response time in the picosecond (ps) range.

1.4.7 Bandwidth (B). The bandwidth of a PD is the modulation frequency of the incoming signal at which the responsivity of the PD is 3 dB (0.707) lower than the peak intensity. A PD with higher bandwidth is desirable for high-speed applications as the PD will accommodate the higher bit rate for data transfer. In a photodetector, optical bandwidth is the range of incident photon wavelength where the responsivity value drops to 70% of its peak value. Therefore, higher optical bandwidth suggests a broader device's operating range with lower selectivity and vice-versa.

1.5 Noise in photodetectors

Any randomness introduced in a system is referred to as noise. In optoelectronic devices, the signal consisting of useful information is superimposed with noise limiting the detector sensitivity. Inconsistency due to the potential fluctuations in the crystal lattice gives rise to electrical inconsistency referred to as noise. Depending upon the physical origin, the noise power, often referred to as a power spectral density (PSD), is dependent on several device characterization parameters, namely frequency, applied bias, and temperature, to name a few. Based on the dependence of PSD on the physical characterization parameters, electrical randomness can be characterized as thermal noise, shot noise, burst noise, generation-recombination (g-r) noise, and flicker noise (1/f) noise to name a few [41]-[44]. For example, in an NW photodetector, potential fluctuations that originated due to unpassivated surface states, vacancies, complexes, and unintentionally introduced impurities during the growth, often referred to as traps, are the prime noise sources. These traps act as a generation-recombination (G-R) center due to their propensity of random trapping and de-trapping of the carriers causing the carrier fluctuations and thus

stochastic conduction referred to as noise. The variety of noise sources observed in real-world photodetectors are listed below:

1.5.1 Flicker (1/f) noise. The flicker noise is often referred to as 1/f noise as the power spectral density (PSD) of this noise spectra depends on frequency as $f^{-\gamma}$, where $\gamma = 1 \pm 0.1$ [45]. It is dominant at a lower frequency and is studied extensively to determine the lowest detection limit for various sensing applications [46]. Flicker noise introduced in a system is attributed to the carrier concentration fluctuations due to the carrier trapping and de-trapping [47] by the defect states, as suggested by McWhorter theory. Also, the potential fluctuations due to defects result in mobility fluctuations as proposed by Hooge, giving rise to the noise with PSD resembling the 1/f characteristics.

1.5.2 Generation-recombination (G-R) noise. Generation-recombination (G-R) noise ensues in a PD due to the carrier exchange between two distinct energy levels, i.e., the band to band or one of the bands to the trap levels resulting in Lorentzian noise PSD [48]. The G-R noise PSD is characterized by a corner frequency related to the emission or the capture time constant of the defect centers with a discrete-time constant. Whereas a wide distribution of the trap states' capture or emission time constant promotes the superimposition of multiple G-R noise spectra resembling the 1/f behavior, suggesting 1/f noise can sometimes be engendered in a system due to the presence of several G-R noise sources [49].

1.5.3 Thermal noise. Thermal noise, also known as the Nyquist noise, originated due to the random motion of the charge carriers in a resistor R at a temperature higher than absolute zero. Its PSD is independent of frequency, i.e., exhibits the white noise characteristics and can be estimated by: $S_T = 4kTR$, where k is the Boltzmann constant, T is the temperature, and R is the

differential resistance. i.e., $R = dV/dI$ where V is the applied bias, and I is the dark current flowing through the PD.

1.5.4 Shot noise. Shot noise is a low-temperature white noise providing an insight into the carrier transport and conduction mechanism. The origin of shot noise is attributed to the electron-phonon scattering mechanism. The shot noise PSD is related as:

$$PSD = 2qI_{PD} = 2q(I_P + I_D) = 2qI_P + 2qI_D \approx 2qI_P \quad (6)$$

Thus, the increased photoresponse of a PD comes with the increased shot noise in the system.

1.6 Gain (G) of a photodetector

In a PD, a gain is defined as the ratio of a number of e-h pairs collected by the electrodes to the total number of generated photocarriers [50]. The e-h pairs generated in a PD are separated effectively under the influence of both the internal electric field and the external bias resulting in the photocurrent. Under the ideal condition, photogenerated e-h pairs reach the electrodes simultaneously, producing a unity gain. But due to inevitable crystal defects, either of the photocarriers gets trapped in those defects prolonging the lifetime. If a hole gets trapped, photogenerated electrons reach the collecting anode earlier than the holes. Thus, another electron would enter the conductive channel to maintain the charge neutrality, resulting in enhanced photoconduction. Moreover, the hole trapped in the localized states causes the Fermi level shift inducing more electrons attributed to the E-field effect of the trapped holes [38]. This increased density of electrons participates in the conduction, causing the flow of higher I_{photo} , leading to the photoconductive gain (G). In other words, for a single photon, more electrons can be extracted,

resulting in a quantum efficiency greater than one. The gain in a PD can be expressed mathematically as [51]:

$$G = \frac{\tau_{photocarriers}}{\tau_{transit}} \quad (7)$$

Here, the $\tau_{photocarriers}$ is determined by the recombination lifetime of the trap states and $\tau_{transit}$ is the time taken by the carriers to reach the external electrode. Thus, in a PD, photo gain is ascribed to the carrier trapping phenomenon imparting a higher life to the photocarriers.

Generally, the enhanced gain is offered by the trap centers present within the NWs, giving a false impression of traps being essential. But it is very much difficult to control the number of traps present within the NWs, compromising the device's reproducibility and the trap-induced gain enhancement comes with increased dark current adding up to the overall noise. In addition, the increased trap density significantly decreases the device response speed. Similarly, depending on the nature of the traps, a semiconductor device demonstrates a positive or negative photoresponse. For example, if an n-type material has hole traps, the photogenerated hole gets trapped, and electrons are free, adding up the overall carrier concentration, resulting in positive photoconductivity.

On the other hand, the existence of electron traps causes the photogenerated electrons to be trapped, and the holes will recombine with the thermal electrons resulting in the reduced free carrier concentration and, thus, negative photoconductivity. Ideally, in n-type material, there will be a dominance of minority carrier traps or the hole trap. This is because the thermal carriers will satiate most charge carrier traps before the photogeneration.

1.7 Photodetector parameters

In addition to the figure of merit, PD performance can be assessed quantitatively based on the following parameters:

1.7.1 On-off ratio. It is the ratio of photocurrent to the dark current flowing through the device calculated at 0 V. A PD with a higher on-off ratio suggests a lower leakage power flowing through the device, ultimately suppressing the overall noise. The on-off ratio can be expressed as:

$$on - off\ ratio = \frac{I_{photo}}{I_{dark}} \quad (8)$$

1.7.2 Turn-on voltage. In a semiconductor device, under the ideal condition, the diffusion force in the charge carriers is balanced by the electric force, thus no conduction without bias. The diffusion force will overcome the electric force by applying the bias, enabling the exponential rise in the device current. The turn-on voltage is the magnitude of external bias beyond which current increases exponentially. Based on the device architecture and application, the magnitude of turn-on voltage aids in developing an understanding of the various electrical phenomenon occurring in the PD.

1.7.3 Reverse saturation current (I_S). The famous ideal diode equation governing the dependence of the magnitude of current with the applied bias is given as:

$$I_D = I_S e^{\left(\frac{qV}{kT}\right)} \quad (9)$$

Where, I_D is the total dark current, I_S is the reverse saturation current, q is the electronic charge, V is the applied voltage, k is the Boltzmann's constant, and T is the absolute temperature. The voltage-independent current flowing through the device under reverse biased conditions is called a reverse saturation current (I_S). It is a characteristic property of a material and is generated

by the flow of minority charge carriers. Under ideal conditions, its value is highly dependent on the material bandgap and the temperature and is almost independent of the illumination and the external bias. However, in a practical scenario, defects present within a device act as a generation center under a reverse biased condition, adding to the overall I_S . Thus, the magnitude and the dependence of I_S with reverse bias can also be utilized to assess the crystal quality of the PD material. Due to these infamous crystal defects, the I_S is no longer independent of external conditions. So, to circumvent the deviation from the ideal state, the ideality factor is introduced in the diode equation, referred to as an ideal diode equation.

1.7.4 Ideality factor (n). The diode equation considering the non-idealities is expressed as [52]:

$$I_D = I_S e^{\left(\frac{qV}{nkT}\right)} \quad (10)$$

Where n is an ideality factor of a diode defining the extent of deviation of a device from the ideal characteristics, the value of n equals one represents the perfect diode condition. In contrast, the larger n suggests the deviation from the ideality. The value of n greater than 1 stem from the non-radiative recombination pathways that depend differently on the number of charge pairs prevalent in the PD that facilitates the free carrier recombination [53]. Thus, the value of the ideality factor helps to develop an insight into the PD material quality.

1.7.5 Rectification ratio. It is a ratio of the forward bias current to the reverse-biased current at a particular voltage to assess the extent of the unidirectional flow of the charge carriers. A device with a higher rectification ratio suggests higher unidirectionality. Therefore, higher unidirectionality is sought in the p-i-n PDs. The rectification ratio of a particular device can be expressed as:

$$\text{Rectification ratio} = \frac{I_{forward}}{I_{reverse}} \quad (11)$$

1.7.6 Series resistance (Rs). A particular device can be modeled electrically into a perfect conductor with a resistance attached in series. Each device offers a certain magnitude of resistance for the charge carriers to flow through it. The ideal device has minimal series resistance, which increases with defects. Augmented series resistance with increased defect density is attributed to the scattering of the charge carriers around those crystal lattice imperfections. Thus, the series resistance is also a parameter defining a PD material quality.

1.8 PIN PD applications

It is well established that the PDs are the key component of the optical receiver, which has a broad spectrum of applications. Due to the intriguing features of the NW PDs compared to their thin-films counterparts, the research interest has been shifted significantly to the former. NW PDs are fabricated in the APD and the pin configuration. The NW PDs in the pin configuration have been established as promising candidates for the next-generation nanostructured applications due to their simpler device geometry, stable and uniform sensitivity, wider dynamic range, and higher tolerance to the ambient light and temperature fluctuations. In addition, pin PDs can be utilized in low-power applications. Some of the applications of p-i-n NW PDs are optical interconnects for supercomputers, autonomous vehicles, and devices for in-situ medical therapy monitoring, image sensing, remote sensing, communication, and environmental monitoring. For example, as the automobile industry is shifting towards autonomous driving to ensure safe driving, p-i-n PDs can be utilized as a rangefinder by calculating the time of flight (TOF).

Similarly, the integration density in the modern IC has risen significantly in the past decades to cope with increasing data traffic, surging the computing power consumption. The

majority of this power is consumed for data transmission along the resistive electrical interconnects. Thus, p-i-n photodetectors are a viable alternative to electrical interconnects because they are capable of reducing the energy consumption, accompanied by higher bandwidth densities, eventually reducing the cost per bit [28].

1.9 Motivation

However, the realization of axial p-i-n NW PD is in its nascent stage due to the stringent challenges impeding their realization in real-life applications [54]. Hence, this work is driven by a quest for high-performance GaAsSb p-i-n NW ensemble PD for near-infrared (NIR) wavelength detection.

There are two widely accepted architectures for the realization of p-i-n NWs, viz. axial and core-shell (CS) architectures. Among these two, the axial configuration has attained significant attention due to the better crystalline quality, minimal shadowing effect, higher degree of tolerance to doping variation, ease of device fabrication, and characterization [13]. On the other hand, the VS growth mechanism employed for radial p-i-n NWs growth results in an uneven doping profile due to the facet-dependent dopant incorporation. In addition, VS-grown NWs are highly defective with poor electrical and optical properties. Therefore, attaining a clean interface without defects in a CS NW configuration poses a challenge, which is critical to high-performance devices. Further, the interface extends to μm in CS configuration, as opposed to the interface area in the axial configuration being in the nm range, suggesting that high-quality NWs can be easily realized in the latter configuration.

Despite these advantages of the axial configuration over CS NW configuration, the growth of NWs in axial configuration has its challenges. Thus, this work is driven by a quest for the high-

performance axial p-i-n GaAsSb NWs operating in the NIR region. There are various challenges in achieving the high-quality p-i-n NWs in the axial configuration listed below:

1.10 Challenges

The successful growth of axial p-i-n GaAsSb NWs and the realization of ensemble NW PD calls to address some of the material quality, doping, and interface challenges encountered in the NW growth. Additionally, the performance of p-i-n axial configured NWs is dictated by several parameters, namely, the individual segment thickness, doping in the neutral region, unintentional doping in the i-segment, sharpness, and quality of the interface. The list of these issues and the approaches adopted in this work to tackle them are briefly discussed below.

1.10.1 Attaining the purely intrinsic GaAsSb i-segment. GaAsSb is intrinsically p-type due to the Sb vacancies present within the NWs. These vacancies interact with the Ga vacancy and get converted into point defects that are acceptor in nature. The origin of vacancies is attributed to the exchange mechanism between As and Sb, promoting radial out-diffusion of Sb towards the NW surface [1]. The intrinsic p-nature of the i-segment requires higher doping in the neutral regions of the n- and p-segments for its complete depletion. However, increased doping introduces the potential fluctuations within the crystal lattice and promotes tunneling-assisted conduction, eventually adding to the overall dark current, detrimental to the PD sensitivity. In addition, the intrinsic p-type nature of the i-segment might also change the interface properties between p and i-segment.

1.10.2 Reservoir effect. In the axial configured NW growth employing the VLS growth mechanism, the realization of the sharp interface is always a challenge due to the accrument of several growth species in the liquid catalyst droplet, referred to as a reservoir effect [14], [55], [56]. The prime consequences of reservoir effect on the axial p-i-n NWs can range from the

reduced magnitude of E-field across the junction to the onset of unintentional doping or compensation mechanism. The interface effects include broadening the interface, the shift of the junction interface, or even an utterly faulty junction [57]. These effects increase parasitic capacitance and dark current, leading to poor detectivity and device response speed.

1.10.3 Defect-free interface. The interface is commonly known as the source of defects in the axial NWs due to junction imperfections [58], [59]. This occurs when the continuous growth is interrupted to grow the subsequent segment of different species. This interruption causes the dangling bond to introduce interface states within the forbidden energy gap acting as the trap states. These have a deleterious effect on the electrical and optical properties of the NWs.

1.10.4 Photoabsorption in the top n-segment. Due to photoabsorption, the axial p-i-n NW under illumination generates e-h pairs in the top neutral segment. These photocarriers generated within the diffusion length at the two edges of the active region within the neutral region will diffuse to the active region and induce the diffusion current and contribute to the noise, while the carriers generated beyond the diffusion region recombine instantly due to the absence of E-field, compromising the overall PD quantum efficiency.

1.10.5 Reduction of dark current. The higher dark current has a detrimental effect on the p-i-n PD performance due to the added noise in the system, decreasing the system signal-to-noise ratio. There are various sources of dark current, namely diffusion, tunneling, G-R, etc. The magnitude of diffusion current is guided by doping variation, whereas tunneling and G-R dark currents originate from the defects in the neutral segment. Due to the infamous reservoir effect, defective interface due to the dangling bonds and the higher growth temperature of the NWs also contribute to the origin of defects. Under the reverse biased condition, these defects act as the G-R centers adding to the overall dark current. The defect density cannot be nullified but can be

minimized by careful growth recipe optimization. Thus, decreasing the dark current in the p-i-n NW configuration is challenging.

1.10.6 Axial selectivity. In an NW growth employing a VLS mechanism, there is always competition between the axial and radial growth. Growth entirely by one growth mode is challenging. Thus, the performance of axial heterostructured NWs is compromised by the parasitic radial growth. This radial overgrowth in the heterostructured NWs will contribute to the additional pathway for the leakage current, introducing the noise in the system.

1.10.7 Optimization of doping in n-segment. The extent of doping optimization in the neutral region is essential for realizing high-performance axial p-i-n NWs. The doping optimization is crucial because if the doping in the neutral region is less, then a complete depletion of the i-segment poses a challenge and gives rise to the diffusion current. However, if the doping is too high, it will eventually induce the tunnel-assisted current conduction mechanism in increasing the dark current.

1.11 Approaches

The following approaches have been developed to address the several challenges discussed above in the growth of axial GaAsSb p-i-n NWs, enabling this dissertation's demonstration of high-performance PD.

1.11.1 Te compensation of i-segment. The intrinsic p-nature of the GaAsSb material system poses a significant challenge in attaining a purely intrinsic segment. Therefore, the intermittent pulsing of Te (n-dopant) for every 2 mins growth of i-segment has been established as a practical compensation approach.

1.11.2 Be pulsing, pre-termination, and supersaturation. Three approaches have been investigated to minimize the possibility of p-type doping of intrinsic segment due to the inevitable

reservoir effect from the preceding p-segment. These are Be prior termination, pulsing, and supersaturation. In the first approach, the supply of Be is terminated 1 min before the completion of p segment growth such that the p-GaAsSb growth for the next 60 secs can progress with the Be atoms present in the seed droplet. Similarly, in the second approach, the Be supply is pulsed for every 5 secs in the last one minute of the growth to limit the supply of Be, and the final approach is to decrease the NW growth temperature to promote the Be supersaturation.

1.11.3 Growth interruption. In this approach, after the p and i-segment, the NW growth is interrupted for 60 secs enabling the surface reconstruction for the clean interface. One can envisage the reduced interface roughness and current leakage with growth interruption. This pause might also serve as an approach to minimize the reservoir effect as the dissolved growth species get a chance to either precipitate out or get reevaporated. Finally, the NW growth is resumed with 2 secs of Ga droplet replenishment.

1.11.4 Higher bandgap n-segment. For the top n-segment, higher bandgap GaAsSb material with lower Sb composition is adopted to decrease photoabsorption. The higher bandgap material will be transparent to the incoming radiation resulting in minimized photoabsorption in the top n-segment, and the maximum light will reach the active region of the p-i-n NWs. Along the same line, the n-segment thickness should be optimum, as the penetration depth of the incident photon decreases with the segment length.

1.11.5 Increased growth and annealing temperature and As/Sb ratio. Three different approaches have been adopted to suppress the parasitic radial overgrowth. First, the subsequent NW segment is grown at the elevated substrate temperature, as the radial overgrowth is promoted by VS growth, favorable at a lower temperature. Moreover, the higher temperature annealing of the heterojunction core might also serve as an effective technique for suppressing radial

overgrowth. In addition, increasing the As/Sb ratio for the subsequent segment growth might also be an approach to suppress the radial overgrowth as the axial growth is promoted by increasing the As flux.

1.11.6 Varying the dopant source temperature. The extent of doping in the n-segment is varied by changing the dopant source temperature. Generally, a higher source temperature corresponds to the higher dopant incorporation, whereas the lower source temperature corresponds to the reduced dopant incorporation. The optimization of dopant incorporation in the n-segment is dictated by the various optical, electrical, and microstructural characterization techniques.

1.12 Dissertation outline

This dissertation is organized into four chapters. The scope of each chapter is discussed below:

Chapter 1 delineates the general overview of p-i-n NWs and their application in PD. Here, we discuss various NW PD figures of merits, PD parameters, different types, and noise sources in semiconductors. Finally, the motivation, objectives, and challenges of recent work are presented.

Chapter 2 elucidates the experimental details followed by the tools and techniques employed to characterize the NWs.

Chapter 3 discusses the influence of droplet consumption and the post-growth in-situ annealing approach on the optical and electrical properties of Te-doped GaAs NWs and proposes an optimized recipe for attaining high-quality NWs.

Chapter 4 summarizes the optimization of GaTe cell temperature to grow high-quality n-segment, which was demonstrated by fabricating high-performance Schottky diode ensemble NW PD. The optimized n-GaAsSb formed the n-segment portion of the axial p-i-n NWs geometry. This work was published in **Nanotechnology** in the year 2020.

Chapter 5 deals with the growth recipe optimization of the heterostructure axial p-i-n NWs and the realization of ensemble NW PD operating in the 1.1 μm region.

Chapter 6 Summarizes the research work and lists the findings. Finally, the dissertation is concluded with a discussion on the possibility of extending this work to realize axial p-i-n NW PD operating in the telecommunication wavelength regime.

CHAPTER 2

Experimental Details

This chapter presents a brief description of the molecular beam epitaxy (MBE) growth of axial GaAsSb NWs in the ultra-high vacuum (UHV) condition, followed by the various characterization techniques employed to assess NW properties.

2.1 Need of ultra-high vacuum (UHV) conditions for NW growth

Generally, NWs are grown using the MBE system in the UHV condition to attain high-quality NWs. The UHV condition is customary in the MBE growth of high-quality NWs because of the reasons listed below:

- ❖ UHV condition increases the contamination time, improving the NW material quality.

Contamination time (t_c) is the time taken by impurities atoms wandering in the growth chamber (GC) to form a monolayer. Contamination time is related to the growth chamber pressure as [60]:

$$\text{Contamination time}(t_c) = \frac{1.86 * 10^{-6}}{\text{Pressure (torr)}} \quad (12)$$

From the above equation, for the GC vacuum of 1 atm, t_c was 3.94×10^{-9} sec, whereas, for 10^{-10} torr, t_c was 7.3 hours. So, the NW growth under UHV conditions improves the material quality.

- ❖ The higher vacuum also enables the ballistic transport of the source flux to the substrate achieving the optimized growth rate.
- ❖ The memory effect will be minimized in UHV conditions, facilitating the realization of heterostructured NWs with an abrupt interface.

2.2 Substrate preparation

The p-Si <111> was chemically treated with piranha solution followed by the hydrofluoric (HF) acid etching before placing inside the MBE. Piranha solution combines sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) in the ratio of 2:1, used to remove the possible organic, metallic, and ionic impurities. First, piranha cleaned substrate was treated with HF solution to etch off the native oxide present on Si as it might be piranha contaminated and alter the NW growth conditions. Next, HF treated Si substrate was rinsed with deionized (DI) water and was dried with nitrogen. This dried substrate was left idle in the cleanroom environment to promote pure native silicon oxide (SiO_x) growth. The prime role of SiO_x is to stop the coalescence of adjacent Ga droplets enabling the NW growth. After achieving appropriate native oxide thickness, the chemically treated substrate was loaded to the intro chamber and was baked. Intro chamber baking of the substrate at 200 °C is instrumental in removing the additional impurities present on the substrate.

2.3 NW growth

GaAs / GaAsSb NWs were grown on chemically treated p-Si <111> substrate using EPI 930 solid-source MBE employing a widely accepted self-catalyzed VLS growth mechanism. The chemically treated substrate baked in the intro chamber was transferred to the growth chamber through a buffer chamber. Before the NW growth, the Si substrate was annealed at the growth temperature of 620 °C for 10 mins to desorb the impurities, accompanied by the creation of pit holes acting as the nucleation sites for the NW growth. NW growth was initiated by 13 secs of Ga predisposition for catalyst droplet formation followed by the catalyst droplet supersaturation. Initially, a short GaAs stem was grown before growing the GaAsSb NWs segment, as the GaAsSb material is weak and could not sustain the desired length independently. Similarly, a widely

accepted two-step approach is utilized in the GaAs / GaAsSb segment growth to enhance the Sb incorporation at lower BEP, as NW density decreases with higher Sb flux. The NW diameter was dictated by the Ga pre-deposition time, and the overall growth duration determined the NW length. After the desired NW length growth, the core VLS growth was terminated by catalyst droplet consumption under the As rich condition using the same As flux as the growth flux, accompanied by dialing down the substrate temperature to 465 °C. The NW was in-situ annealed after the dual passivation shell growth. GaAs passivation shell referred to as the skin is grown on the top of AlGaAs to prevent the possible oxidation of Al.

2.4 Measurement of substrate temperature using radiation pyrometer

In the MBE growth of NWs, it is customary to keep track of the substrate temperature. However, the slight change in the growth temperature can alter the vertical yield of the NWs due to the alteration in the growth condition. Therefore, the IR radiation pyrometer measured the substrate temperature during GaAs/GaAsSb NWs growth. We employ the two-step approach, i.e., two different temperatures for the stem and the core growth. In addition, the passivation shell is grown, and the NW core is in-situ annealed at an even lower temperature than the core growth temperature. The accuracy of all these temperatures is essential for achieving superior quality NWs with a higher yield. Furthermore, all the required temperatures must be noted before the growth i.e., the material deposition. The substrate emissivity changes with material deposition resulting in a false temperature reading, affecting the growth condition and eventually the NW quality and yield.

2.5 Influence of substrate rotation on the NW density

In the self-catalyzed VLS growth of the NWs, substrate rotation, essential for the flux uniformity, directly influenced the density of NWs. Therefore, we meticulously investigated the effect of the timing of the substrate rotation on the NW density. We tried three different approaches: no substrate rotation, rotation before the seed droplet formation, and rotation after the seed droplet formation. The vertical NW yield was higher in the sample with substrate rotation after the seed droplet formation, attributed to the unstable catalyst droplet in the NW sample with substrate rotation before the Ga droplet predisposition. Whereas there was no isotropic impingement of the flux without substrate rotation, resulting in the compromised NW density. Initiation of the substrate rotation before the Ga droplet formation resulted in the unstable seed droplet enabling them with the neighboring droplets causing the thin film growth. Thus, from our investigation, the substrate rotation after Ga droplet formation was a practical approach for attaining higher density NW growth.

2.6 The need for NW passivation

The potential applications of the NWs in the next generation nanostructured devices are compromised by the origin of deleterious surface states, entailing the need for NWs passivation. A higher surface-to-volume (S/V) ratio in the NWs increases the surface sensitivity degrading the NW properties as the surface states promote the non-radiative recombination path and act as a source of potential fluctuations. The existence of surface states causes the Fermi level pinning and the introduction of midgap states. Increased density of surface states depletes the charge carriers in the NW core [61]. The depletion region might extend throughout the NW length and diameter, making the NW highly resistive or semi-insulating. Therefore, the passivation of surface states is customary to attain higher quality NWs. The influence of surface states can be mitigated by

depositing a higher bandgap material on the NW surface, preventing the carrier annihilation due to the spatial separation of the NW core electronic states from that of the surface. Moreover, the choice of higher bandgap material stems from the call for minimal light absorption in the passivation shell. The vapor-solid (VS) growth is favored at lower temperatures. Thus, the passivation shell is grown at the substrate temperature of 465 °C for 5 mins. The inner shell of AlGaAs was grown for 3 mins, and the outer shell of GaAs was grown for 2 min.

2.7 Molecular beam epitaxy (MBE) system

The MBE system was introduced in the late 1970s in Bell laboratories by J.R. Arthur and J.J. LePore and is established as a proper deposition capable of producing abrupt interface and controlled doping profile because of its lower growth temperature and suppressed growth rate. However, its limitations lie in a lower yield stemming from a lower growth rate and the wafer capability. MBE is a cold-walled technique; the liquid nitrogen cryo panels surround the main chamber and the source flange. These cryo panels are cooled by the continuous flow of the liquid nitrogen (LN₂), preventing the gas species' re-evaporation from the chamber walls. In addition, LN₂ can thermally isolate the adjacent sources as well as the the additional pumping of the residual gas. In the MBE system, the effusion cells are the key components They provide stable, pure and uniform material fluxes at the higher growth temperature for a extended period of time. These source are placed on the source flange and are positioned such that the beam flux leaving the sources is focused on the substrate heater for flux uniformity. During the deposition, material flux is modulated using a mechanically operated pneumatic shutter. MBE system being a UHV thin-film deposition technique, several pumps work in conjunction to pump out the residual gas. These pumps involve scroll pumps, often referred to as roughing pumps, turbo molecular pumps (TMP), cryogenic pumps, and ion pumps. The cryogenic pumps are generally used to pump

particular species of gas. The pumping systems are responsible to reduce the residual impurities of the growth chamber to a minimum. The MBE system is equipped with a residual gas analyzer (RGA) to assess the partial pressure of residual gas in the GC.

The NW samples studied here were grown by a Veeco EPI 930 in the cleanroom environment, as depicted in figure 2.1. The MBE system accommodates nine sources of “tilted” orientation GC source flange. The GC’s center axis is oriented $\sim 20^\circ$ off the horizontal axis, and the substrate is positioned coaxially along with the chamber’s tilt. The sources producing the molecular beams by thermal evaporation were placed radially around the source flange. This orientation directs the beam flux towards the substrate at an angle of $\sim 33^\circ$ from the chamber’s axis. The focal point of all the sources mounted on the source flange is at the sample plane on a substrate heating stage, capable of continuous rotation up to 120 rpm for growth uniformity. The MBE system consists of three chambers: the intro chamber for loading and unloading the substrates, the buffer chamber, the intermediate chamber providing the clean UHV environment between the growth chamber and the intro chamber, and the growth chamber. The growth chamber, 18”/450 mm in diameter, with a total volume of approximately 140 liters where the thin film deposition occurs, consists of a vertically oriented ion pump and a horizontally oriented cryopump to pump the residual gas species and attain the UHV condition. The UHV gate valve separates all these chambers.



Figure 2.1. EPI 930 MBE system

2.8 Characterization techniques

The MBE-grown GaAsSb NWs were characterized using various characterization tools to assess the morphological, optical, electrical, and crystallographic properties. In addition, these characterization tools were used as feedback for optimizing the GaAsSb NW growth recipe.

2.8.1 Scanning electron microscopy (SEM). Morphological properties of all the NWs grown were studied using Carl Zeiss Auriga-BU FIB FESEM microscope. The NW samples were mounted on the aluminum stubs using double-sided carbon tape. This carbon tape provides a conductive path for the accumulated electrons to prevent charging, which is detrimental to the image quality. The typical electron gun voltage of 5 kV was used during imaging with the stage tilt angle of 45° and the working distance of 6 mm.

2.8.2 Photoluminescence (PL) spectroscopy. The optical properties of GaAsSb NWs were probed using the μ -PL setup. The PL system was equipped with a solid-state He-Ne laser with a 633 nm excitation wavelength and a power density of 35 mW. A fiber was coupled with the

confocal microscope and the sample stage to focus the laser beam to the NW sample and collect the emission from the NWs. A cryostat from Montana instruments was used to cool the sample stage enabling the 4K PL measurement. 50X objective lenses collected the photoemission from the sample and thus collected optical signal was dispersed by Horiba Jobin Yvon iHR 320 monochromator. Liquid nitrogen cooled InGaAs detector was used to detect the signal from the monochromator. The output of the InGaAs detector was fed to the input of the lock-in amplifier to detect the emission from the sample, and the output was displayed on the computer monitor using Jobin Yvon GUI.

2.8.3 Raman spectroscopy. Raman scattering analysis on the NWs was performed at room temperature (RT) on the Horiba YVON LabRam ARAMIS instrument at the SMIF facility of the Duke University, which has a spectral resolution of 0.6 cm^{-1} and 1800 grating/mm at 633 nm wavelength. A He-Ne laser with a wavelength of 633 nm was used as the excitation source. Before experimenting, the instrument was calibrated using a standard Si sample, and a multichannel air-cooled charge-coupled device detected the Raman signal. Raman spectroscopy is a widely adopted characterization tool as it does not require a complex sample preparation process, not to mention this being a non-destructive technique.

2.8.4 Transmission electron microscopy (TEM). The microstructural properties were assessed by high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) on JEOL 2010F field emission gun microscope with operating voltage set at 200 kV. EDS line scan on the NWs was performed using probe aberration-corrected FEI Titan G2 system with ChemiSTEM Technology operated at 200 kV. TEM characterization of the NW samples was carried out in the Analytical Instrumentation Facility (AIF) at North Carolina State University.

2.8.5 Fabrication of ensemble device. The NW sample was spin-coated with poly (methyl methacrylate) (PMMA) and hexamethyldisilane (HMDS). PMMA acts as a filler providing the mechanical support and insulation among the NWs. The spin-coated NW sample was soft baked and oxygen plasma etched to expose the NW tips for the spin coating of the AgNWs serving as the top contact, and the Ag paste is used as the back contact of the ensemble device.

2.8.6 Current-voltage (I-V) characterization. Temperature-dependent I-V characteristics of the ensembled NWs were investigated using a Keithley 4200 semiconductor parameter analyzer system accompanied by a Lake Shore TTPX probe station in an N₂ purged environment for two-probe measurements [62]. Also, conductive atomic force microscopy (CAFM) operating in contact mode was used for the single nanowire (SNW) room-temperature (RT) I-V characteristics. A Pt coated Si cantilever with a radius of 20 nm, and a spring constant of 18 Nm⁻¹ was used by placing the AFM probe on the NW tip and providing the back contact on the substrate. The voltage sweep was used during the measurement from -1V to +1V [20].

2.8.7 Low-frequency noise (LFN) spectroscopy. The low-frequency noise setup comprises low-noise preamplifiers (LNA) and the dynamic signal analyzer (DSA) with proper shielding to prevent the DSA from catching the external noise. The input terminal of LNA is used to bias the PD sample. The output of LNA was fed to the input of DSA, where the noise signal is Fourier transformed to the power spectral density using the cross-correlation technique.

CHAPTER 3

Effect of Post-Growth Annealing and The Droplet Consumption on the Te Doped GaAs

Nanowires Properties

3.1 Tellurium (Te) doping

Achievement of high-performance optoelectronic devices calls for a well-behaved dopant, namely low ionization energy and minimum diffusion coefficient [20]. As the NW growth progresses utilizing the widely accepted VLS growth mechanism, the choice of dopants becomes more crucial because the incorporated dopant species in the seed droplet can modulate the growth kinetics. The choice of Te as the dopant amongst the other commonly used n-type dopants, for example, Sn, Si, Se, and S, stems from its high solubility in the Ga droplet associated with the VLS mechanism and a significantly increased level of doping that can be achieved at a lower temperature than most of the dopants [63]. Other key advantages of Te-doping include high incorporation efficiency and low diffusion coefficient [64], [65]. Further, selecting a GaTe captive dopant source in molecular beam epitaxy (MBE) was dictated by its ability to control doping level, suppressed cell crosstalk, and associated memory issues [66].

There are numerous reports of n-doping using GaTe source in GaAs[20-25] NWs and a study on InAs [67] NWs by Gusken et al. The central ideal of these reports is to calculate the carrier concentration employing a variety of characterization techniques [68]. In addition, the effects of GaTe cell temperature (T_{GaTe}) on different properties have been carried out by Soulemenin et al. [24] and Gusken et al. [67], and the wide range of T_{GaTe} varying from 401 °C - 640 °C is reported in the literature.

After the successful growth of the NW core with the desired length, VLS growth is terminated by the consumption of seed droplets under the As-rich condition. The BEP of As used for the droplet consumption is found to directly influence the optical, electrical, and microstructural properties of the NW core. In addition, the in-situ post-growth UHV annealing can provide additional energy for atomic intermixing, influencing the NW properties. There are numerous reports on the Te doped GaAs NWs [68]-[73] in the literature, primarily focusing on the carrier concentration calculation but has not addressed the effects of droplet consumption and in-situ post-growth annealing.

This chapter investigates the influence of the As flux used in seed droplet consumption and in-situ post-growth annealing on the Te-doped GaAs' microstructural, optical, and electrical properties. Our findings indicate that higher As flux utilized for the seed droplet consumption and the NW post-growth annealing resulted in the degradation of the optical properties, as evidenced by suppressed 4K PL emission intensity with increased FWHM and reduced photocurrent observed in SNW. In addition, the RT ensemble NW I-V characteristics were transformed from the rectifying in as-grown to leaky in annealed NWs.

3.2 Growth conditions

Te doped GaAs NWs were grown on p-Si (111) substrate at 620 °C using the group III flux of 2.4×10^{-6} Torr and the group V flux of 4.8×10^{-7} Torr. To study the Te-doping of GaAs NWs and optimize the gallium-telluride cell temperature (T_{GaTe}), GaAs NWs were doped at the T_{GaTe} varying from 200 °C to 570 °C [41]. Finally, the NW growth was terminated by closing the Ga shutter, followed by the droplet consumption under As-rich conditions and the constant supply of Te. We adopted three different approaches for the droplet consumption, i.e., using double, same,

and half the As flux used during the NW core growth. Similarly, the NW core was annealed in-situ after the passivation shell growth at the substrate temperature of 465 °C for 5 mins.

The effect of droplet consumption on the optical, electrical, and microstructural properties is investigated using 4K PL spectroscopy, SNW AFM, and high-resolution transmission electron microscopy (HRTEM) images.

3.3 Result and discussion

The 4K PL emission of Te-doped GaAs NWs was compared with that of the intrinsic NWs, as depicted in figure 3.1, revealing that the PL emission is enhanced significantly for T_{GaTe} above 500 °C, suggesting that the dopant atoms are markedly incorporated at the T_{GaTe} above 500 °C.

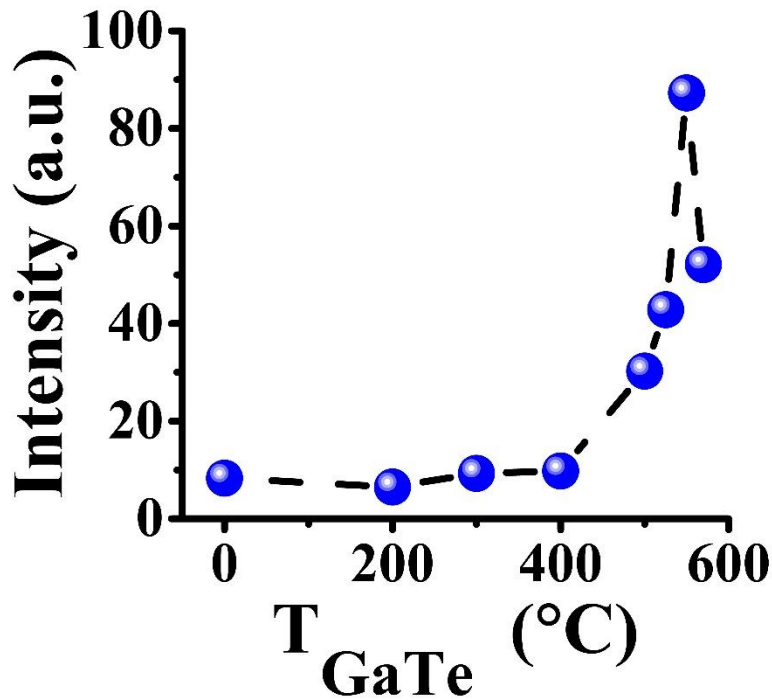


Figure 3.1. 4K PL emission variation in Te doped GaAs NWs at different T_{GaTe} .

The NW core doped at T_{GaTe} of 550 °C was chosen for this detailed study due to the highest PL intensity observed at this cell temperature and based on the optimization in our previous work [20].

3..3.1 Morphological properties. The average length and diameter of NWs were $\sim 1.75 \mu\text{m}$ and $\sim 153 \text{ nm}$, respectively, with no effects of annealing on axial and radial growths, NW density, and morphology as displayed in SEM images (Fig. 3.2(a) and 3.2(b)). Similarly, the droplet consumption approach had no effect, though the images are not shown here.

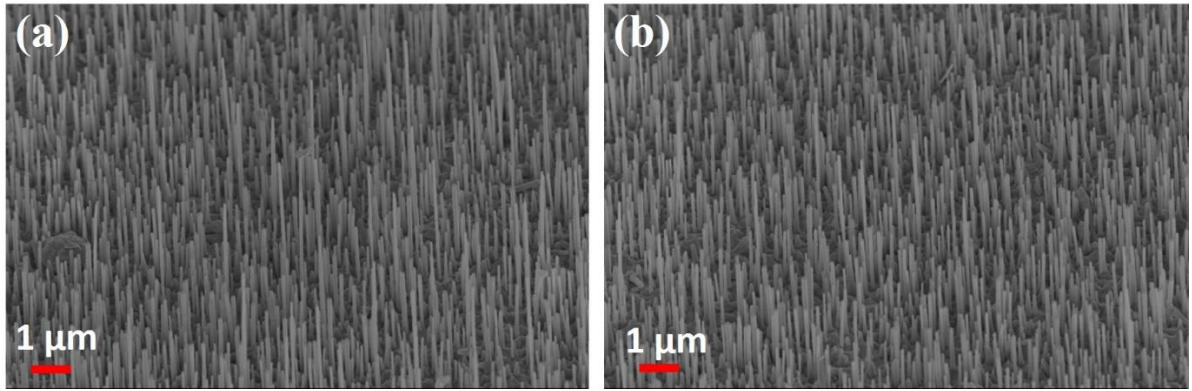


Figure 3.2. SEM images of (a) as-grown and (b) annealed n-GaAs nanowires

2.8.8 Effect of droplet consumption. The seed droplet consumption is a requisite for the termination of the VLS growth mechanism before the passivation shell growth around the NW core to suppress the axial growth. NW seed droplet is consumed after desired core length is achieved, and the growth of $\sim 20 \text{ nm}$ is achieved during the droplet consumption in this study. The NW tip is a critical segment of the NW core, as the optical absorption and the electrical conduction in the ensemble NW configuration are initiated there. Generally, the seed droplet is consumed under the As-rich condition by shutting the supply of Ga while keeping the supply of all the growth species constant, as shown in figure 3.3(a)-3.3(c). The droplet in these NW samples was consumed using the half, same, and double the As flux used during the growth. The first approach was ineffective in consuming the droplet, as the As flux was not enough in consuming the seed droplet

with the droplet consumption for 8 mins. In contrast, the droplet was consumed effectively employing the remaining two approaches, and hence only the effects of these two were studied.

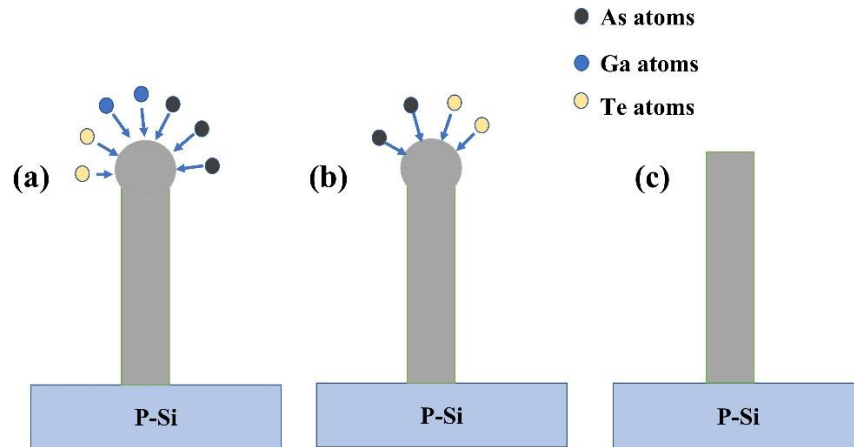


Figure 3.3. Schematic of (a) regular NW core growth, (b) NW growth during the droplet consumption, and (c) NW core after the droplet consumption

The 4K PL spectroscopy depicted in figure 3.4a revealed that the optical emission from the NWs using the same As flux resulted in ~ 3 folds enhancement in the PL intensity with FWHM reduction by 50 meV compared to its higher As flux counterpart.

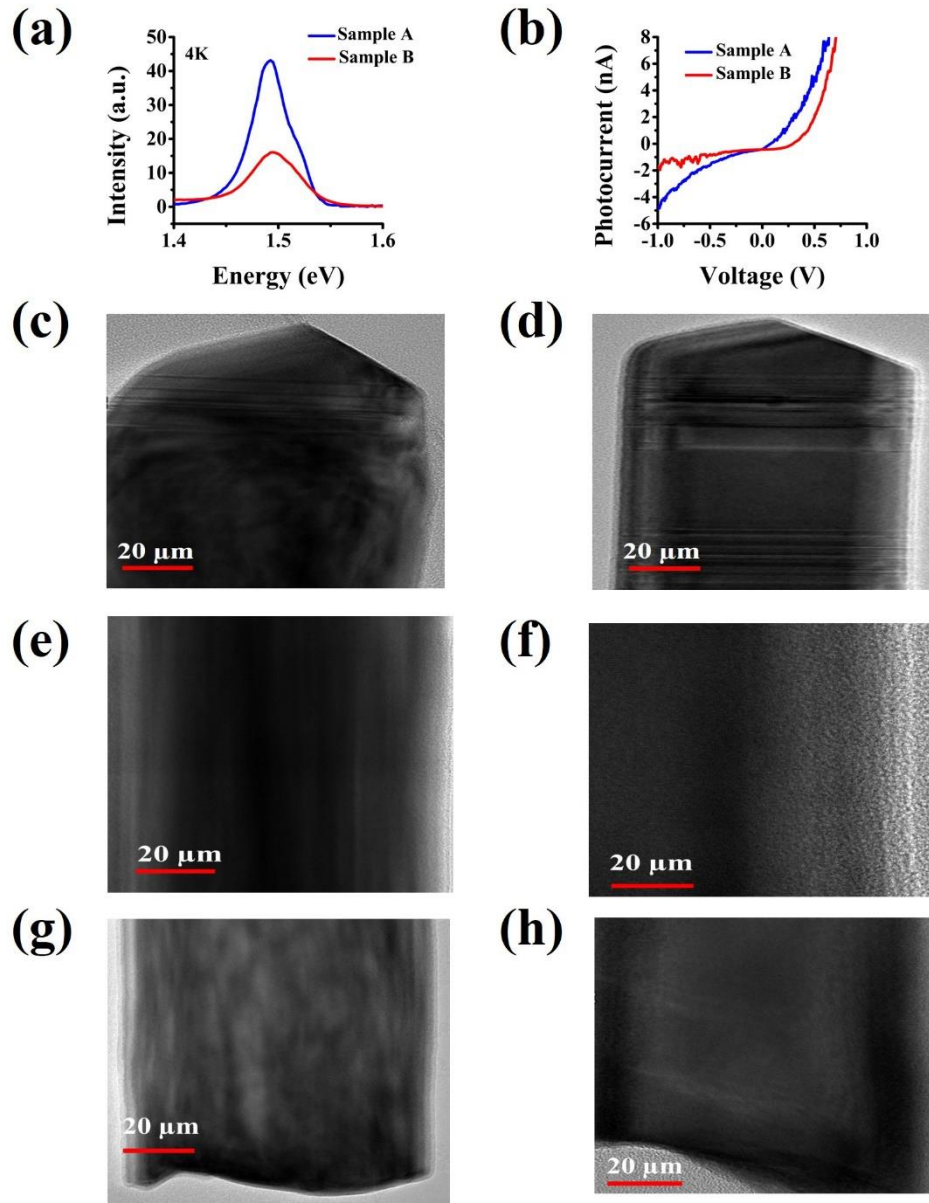


Figure 3.4. (a) Superimposed 4K PL spectra, (b) superimposed SNW I-V characteristics under illumination, (c, e, g) and (d, f, h) HRTEM images of NW top, middle, and bottom segments of Te doped GaAs NWs with two different droplet consumption approaches.

Similarly, the SNW photocurrent exhibited ~ 2 folds enhancement measured at 1V reverse bias in the NWs using the same As compared to those using the higher As flux as shown in figure

3.4b. This 4K PL emission reduction, increased FWHM, and the suppressed photoemission might be attributed to the increased defect density. These defects act as a non-radiative recombination center suppressing the radiative recombination channels. In addition, the defects within the crystal lattice are capable of scattering photogenerated carriers, reducing photoconduction. This assertion of the increased defect density with increased As flux is supported by the HRTEM images in figures 3.4c and 3.4d, respectively, which revealed higher density of stacking faults. The NW bottom and middle segments were devoid of stacking faults, suggesting the defects were introduced during the droplet consumption (figures 3.4(e-h)). These stacking faults are identified by horizontal contrast stripes depicted in the figure, causing the potential fluctuations, thus increasing the PL FWHM and degrading the overall optical emission and photoconduction. Therefore, utilization of the same flux as that of the growth during the droplet consumption is an effective VLS NW growth termination approach with suppressed defect density. Hence all the investigation discussed below pertains to the samples that were terminated using the same As flux.

2.8.8 Effect of post-growth annealing. This section will discuss the impact of post-growth annealing on the optical and electrical properties of the Te-doped GaAs NWs. Annealing is a fundamental approach in NW growth, as it provides an additional amount of energy for the atomic intermixing to alter the NW properties. The comparison of PL emission of intrinsic and Te doped NWs is depicted in figure 3.5a. In figure 3.5a, the sample I (intrinsic) exhibited a single prominent peak at 1.5 eV. In contrast, sample D (n-GaAs) demonstrated a lower energy peak at ~ 1.35 eV in addition to the intrinsic peak. The presence of a lower energy peak ~ 0.15 eV below the inherent GaAs peak in sample D is assigned to the transition of photoexcited electrons from the conduction band to the acceptor level complex ($\text{Te}_{\text{As}}\text{V}_{\text{Ga}}^-$) formed in Te doped GaAs [74], [75] as depicted in the band diagram (figure 3.5b).

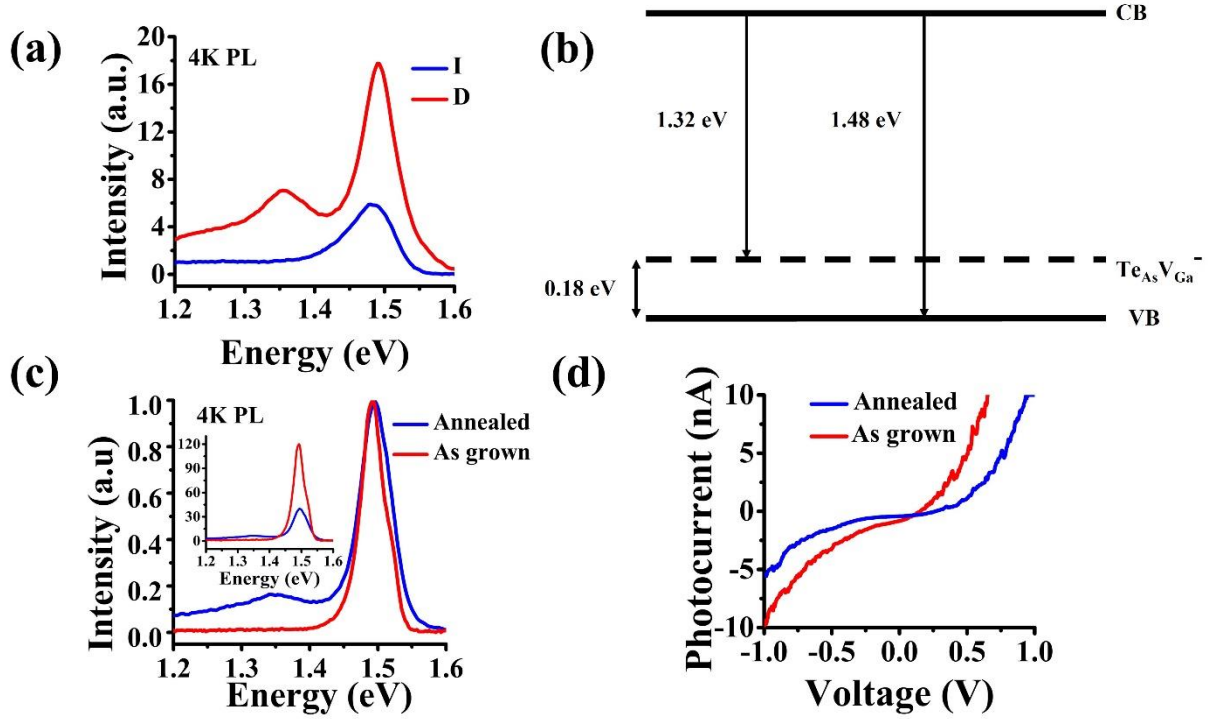


Figure 3.5. (a) 4K PL spectra of intrinsic and Te-doped GaAs at GaTe source temperature (550 °C), (b) band diagram of n-GaAs NWs, (c) comparison of regular (inset) and normalized 4K PL, and (d) SNW I-V spectra of annealed and as-grown nanowires

The origin of this complex is speculated to arise during the NW growth from Te occupying the As lattice site (Te_{As}) [76], and post-growth annealing promoting its interaction with the Ga vacancy (V_{Ga}) to form the acceptor level. The effect of post-growth annealing on Te doped GaAs NWs was assessed using the 4K PL and the SNW I-V characteristics. The superimposed 4K PL emission of annealed and as-grown nanowires in figure 3.5c exhibiting ~ 3-fold intensity decrease (inset figure 3.5c) with broader FWHM in annealed NWs indicates the quality degradation. In the GaAs material system in thin-film configuration, it has been reported that post-growth annealing results in the formation of additional V_{Ga} by the Frenkel reaction [76], which combines with the Te_{As} increasing the density of $\text{Te}_{\text{As}}\text{V}_{\text{Ga}}^-$ with pronounced lower energy PL peak in annealed NWs. The presence of a lower energy peak only in annealed NWs, as depicted in figure 3.5 c, further

supports this assertion. Similarly, the SNW I-V characteristics in figure 3.5d displayed a significant reduction in the photocurrent with annealing.

The effect of post-growth annealing on the electrical properties of the ensemble of Te doped GaAs NWs was assessed using the RT I-V characteristics as shown in figures 3.6a and 3.6b, respectively. The as-grown NWs demonstrated a rectifying dark I-V characteristic, whereas the annealed NWs displayed leaky behavior. The latter characteristics again point to the defect states acting as the generation-recombination centers under reverse biased conditions and contributing to the overall dark current [30]. Similarly, the photoresponse of n-GaAs NWs was significantly influenced by post-growth annealing, resulting in negative photoresponse as depicted in figure 3.6b [45].

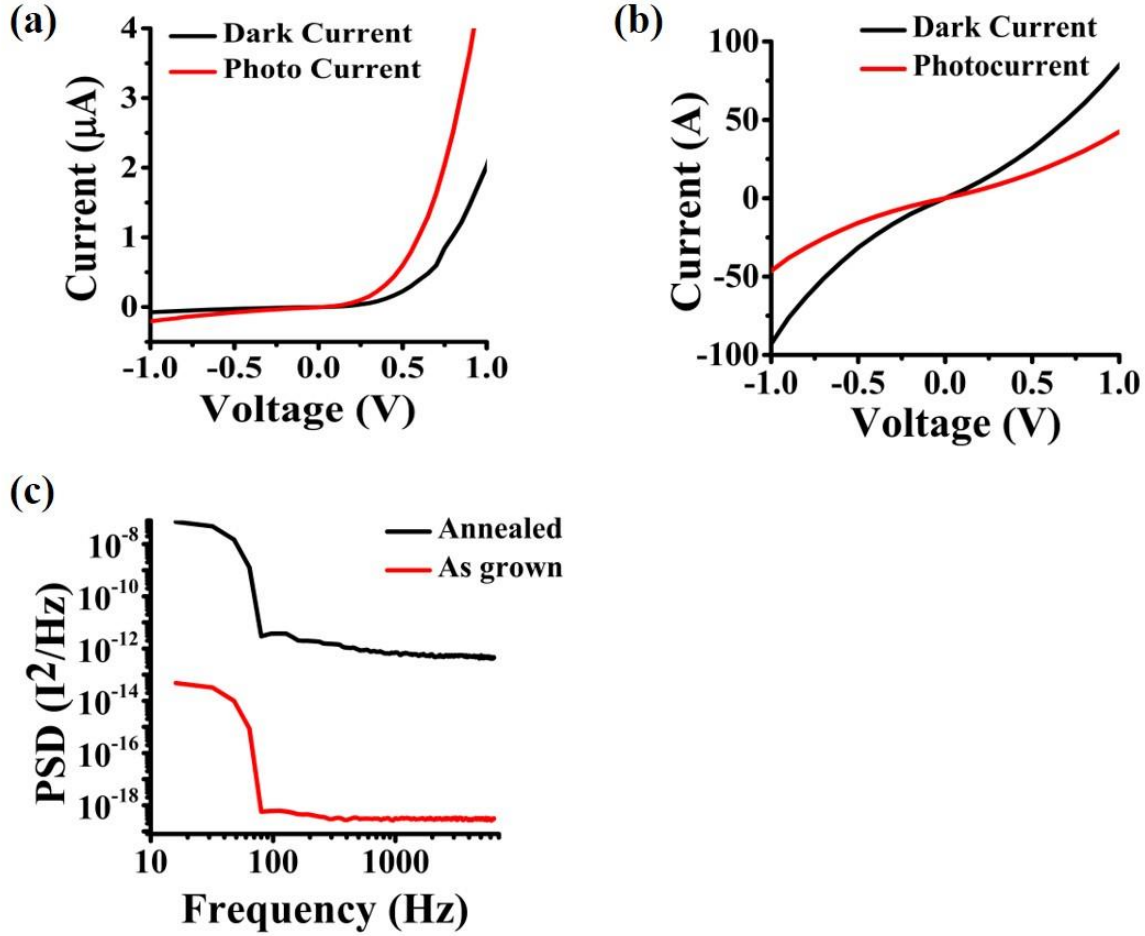


Figure 3.6. Ensemble NW IV characteristics of (a) as grown GaAs-Te NWs and (b) annealed GaAs-Te NWs, (c) low-frequency noise (LFN) spectroscopy.

The low-frequency noise (LFN) spectroscopy in figure 3.6c demonstrated a higher noise level in annealed NWs than as-grown NWs with the generation-recombination noise characteristics up to 100 Hz and white noise beyond. All these attest to the Te-induced defect states being trap states, very likely electron and slow trap states. In addition, the photogenerated holes had the propensity of recombination with the thermal electrons resulting in reduced overall carrier concentration [77] resulting in negative photoconductivity, suppressed band to band PL emission, and enhanced noise level caused by increased trap induced potential fluctuations and free carriers.

3.4 Activation energy

It is the energy required by the charge carriers for radiative recombination. The value of activation energy is governed by the energy level of the crystal defects in the bandgap. These crystal defects act as the photocarrier trap centers, and the energy to detrap the carrier to the bands is termed activation energy. The charge carriers with an energy greater than the activation energy will be detrapped from the traps and promote the conduction. This describes the quenching of the PL emission intensity and the reduced photoemission in the defective NWs. As a result, the density of electrons capable of the band-to-band transition decreases in the defective NWs, and the overall conduction will be reduced. Activation energy can be calculated using temperature-dependent I-V and PL spectroscopy. The effect of traps will be minimized at the lower temperature due to the freezeout. Whereas at the higher temperature, traps are activated, confining the photocarriers suppressing the conduction. In addition, lattice defects cause potential fluctuations scattering the charge carriers and quenching the overall conduction. For n-type semiconductors, the donor levels require thermal energy to push the electrons from the donor states to the conduction band. Likewise, the p-type materials need additional energy to accept an electron from the acceptor level to the valence band. This extra energy is referred to as activation energy. Alternately, the activation energy is defined as the energy required by the charge carriers (electrons/holes) to get detrapped from the defect states and move to the conduction/valence band.

3.5 Temperature-dependent I-V characteristics

Similarly, the temperature dependence of dark current was investigated to develop an insight into the activation energy. The temperature-dependent dark current variation of the as-grown and the annealed NWs at the forward bias of 0.2 V is depicted in figures 3.7a and 3.7b, respectively. The value of activation energy in annealed and as grown Te doped NWs was

calculated from the Arrhenius plot as shown in figure 3.6 using the following equation assuming the presence of only one defect state.

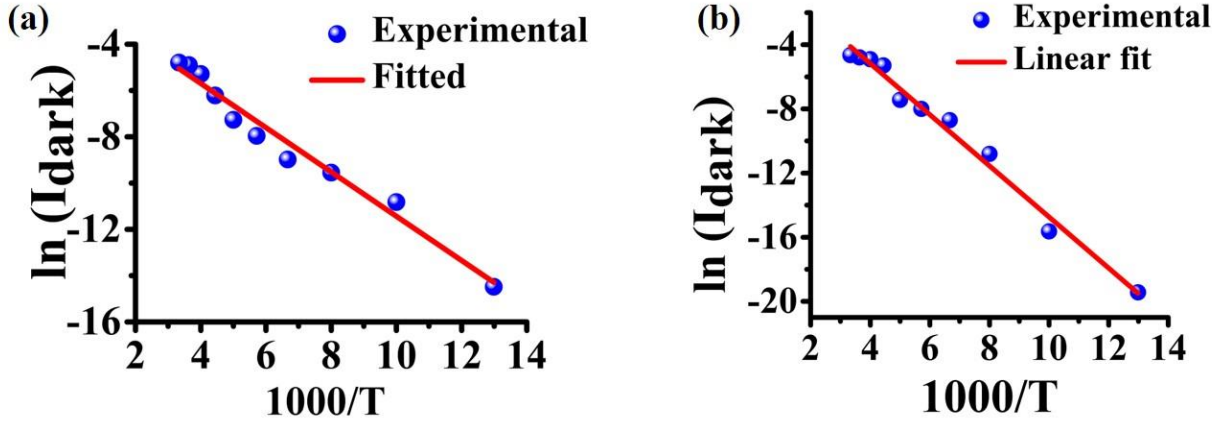


Figure 3.7. Temperature dependence of dark current at 0.2 V forward bias in (a) as-grown and (b) in-situ annealed Te doped GaAs NWs.

$$I \sim e^{-\frac{E_A}{k_B T}} \quad (13)$$

Where I is the experimentally measured dark current, E_A is the activation energy, k_B is the Boltzmann constant, and T is the temperature. Equation 13 can be simplified as:

$$\ln(I) \sim -\frac{E_A}{k_B} \frac{1}{T} \quad (14)$$

The experimental dark I-V was fitted against equation 14 using the linear approximation, and the slope of the best linear fit corresponds to the activation energy. The value of activation energy was computed to be ~ 80 meV and ~ 230 meV in as grown and annealed NWs, respectively. The lower value of activation energy suggests the existence of shallower energy levels in as-grown NWs, whereas the deeper traps in the annealed NWs. Hence, the shallower energy level might be

attributed to the donor states, whereas the deeper energy level corresponds to the annealing assisted acceptor states.

3.6 Conclusion

The As flux used for droplet consumption and the post-growth annealing were found to strongly influence the optical and electrical properties of Te-doped GaAs NWs. As flux exceeding the growth flux for termination resulted in the stacking faults adversely impacting the NW optoelectronic properties. Likewise, the in-situ annealing of doped NWs had a detrimental effect on the electronic properties. This has been assigned to the annealing induced non-radiative recombination channels evidenced by the presence of a broad lower energy PL peak with 3-fold decrease in the PL intensity negative photocurrent in the corresponding annealed SNW in comparison to the as-grown NWs. The trap level has been assigned to $\text{Te}_{\text{As}}\text{V}_{\text{Ga}}^-$ complex acceptor with an activation energy of 230 meV as determined from the temperature dependence I-V and the low energy level PL peak shift from the band-to-band transition. Thus, this study shows seed droplet consumption using the same As flux without any post-growth annealing is the optimized growth condition for attaining high-quality Te doped GaAs NWs.

CHAPTER 4

Optimization of n-GaAsSb NWs and Realization of Ensemble Schottky Barrier

Photodetector

4.1 Schottky barrier photodetector

In a photodetector (PD) configuration, the device architecture significantly influences the photodetection ability and the detection limit. Conventional photodetectors employing the ohmic contacts require higher external bias to effectively separate the photogenerated carriers, limiting their self-powered applications irrespective of a higher figure of merit [34]. Substituting either one or both of the ohmic contact devices by a Schottky metal contact results in a Schottky barrier PD. Work function difference between semiconductors and metal contact initiates the carrier diffusion, causing a band to bend at the interface, giving rise to the built-in potential and the depletion region. The built-in potential in the Schottky junction PDs can effectively separate the photogenerated carriers, improving the photoresponse [78], [79]. In contrast to ohmic contact, Schottky devices possess higher sensitivity and response speed [34] engendered by the built-in potential. The lower turn-on voltage of Schottky contact devices also makes them a strong candidate for low-power applications.

Generally, the Schottky junction-based NW PD has a broad scope ranging from biomedical applications to environmental monitoring devices [80]-[82]. Based on the illumination measurement reported in the literature, implementing the Schottky junction resulted in reduced photocurrent decay time compared to its ohmic contact counterparts [80]. The Schottky junction NW PD were realized in the GaAsSb [20], [39], [83], [84] material system in the literature, demonstrating the significantly higher figure of merit. The ensemble NW PD fabricated by capitalizing on GaAsSb NWs grown on the monolayer graphene exhibited demonstrated the device

responsivity of 110 A/W and the detectivity of 1.1×10^{14} Jones [84], [85]. Similarly, the dilute nitride GaAsSb ensemble NW PD demonstrated the optical responsivity of 3800 A/W and the detectivity of 3.2×10^{10} Jones [43], suggesting that the higher responsivity is achieved at the expense of device detectivity. Similarly, in our earlier work employing p-i ensemble NW PD, the responsivity of ~ 311 A/W and the detectivity of 1.9×10^{10} Jones was achieved [39]. However, very little work has been done in the literature to fabricate ensemble NW PDs. The ensemble NW PD fabricated in the AlGaAs/GaAs, and the nanopillars of InGaAs demonstrated the device responsivity ~ 0.7 A/W and 0.28 A/W without reporting the detectivity [86], [87].

This chapter discusses the growth of high-quality Te-doped GaAsSb NWs and the determination of the optimum Te doping in the GaAsSb system. The purpose of this work is to utilize the optimized n-GaAsSb growth recipe for the n-segment growth in the axial p-i-n GaAsSb NWs. The optimized Te doping in the GaAsSb NWs will be determined after carefully assessing the structural, optical, electrical properties of the doped NW samples. Finally, the performance of ensemble NW PD operating in the NIR region fabricated capitalizing the optimized n-GaAsSb NWs will be discussed.

4.2 Experimental details

The GaAsSb NWs growth conditions are extensively discussed in chapter 2. Based on the previous work, n-GaAsSb NWs were realized by doping the GaAsSb core at the T_{GaTe} of 550 °C [20] and 570 °C will be studied extensively in this work. The influence of doping on the NW properties will be identified by comparing the structural, optical, electrical, and microstructural properties of the doped NW samples with their intrinsic counterparts. In addition, the n-GaAsSb ensemble NW PD was fabricated by spin coating the polymethyl methacrylate (PMMA) followed

by the oxygen plasma etching for the metal contact deposition on the NW sample with optimized doping. The details on the fabrication of ensemble NW PD can be found elsewhere [62].

4.3 Results and discussion

4.3.1 Structural properties. The incorporation of Te within the NW crystal lattice significantly influenced the structural properties revealed by the high magnification SEM images in figure 4.1 (a-c) and table 4.1. In this chapter, intrinsic NWs, doped at T_{GaTe} of 550 °C and 570 °C, will be identified as samples R, 550, and 570. The SEM images in figure 4.1a-c reveal high-density vertical NWs suggesting that the NW density was independent of T_{GaTe} . With Te incorporation, the axial growth rate was abated, and the radial growth rate was augmented, lowering the NW aspect ratio as depicted in figure 4.1d. The variation of NW length and diameter with Te doping due to its surfactant nature is listed in table 4.1. In the NWs, incorporated Te atoms occupy the As sites [76] where they are strongly bonded to the NWs crystal lattice, impeding the adatom migration while decreasing the adatom surface diffusion length (SDL) [88]. This decreased SDL is responsible for the reduced axial growth rate and increased radial growth. However, tapering of any kind was not observed in the Te doped NWs suggested by the uniform NW diameter along the NW axis, as shown in figure 4.1e.

Table 0.1: Variation of the NW physical dimensions with T_{GaTe}

Sample	Length (μm)	Diameter (nm)
R	2.4 ± 0.12	136 ± 6
550	1.7 ± 0.08	152 ± 7
570	1.75 ± 0.1	157 ± 5

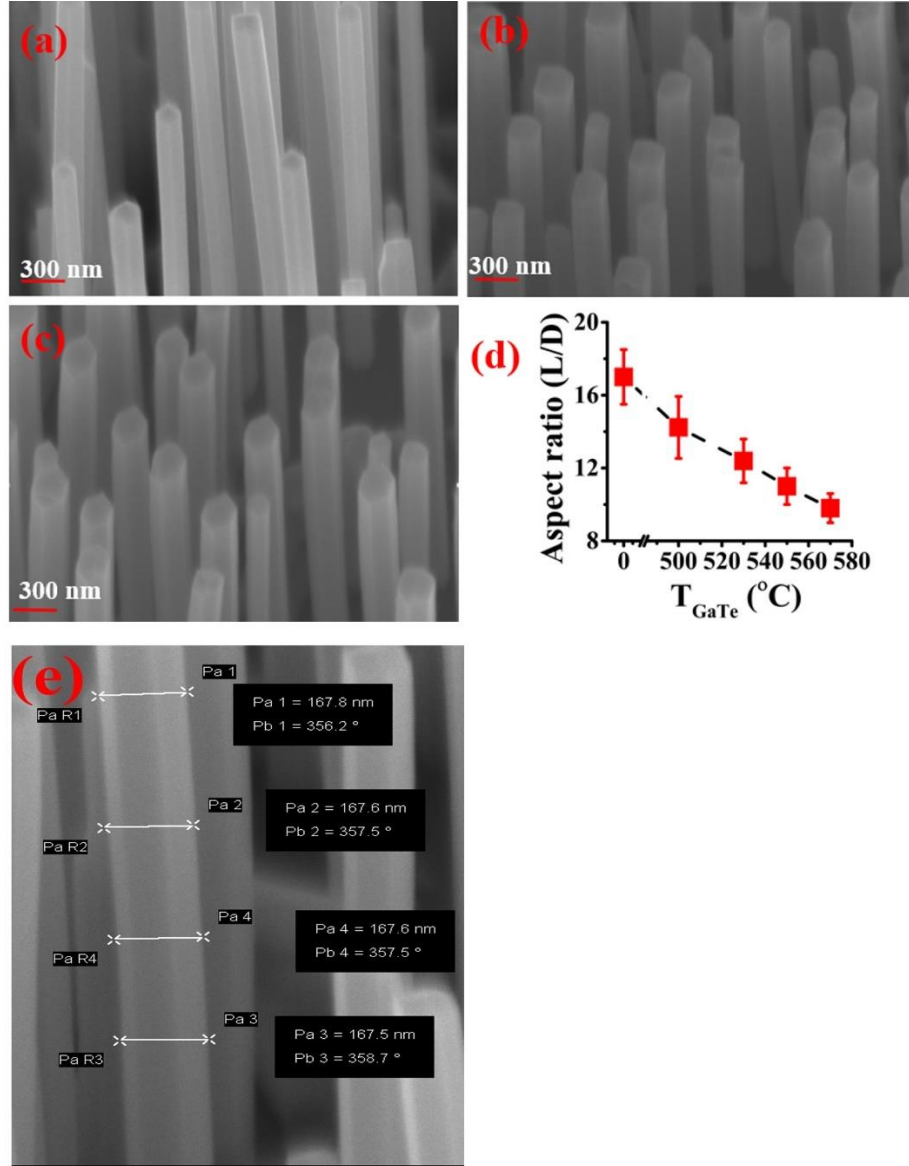


Figure 4.1. High magnification SEM images of GaAsSb NWs: (a) intrinsic, (b) 550, (c) 570 samples, (d) variation of the aspect ratio of the NWs with T_{GaTe} , and (e) diameter variation of the 550 sample along the NW axis.

4.3.2 Optical and vibrational properties. Next, the effect of Te-doping on the optical properties of the doped NWs in relation to intrinsic ones was assessed at 4K and RT via PL spectroscopy. The variation of the 4K PL peak energy and its intensity as a function of T_{GaTe} is depicted in figure 4.2a. The PL emission energy demonstrated a gradual redshift (a maximum of

90 meV) accompanied by significant intensity enhancement. Also, the RT PL spectral shape transformation from symmetric for intrinsic NWs to an asymmetric shape in the doped NWs accompanied by a high-energy PL tail (figure 4.2b). The early onset of PL emission in 550 sample compared to sample R suggests the presence of a low-energy shoulder, potentially due to defects, attributed to acceptor vacancies [74], which are filled up by doping and therefore vanishes for the doped samples. Furthermore, the long exponential decay tail is associated with radiative recombination occurring from Te-bound impurity localized states [89]. Among the R and doped NWs, sample 550 displayed the best PL characteristics with the highest PL emission intensity at 4K (figure 4.2c) and low FWHM at RT and 4K, suggesting that T_{GaTe} of 550 °C be the optimum doping temperature with superior optical properties.

The influence of Te incorporation on the NW crystal lattice was further assessed by using Raman spectroscopy. The RT Raman spectra for samples R, 550, and 570 exhibited distinct GaAs-like transverse optical (TO) and longitudinal optical (LO) vibrational modes, as demonstrated in figure 4.2d. The incorporation of heavier Te atoms within the NW crystal lattice resulted in the redshift of Raman vibrational modes of sample 550 relative to intrinsic NWs, speculated due to dampening of the lattice vibration frequency. Furthermore, an increased LO/TO signal ratio in the 550 sample very likely originated from the combined effect of increased density of ionized species leading to higher electric field coupling and increased NW diameter, which manifests in the enhanced LO mode [90].

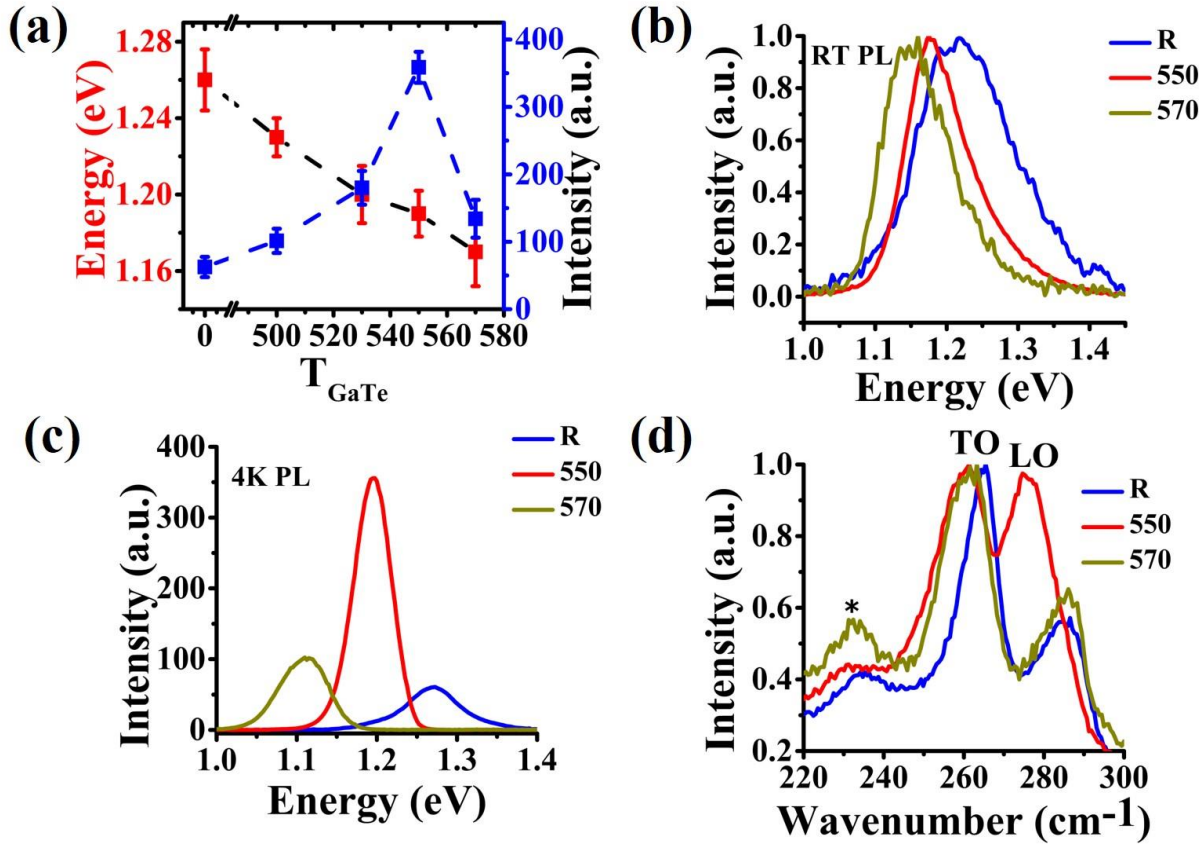


Figure 4.2. (a) Variation of 4K PL peak energy (red boxes) and its intensity (blue boxes) with T_{GaTe} (dotted black and blue lines are guides for the eye), superimposed (b) normalized RT PL, (c) 4 K PL, and (d) RT Raman spectra of samples R, 550 and 570. The asterisk at $\sim 232 \text{ cm}^{-1}$ represents the GaSb-like TO mode.

An additional peak positioned at $\sim 232 \text{ cm}^{-1}$ is assigned to the GaSb-like TO mode, commonly observed for higher Sb concentration in the GaAs matrix [91], [92]. The increased intensity of GaSb-like TO in the doped NWs hints at the increased Ga-Sb interaction as the Te occupies As lattice sites. All the above changes in the 550 sample relative to intrinsic ones, namely, the decrease in aspect ratio, enhanced PL emission accompanied by the asymmetric line shape with the high energy band tail and increased LO/TO mode ratio in the Raman spectra of the doped NWs support Te incorporation in the host lattice. However, the Raman spectra of the 570 sample

shift closer to the intrinsic sample with a broader linewidth and asymmetric line shape of LO peak. This reversal in the peak shifts and LO/TO signal ratio with increased GaTe cell temperature is speculated to be caused by Te-induced defects, which is also corroborated by increased planar defects on the tip of the NWs, as evidenced from the HRTEM images in the supporting information figure S3. It is to be noted that the repeated growths ensured that this reversal of the characteristics at higher T_{GaTe} of 570 °C is reproducible and is not a result of the artifact of source depletion or any growth sequence.

4.3.3 Single nanowire electrical properties. The I-V characteristics of the intrinsic and doped vertical SNW for varying T_{GaTe} were investigated using C-AFM. The schematic of SNW I-V measurements using AFM is depicted in figure 4.3a. Doped NWs were characterized by a lower turn-on voltage (figure 4.3b) due to the doping-induced reduction in the depletion region width. Amongst all the doped samples, 550 showed superior photoconductivity, as evidenced by the higher photocurrent to the dark current ratio ($I_{\text{P}}/I_{\text{D}}$) at a reverse bias of -1 V (figure 4.3c). The exponential dependence of the dark current under reverse bias in 550 (figure 4.3d) with a concomitant reduction in the turn-on voltage is indicative of the tunneling assisted conduction being the dominant transport mechanism. Sample 550 demonstrated a responsivity and a detectivity of 0.3 A/W and 4.8×10^8 Jones, respectively.

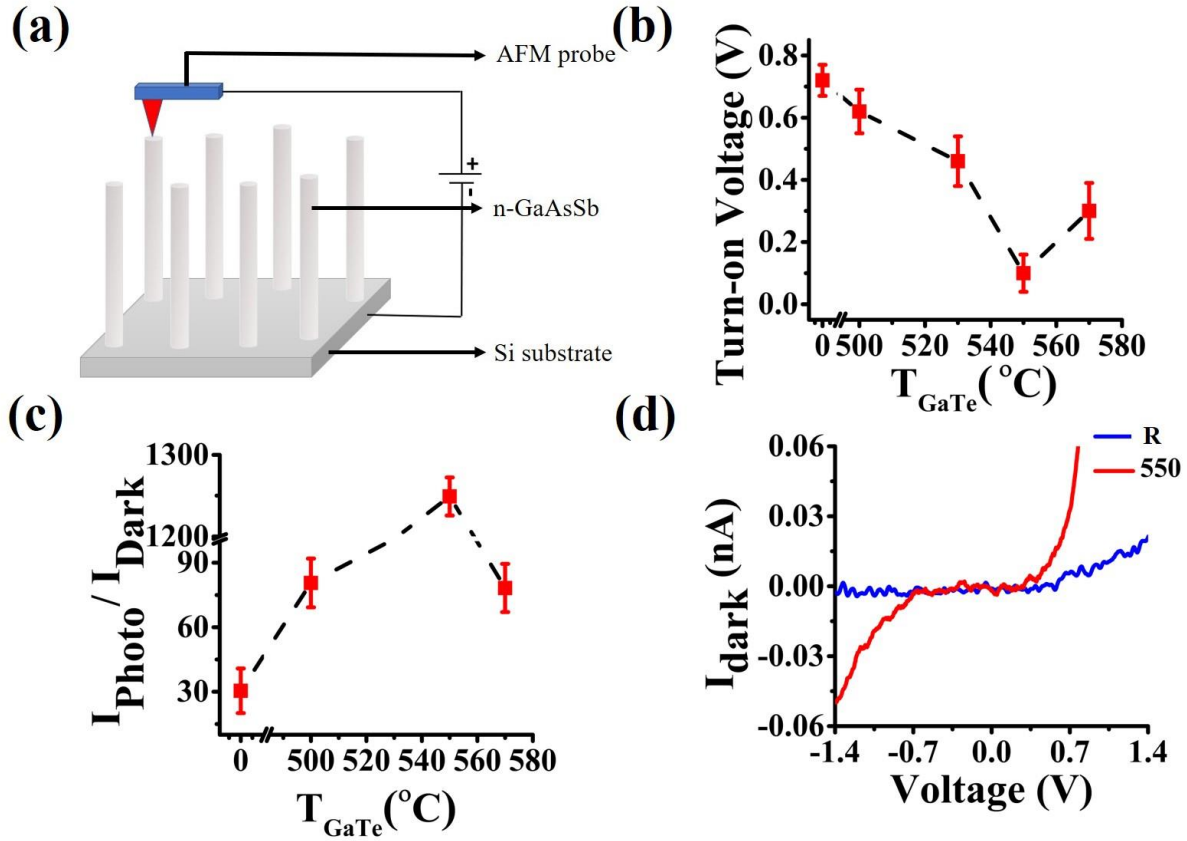


Figure 4.3. (a) Schematic of SNW C-AFM I-V measurement, variation of (b) photocurrent turn-on voltage, (c) photocurrent to the dark current ratio (I_P/I_D) with T_{GaTe} , and (d) superimposed dark current of the samples R and 550.

4K PL spectra carried on SNW of 550 were similar to that for corresponding ensemble NWs, indicating good compositional homogeneity amongst the NWs. As these optical and electrical observations indicate that sample 550 has the optimized doping level with good PL emission and photoconduction, the following structural analysis using TEM and PD fabrication on ensemble NWs was confined to sample 550 only.

4.3.4 Microstructural properties. The influence of Te doping in the crystallographic properties of the NW is studied utilizing the HRTEM, EDS, and the SAED pattern. The representative NW for microstructural properties investigation is depicted in figure 4.4a. The

HRTEM image (figure 4.4(b-d)) and SAED pattern (figure 4.4(e-g)) confirm the single-phase zinc-blende (ZB) crystal structure of n-GaAsSb NWs.

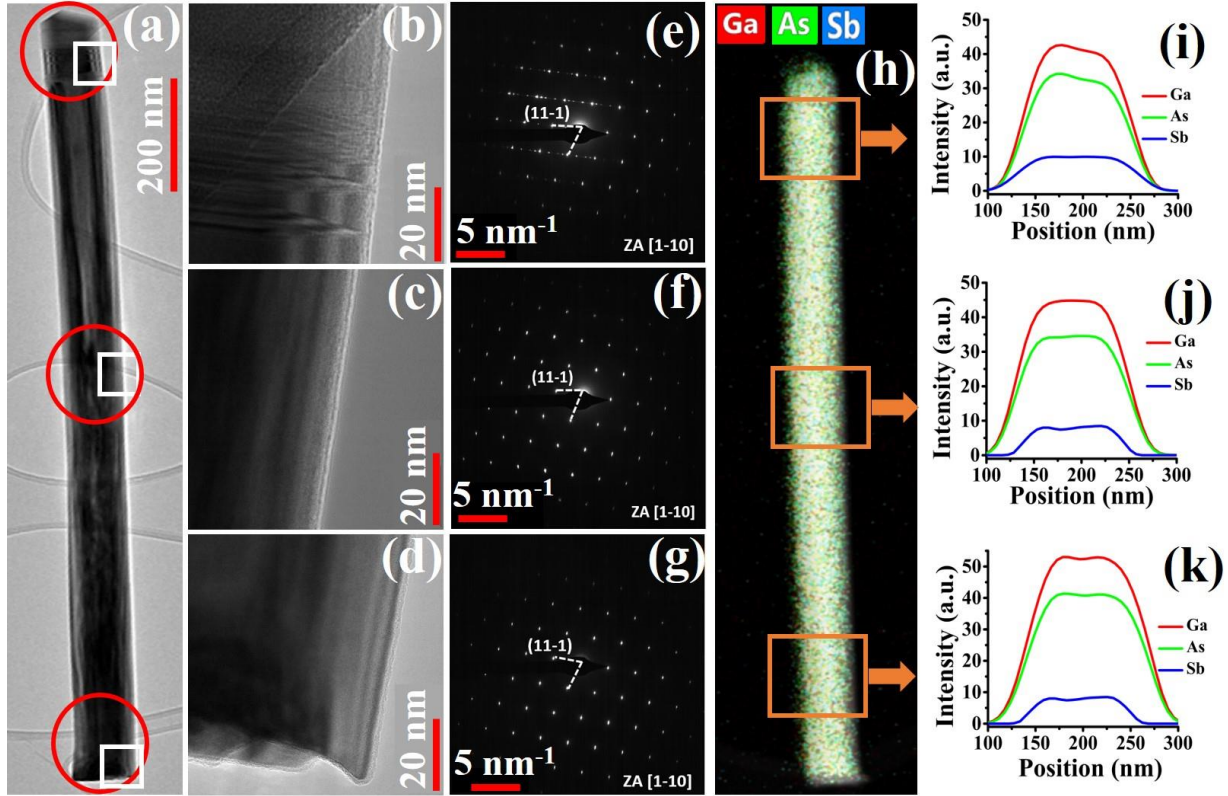


Figure 4.4. Optimized n-GaAsSb NW : (a) TEM image, (b-d) HR-TEM images of the selected areas marked with the white squares, (e-g) SAED patterns of the selected regions of NW in figure (a) marked with red circles viewed from the zone axis of $[1\ -1\ 0]$, (h) False color mapping of HAADF STEM image of the corresponding NW, and (i-k) EDS line scans taken at the top, middle, and bottom segments marked with orange rectangles in figure (h).

The bottom and middle segments of the NWs were free of any planar defects, while the top segment revealed stacking faults of ~ 20 nm, distinctly seen as horizontal contrast stripes (figure 4.4b). These structural defects near the NW tip are very likely due to the procedure adopted for the Ga droplet consumption, which was carried out under As ambient. The increased concentration

of As favors the wurtzite (WZ) crystal phase, and it is well established that stacking faults originate from transformation from ZB to WZ phase [93].

The EDS compositional line scans (figure 4.4(i-k)) performed at the top, middle, and bottom segments are depicted in the high angle annular dark-field (HAADF) STEM image in figure 4(h). The extended plateau of all the constitutional elements in the EDS line scan at the bottom and middle segments suggests radial compositional homogeneity. However, the top segment of the NW shows radial compositional inhomogeneity, which is again attributed to the termination of the Ga droplet. In addition, EDS line scan at the middle and bottom segments of the NW reveals an Sb deficiency at the surface resulting from the As-Sb exchange mechanism due to the extended exposure of NWs to the group V fluxes causing out-diffusion of Sb [1].

It is to be pointed out that the HRTEM of 570 samples revealed a similar planar defect-free structure in the bottom and middle segments (not shown) while showing a higher density of stacking faults at the top, indicating the doping induced disorder for higher T_{GaTe} . This explains the observed degradation in the PL intensity and the photocurrent in 570 samples and demonstrates that a high density of stacking faults at the NW tip can have a deleterious impact on the optoelectronic characteristics of the NWs.

4.4 Schottky barrier ensemble NW photodetector

The performance of ensemble PD fabricated using sample 550 was assessed using RT I-V characteristics under dark and illumination conditions. First, the dark I-V was examined for the prevalent current transport mechanism. An ideality factor of 8.8 and series resistance of $\sim 320 \text{ k}\Omega$ was extracted from the slope and intercept, respectively from the plot of differential change in the voltage (dV) to differential change in current (dI) versus reciprocal of current ($1/I$) under forward bias above the turn-on voltage. The large series resistance is attributed to the contact resistance as

no special process such as annealing after metal deposition was performed. The higher ideality factor corroborates our earlier discussion on tunneling being the dominant current conduction mechanism in a single NW. Alternatively, we can model the I-V data based on a non-ideal Schottky diode equation to estimate the carrier concentration by best fitting the experimental dark I-V curve using a generalized expression for an exponential fit in forward bias (figure 5a inset), as shown below.

$$I = A \exp(B \times V) \quad (15)$$

Here, A is the reverse saturation current. Then, is used to determine the Padovani-Stratton parameter (E_{00}), also known as the tunneling parameter employing the following equations [94]:

$$B = \frac{1}{E_{00} \coth\left(\frac{E_{00}}{KT}\right)} \quad (16)$$

$$E_{00} = \frac{qh}{4\pi} \sqrt{\frac{N_d}{m^* \epsilon}} \quad (17)$$

Here m^* represents the electron effective mass, q the electronic charge, h the Planck's constant, and ϵ the semiconductor permittivity. The best experimental data fit resulted in an E_{00} of ~ 0.3 eV from which a carrier concentration of $4 \times 10^{19} \text{ cm}^{-3}$ was extracted. The high carrier concentration estimated from the simulation fits very well with the value of $3.3 \times 10^{19} \text{ cm}^{-3}$ and $2.3 \times 10^{19} \text{ cm}^{-3}$ determined from other surface analytical techniques x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS), respectively [95]. Further, the value of carrier concentration is also in excellent agreement with those reported earlier by

Bennet et al. [96] on GaAs and GaSb thin films at this GaTe cell temperature. A good agreement between the simulated data and the value obtained from surface analytical techniques suggests that Te is not amphoteric as Si suggested by Dubrovskii et al. [59]. The incorporation predominantly occurs through the droplet via the vapor-solid-liquid mechanism. The absence of Te-related distinct vibrational modes in Raman spectra corroborates the carrier concentration to be less than 10^{20} cm^{-3} in our doped NWs and Te not being incorporated in Ga lattice sites [97], [98]. The value of $E_{00} \gg kT$ indicates current transport by field emission (FE) [99] being the dominant mechanism. Operating under RT conditions, excellent photosensitivity was revealed by a significant I_P/I_D of $\sim 1.3 \times 10^5$ at $\sim 1.07 \text{ } \mu\text{m}$ illumination corresponding to the bandgap of GaAsSb ($\sim 8\%$ Sb) at a reverse applied bias of -1 V (figure 4.5a). The PD spectral response was broad, covering the visible region with a longer wavelength cutoff at $\sim 1.2 \text{ } \mu\text{m}$ (figure 4.5b). The estimated responsivity is $\sim 620 \text{ A/W}$ with an external quantum efficiency (EQE) of $7 \times 10^4 \%$. At higher wavelengths, the roll-off of the photocurrent occurs slightly above the bandgap of GaAsSb when the energy of incoming photons becomes less than the bandgap and is not absorbed. The reduction in the photocurrent on the lower wavelength side of $\sim 0.5 \text{ } \mu\text{m}$ is dictated by a combination of thermalization of hot carriers, screening of the electric field by the photogenerated carriers, and enhanced surface absorption [100].

Excitation power dependence of the photocurrent at different bias voltages is depicted in figure 4.5c. The photocurrent shows a slight dip above specific excitation power, more pronounced with step-like behavior at lower bias. We attribute this response to the trap filling effects [101]. The lower voltages enable probing of shallow traps, while at higher biases, carriers are detrapped from shallow traps due to the large electric field.

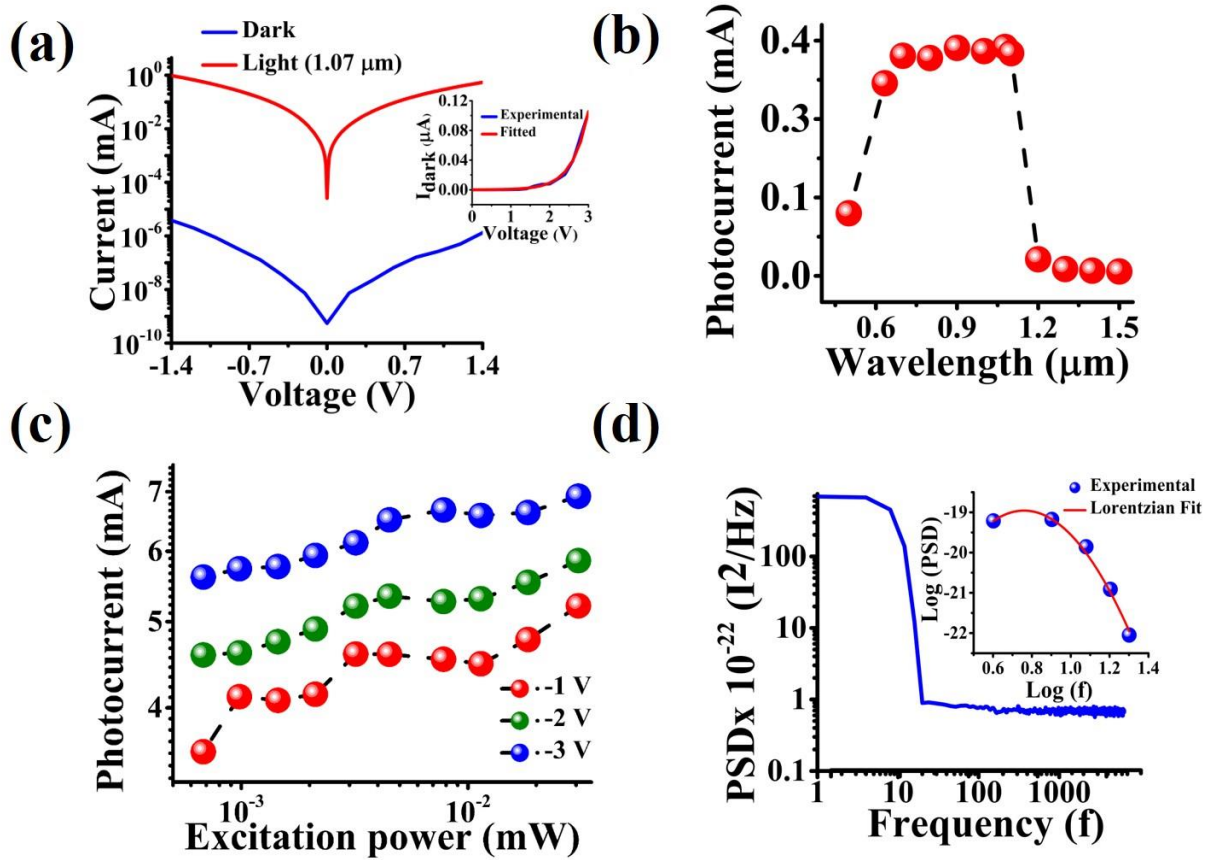


Figure 4.5. N-GaAsSb NW ensemble PD device: (a) dark and photocurrent (at $\sim 1.07 \mu\text{m}$) superimposed in semi-log scale and the inset shows the Schottky diode fitting to calculate tunneling parameter (E_{00}), (b) spectral response, (c) excitation power dependent photocurrent at -1 V, -2 V and -3 V bias for $0.63 \mu\text{m}$ laser excitation, (d) dark current noise spectra (S_I) at the reverse applied bias of 1 V, and the inset shows the Lorentzian fit of dark current noise after the roll-off.

Low-frequency noise (LFN) spectroscopy (figure 4.5d) exhibited a noise power spectral density (PSD) roll-off after 4 Hz. The best Lorentzian fit of the roll-off data up to 20 Hz (figure 5d inset) suggests generation-recombination noise as the principal contributor. Beyond 20 Hz, frequency-independent noise is observed. Based on the PL spectral shape and power dependence of photocurrent, we attribute the presence of generation-recombination noise to a shallow trap

arising from band tail states. Under reverse biased conditions, traps act as generation-recombination centers affecting the device performance and adding to overall device noise [102].

Photodetectors with responsivity variations from 580 – 620 A/W, noise equivalent power (NEP) in the range of $2.3 - 4.7 \times 10^{-13}$ W, and associated detectivity of $1.2 - 3.8 \times 10^{12}$ Jones were obtained in the spectral range of 0.63 μm to 1.1 μm . Thus, our device metrics in this report, namely responsivity, and detectivity, are significantly higher than those reported in ensemble NW configuration thus far. However, there is significant room for improvement in the device performance by using high transmittance transparent contacts and contact annealing and the arrayed NW configuration that would significantly enhance uniformity amongst the NWs.

4.5 Conclusion

Te-doping using a GaTe captive source has been successfully demonstrated to be a suitable dopant for n-type doping in GaAsSb NWs, as evidenced by enhanced PL emission and the increased photocurrent with the significant reduction in turn-on voltage. Replication of PL and I-V characteristics in an SNW, in ensemble NWs and S/TEM studies, attest to the compositional homogeneity in the NWs. Te-bound shallow tail states are responsible for an asymmetric PL line shape with a tail extending on the high energy side and correlate well with a field emission tunneling transport electrical conduction mechanism and low-frequency generation-recombination noise. The ensemble PD fabricated exploiting the optimized n-GaAsSb NW characteristics demonstrated a broad spectral response with a long cut off wavelength of 1.2 μm and improved responsivity of 580 – 620 A/W with detectivity in the range of $1.2 \times 10^{12} - 3.8 \times 10^{12}$ Jones, compared to the reports in the literature in this and other material systems in this NIR wavelength region. Prospects for further improvement in the device performance are very promising with

better transparent contact and annealing and fabricating the device using patterned nanowire configuration.

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CHAPTER 5

Optimization of GaAsSb Axial p-i-n NWs and Realization of Ensemble NW Photodetector

5.1 Overview

NW's capability of elastic strain relaxation ascribed to their smaller footprint enables the NW growth in an axial and radial configuration. As the radial junction suffers from the inevitable shadowing effect and the increased defect density due to the dominant VS growth mechanism, considerable interest has been gained by the axial configuration for nanostructured photodetector (PD) application. In a nanostructured optoelectronic device, junction plays a vital role in photocarrier separation ability. Based on the mechanism of electrical charge separation in the junction, the semiconductor junction can be divided into the Schottky junction and the p-n junction. The Schottky junction is discussed in detail in chapter 4, and this chapter will mainly focus on the p-n and p-i-n junction NWs. The p-n junction NWs have gained significant attention for the next generation PDs attributed to lower dark current, capable of determining the minimum detectable limit of the PD often referred to as a detectivity.

Furthermore, in the p-n junction device, the value of reverse saturation current is significantly lower than its Schottky junction counterparts, increasing the overall device SNR eventually enhancing the device sensitivity. This might be because the dark current in the p-n junction is dominated by the generation-recombination (g-r) current. In contrast, the thermionic, thermionic field, or field emission conduction mechanism is prevalent in the Schottky junction, adding up to the overall NW dark current.

An axial p-n junction is formed in an NW configuration when a p-type material is grown on top of n-type material. Charge carriers' concentration gradient between the p and n- segment induces the diffusion leaving behind the immobile ions creating the depletion region. The spatial

separation of these ions sets up an electric field called the built-in potential. Thus, there are two distinct regions within a p-n junction, i.e., a depletion region and a neutral region. In the p-n junction NWs, the depletion region is called the active region due to the E-field capable of effectively separating the photocarriers contributing to the photocurrent.

Similarly, the diffusion of the charge carriers cannot continue indefinitely and stops when the diffusion force on a charge carrier is balanced by the electric force acting in the opposite direction, achieving a thermal equilibrium condition. The schematic of the p-n junction and the several forces acting on a charge carrier is demonstrated in figure 5.1.

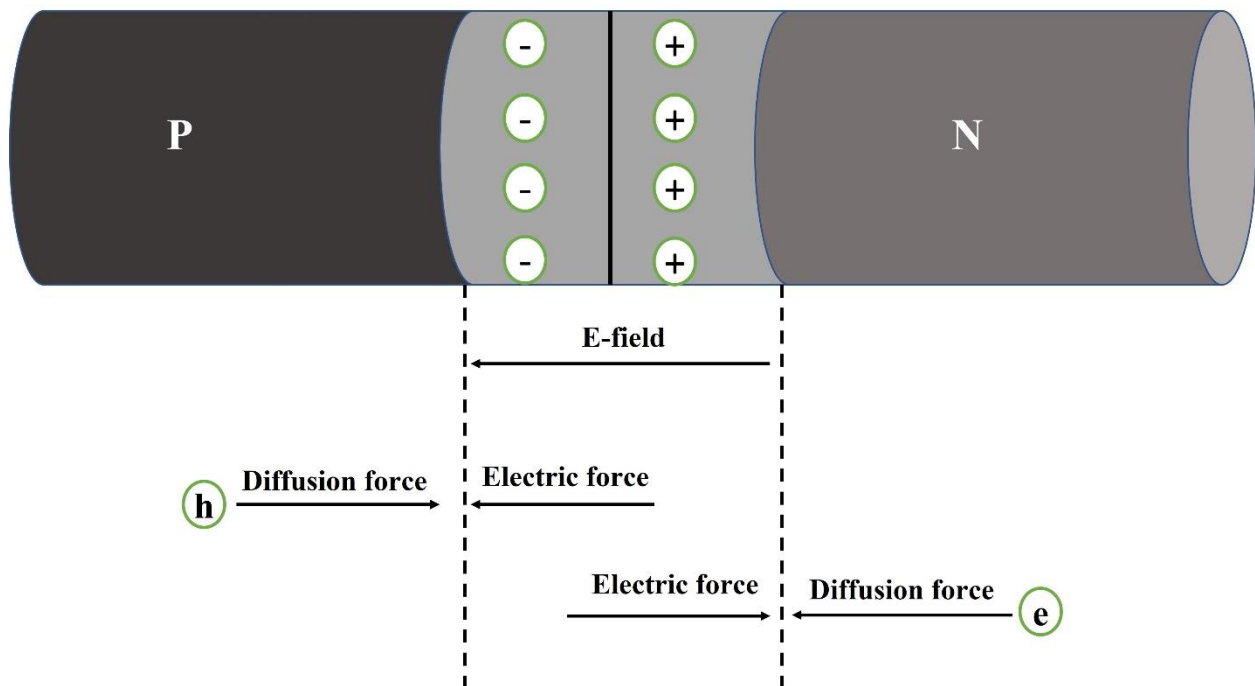


Figure 5.1. Schematic of p-n junction in the NW configuration indicating the built-in electric field and the diffusion force acting on the charge carriers

5.2 Built-in potential

Diffusion of charge carriers across the neutral region unveils the bulky immobile ions. Their spatial separation sets up an electric field directed from the positive ions to negative ions,

i.e., from n-region to p-region called the built-in potential. This potential can effectively separate the photogenerated carriers improving the device photoresponse. Similarly, the built-in potential can also be realized in the band bending at the heterointerface. When the two different semiconductor materials are brought side-by-side, band bending occurs at the interface to attain the constant fermi level throughout the sample. Band bending at the interface engenders a potential that electrons in the conduction band see for conduction, referred to as the built-in potential. When this potential seen by the electrons in the conduction band equals or exceeds the diffusion force, the thermal equilibrium is achieved. This E-field exerts a counterintuitive force on the diffusing carriers to bring the p-n junction NWs to thermal equilibrium. In the non-ideal condition, when the p-n junction NWs are biased, the conduction occurs when the value of the external bias exceeds the built-in potential. For the bias larger than the built-in potential, the current increases exponentially. The value of the built-in potential can be computed mathematically using the following relation [30]:

$$V_{bi} = V_t \ln\left(\frac{N_a N_d}{n_i^2}\right) \quad (18)$$

Where V_t is the thermal voltage, N_a is the acceptor concentration in the p-region, N_d is the donor concentration in the n-region and n_i is the intrinsic carrier concentration. From equation 18, the magnitude of built-in potential is dictated by the donor and the acceptor concentration in the neutral region, suggesting that the increased doping increases the magnitude of the built-in potential.

5.3 Depletion region

The onset of built-in potential within the p-n junction results in sweeping the charge carriers within the potential field, resulting in the depletion of charge carriers. The region within

the p-n junction where charge carriers are absent due to E-field is referred to as a depletion region. Basically, in a p-n junction NWs, there are two regions, viz. neutral region, and the depletion region, as demonstrated in figure 5.2a. The neutral regions are represented by the letter N, whereas the depletion region is represented as D. This region is called the depletion region, lacking charge carriers. In the p-n junction device, the depletion region is called the active region because only the photo carriers generated within the neutral region contribute to the photocarriers. The photogenerated charge carriers within the depletion region get separated effectively in E-field and contribute to the photocurrent. But the photocarriers generated in the neutral region recombine instantly. The mechanism of photocurrent generation is demonstrated in figure 5.2b. The photogenerated holes and electrons in the depletion region are analogous to the air bubble and the water droplet, respectively. Thus, the water bubble travels downhill, whereas the air bubble travels up the hill giving rise to the photocurrent, as demonstrated in figure 5.2b. The depletion region of the p-n junction device can be expressed mathematically as [30]:

$$W = \left\{ \frac{2 \epsilon_s V_{bi}}{e} \left[\frac{N_a + N_d}{N_a N_d} \right] \right\}^{1/2} \quad (19)$$

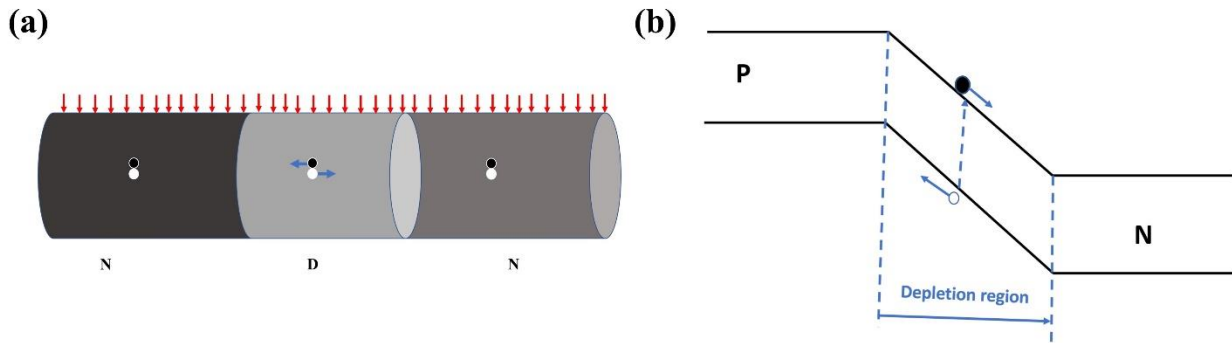


Figure 5.2. Schematic of (a) photocarrier dynamics in the neutral and the depletion region of the p-n junction, (b) photodetection mechanism in the p-n junction

Depletion region being the active region of the p-n junction devices, there is always a quest to increase the active region area. So, one of the practical approaches to increase the active region area is to sandwich a low-doped i-segment between the highly doped p and n-segment, resulting in the p-i-n NW architecture. In the p-i-n structure, the i-segment acts as a depletion region. In the NW configuration, the p-i-n junction can be grown in two different configurations, i.e., axial, and radial configuration, as demonstrated in figure 5.3. In the axial configuration, the p-i-n junction is in the longitudinal direction, whereas the junction lies in the lateral direction in a radial configuration. In this dissertation, we will discuss the axial configuration of p-i-n NWs in detail.

Furthermore, the careful investigation of the p-i-n junction can be modeled as the two one-sided junctions in series.

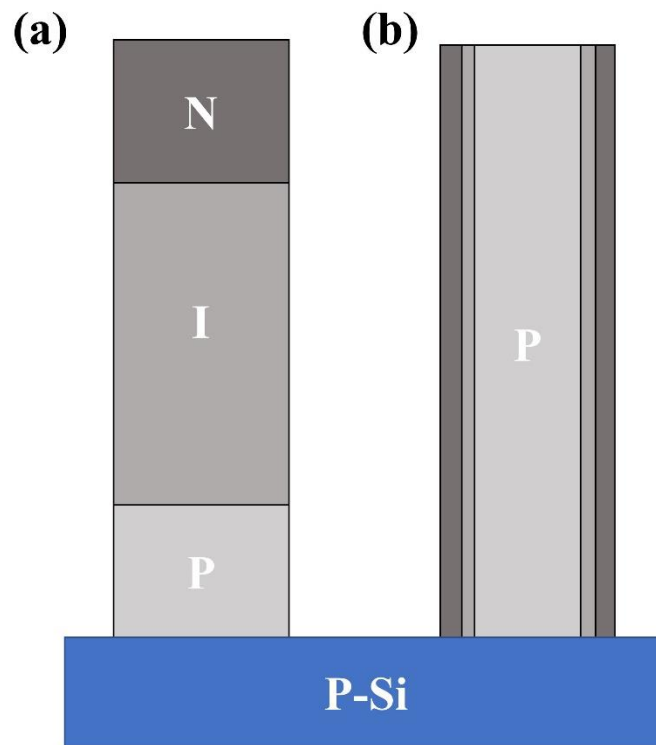


Figure 5.3. Schematic of p-i-n NWs in (a) axial, (b) radial configuration.

5.4 One-sided junction

One-sided junction is a special type of p-n junction when doping in one region is significantly higher than in another. There are two junctions in a p-i-n configuration, i.e., between p and i-segment and the junction between i and n-segment. In p-i-n NWs, doping of the p and n-segment is significantly higher than that of the i-segment. Thus, there are two one-sided junctions in series within the p-i-n NWs. As it is well established that the depletion region extends deeper into the low doped region, with optimized doping in p and n-segment, complete depletion of the i-segment can be achieved. The depletion width of a one-sided junction can be expressed mathematically as [30]:

$$W = \left(\frac{2\epsilon_s (V_{bi} + V_R)}{en_i} \right)^{1/2} \quad (20)$$

Where w is the depletion region width, V_R is the reverse-biased voltage, and V_{bi} is the built-in potential. Similarly, the one-sided junction's C-V measurement helps calculate the unintentional doping in the i-segment. The guiding mathematical expressions to calculate the unintentional doping in the i-segment is [30]:

$$\frac{1}{C^2} = \frac{2(V_{bi} + V)}{q\epsilon N_i} \quad (21)$$

Where C is the experimentally measured capacitance, V_{bi} is the built-in potential, V is the applied voltage, q is the electronic charge, ϵ is the permittivity of the semiconductor NWs and N_i is the unintentional doping in the intrinsic region of the axial p-i-n NWs. Thus, a one-sided junction approximation can be utilized to calculate the unintentional doping in the i-segment.

5.5 Axial p-i-n NWs

The p-i-n NWs can be grown in an axial and radial configuration. Axial p-i-n NWs are preferred over the radial configuration because the active region is perpendicular to the illumination such that the photoabsorption is enhanced. In addition, the active region area is significantly higher, and it can be tuned with ease. Similarly, in the axial configuration, the VLS growth mechanism is the dominant mechanism, whereas the VS growth mechanism dominates the growth mechanism in the radial configuration. It is well established that the VLS growth mechanism engenders lower defect density than the VS growth mechanism. Thus, the axial configuration has improved crystallographic properties compared to the radial counterparts and increased active region area [103].

Similarly, the axial configuration is tolerant to doping variation and shadowing effect. Inevitable shadowing effect in NW configuration results in the discontinuous junction formation as demonstrated in figure 5.4b. Discontinuous junction towards the NW base might compromise the device properties.

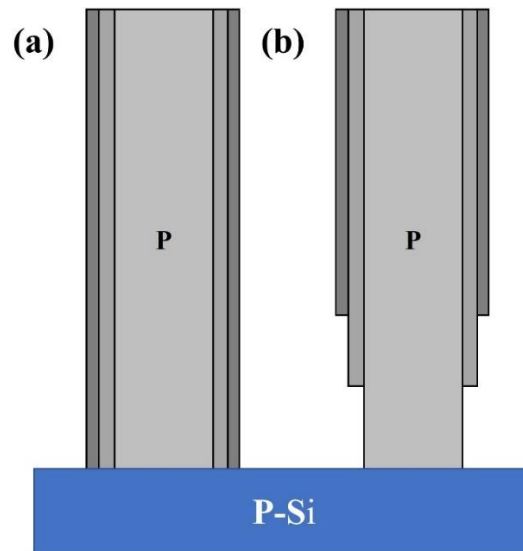


Figure 5.4. Schematic of (a) ideal core-shell p-i-n NWs, and (b) shadowing effect in the core-shell p-i-n ensemble NWs.

Although axial p-i-n NWs do not suffer from the shadowing effects, some of the tough challenges degrade the overall optoelectronic performance of the p-i-n NWs. Thus, in the following section, we will discuss the challenges of axial p-i-n NWs and the approaches taken to address those challenges.

5.6 Bandgap induced photo interaction

The bandgap of material is found to influence the photoresponse of the NWs significantly. If the incident photon's energy is equal to or higher than the material's bandgap, these photons are absorbed, resulting in the generation of e-h pairs figure 5.5a. However, if the incident photon's energy is less than the material bandgap, the material will be transparent to the incoming radiation (figure 5.5b). The variation of the material bandgap-induced photo interaction is depicted in the figure.

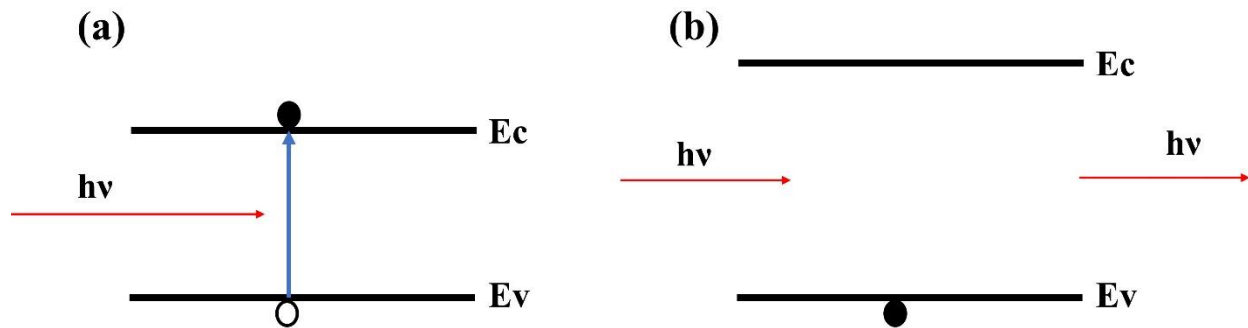


Figure 5.5. Schematic of photon interactions in (a) low-bandgap and (b) high bandgap material

So, this chapter will introduce a new approach of using the higher bandgap n-segment and the lower bandgap i-segment to increase the photoabsorption in the active region. The NW grown utilizing this approach will be referred to as the heterojunction, whereas the NWs growth with the same bandgap in p, i, and n-segment will be referred to as the homojunction. The performance of both the homojunction and heterojunction p-i-n NWs will be discussed extensively in this chapter.

5.7 Axial p-i-n NW growth recipe optimization

In this section, we will be discussing the various challenges in the growth of the axial GaAsSb p-i-n NWs and the approaches to achieve the optimized results.

5.7.1 Addressing the intrinsic p-type nature of GaAsSb. It is well established that the intrinsic GaAsSb is p-type in nature [1], detrimental to the realization of heterostructured axial p-i-n NWs. The p-type nature of the i-segment might introduce the potential fluctuations in the crystal lattice and requires higher doping in the neutral region for complete depletion. Increased potential fluctuations introduce the noise in the PD, whereas the existence of the undepleted region will increase the overall dark current and decrease the photoresponse. The intermittent supply of the donor Te atom during the i-segment growth is established as a practical compensation approach. The efficacy of compensation is assessed by the characterization of both the compensated and the uncompensated i-segment. The compensated i-segment demonstrated the optical emission enhancement by ~ 8 folds compared to the uncompensated sample suggesting the enhanced optical properties as shown in figure 5.6a. As shown in figure 5.6a, the FWHM of 4K PL spectra is broader in the uncompensated sample than the compensated. The broader PL spectra in the uncompensated sample might be due to the emission from the intrinsic defects convoluted with the band-to-band emission resulting in the wider PL FWHM. These intrinsic defects are annihilated with the Te compensation such that 4K PL spectra demonstrate the lower FWHM with the early onset of the band-to-band emission with enhanced emission intensity. The FWHM of a PL spectrum corresponds to the available energy states within the semiconductor bandgap. A larger FWHM suggests a broader distribution of the available states within the NWs bandgap attributed to the Sb vacancies related acceptor level complex causing the potential fluctuations and eventually increasing the FWHM. Gaussian fitting of the experimental 4K PL peak of both the

compensated and the uncompensated i-segment demonstrated the FWHM of 0.03957 eV and 0.068 eV, respectively. The FWHM of the uncompensated core is almost double the compensated core, as depicted in figure 1a.

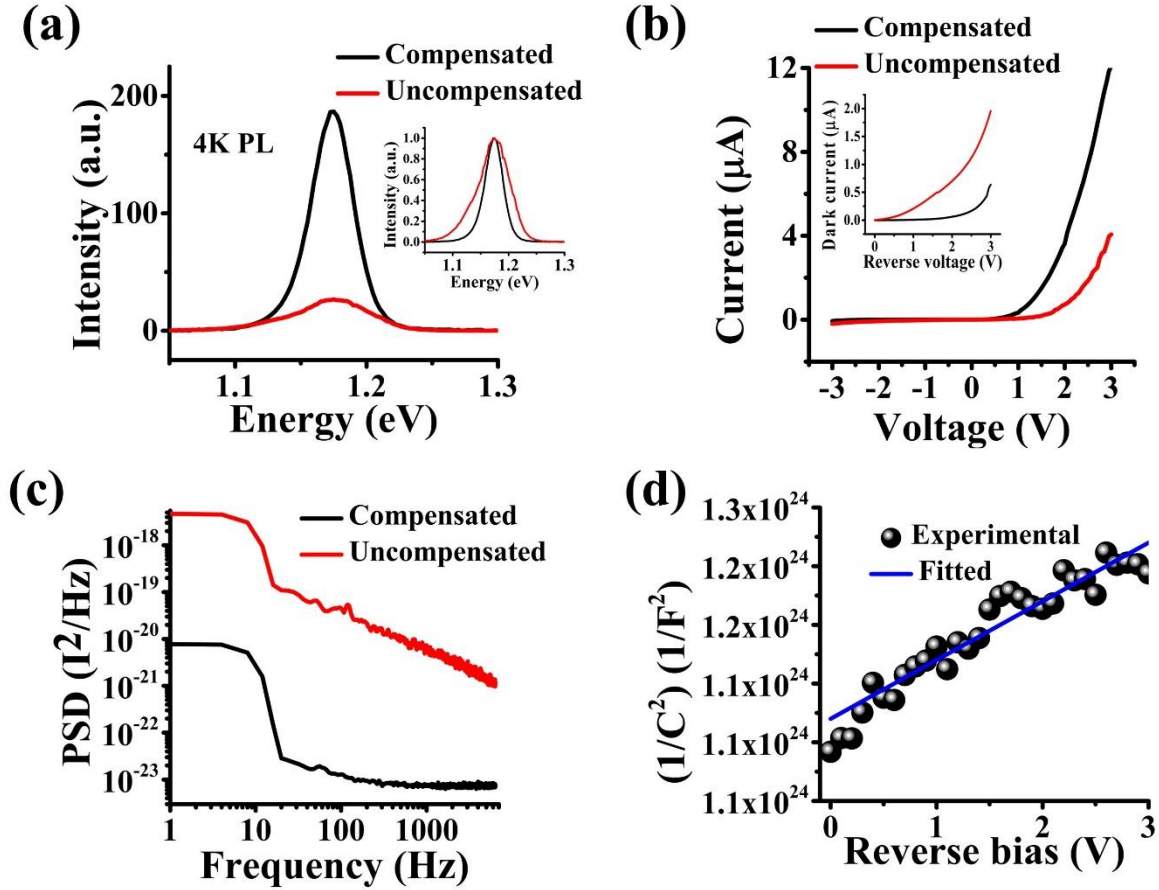


Figure 5.6. Superimposed (a) 4K PL spectroscopy, (b) dark current variation with the reverse bias voltage, (c) LFN noise spectroscopy at -1 V bias of the compensated and uncompensated i-segment, and (d) plot of $1/C^2$ vs. V in the forward bias to calculate the unintentional doping in the i-segment.

Similarly, the influence of compensation on the electrical characteristics is investigated using the RT I-V (under reverse biased condition) and LFN spectroscopy. The reverse bias dark I-V characteristics transformed from the voltage-dependent in the uncompensated to voltage-

independent in the compensated sample as depicted in figure 5.6b. The increased potential fluctuations due to increased acceptor states act as generation centers in the reversed biased condition [48]. This generation current adds to the ideal reverse saturation current, demonstrating a leaky behavior with the added dark current, undesirable in the optoelectronic device application. The compensation-assisted reduction in the dark current is further backed by the reduced noise level with compensation, depicted by the LFN spectroscopy study in figure 5.6c. Both the compensated and the uncompensated core demonstrates the G-R noise as the dominant noise source with the corner frequency of ~ 20 Hz, suggesting that the dominant noise source is independent of compensation. After the corner frequency, the noise level is transformed from frequency-independent in the compensated to strongly dependent on the uncompensated i-segment. The increased noise level with voltage-dependent spectra might be due to the potential fluctuations in the uncompensated sample due to the presence of acceptor states. In addition, the efficacy of Te compensation is evaluated by calculating the unintentional dopant concentration in the i-segment from the C-V characteristics (figure 5.6d). Using the one-sided junction approximation, experimental C-V characteristics of the uncompensated sample were fitted with equation 20, resulting in the i-segment of $\sim 6 \times 10^{15} \text{ cm}^{-3}$, whereas that was found to be $\sim 3.2 \times 10^{15} \text{ cm}^{-3}$ with compensation. Thus, the intermittent supply of Te during the i-segment growth was established as a practical approach to compensate for the intrinsic p-type nature of the i-segment. The batch-induced carrier concentration variation of i-segment is studied in 34 samples. The variation is depicted in figure 5.7a and 5.7b, respectively—the minimal variation in carrier concentration with the batch hints at the repeatability of the optimization process.

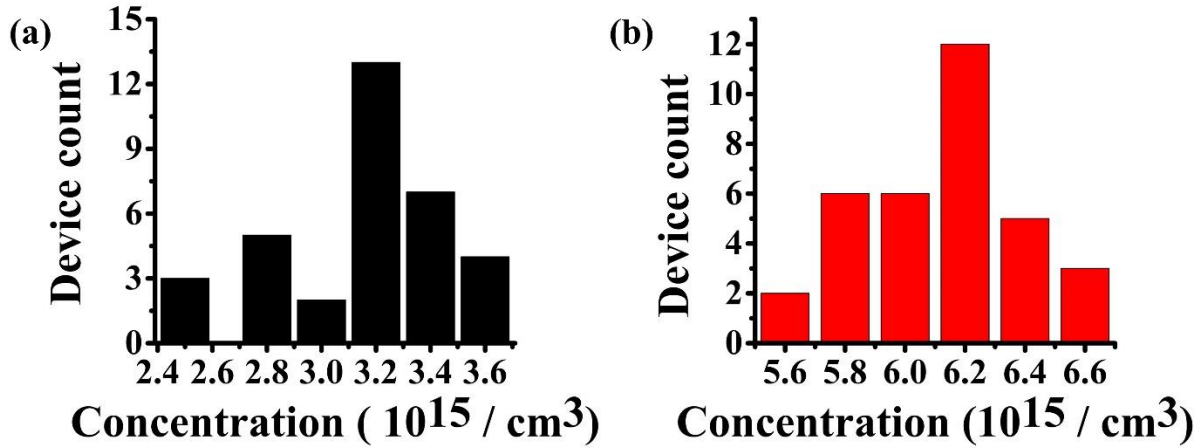


Figure 5.7. Variation of i-segment carrier concentration with sample batch in (a) compensated and (b) uncompensated p-i-n NWs.

5.7.2 Optimization of respective segment length. Sensitivity and device speed are the two critical parameters in the p-i-n NWs PDs. The segment doping determines the magnitude of the E-field, and the segment thickness influences the photoresponse. Another factor that influences the performance of axial p-i-n NWs is the individual segment thickness, as each segment affects the NW properties differently. The thickness of the top n-segment modulates the number of photons reaching the active region, as the penetration depth of the incident light decreases with increased segment length. The penetration depth of the incident photons with segment thickness is governed by:

$$I = I_0 \exp(-\alpha x) \quad (22)$$

Here, I is the light intensity in the active region, I_0 the initial intensity, α the absorption coefficient, and x the distance from the top of NWs. If the n-segment thickness is too small, then the doping in the n-segment might not completely deplete the i-segment, whereas the longer n-segment reduces the intensity of light reaching the active region. Thus, to minimize the

photoabsorption in the n-segment, the n-segment length is chosen to be ~ 200 nm guided by the COMSOL fitting. The n-segment thickness could not be suppressed below 200 nm due to the limitations of the device fabrication, as we don't want the top NW contact to touch the i-segment.

As i-segment is the active region of the axial p-i-n NWs, optimization of i-segment thickness is crucial in realizing axial p-i-n NWs with improved optical and electrical properties. In this study, the i-segment length was varied from 1 μm to 180 nm, and the corresponding variation in the magnitude of dark current and the shape of the curve is studied as depicted in figure 5.8a.

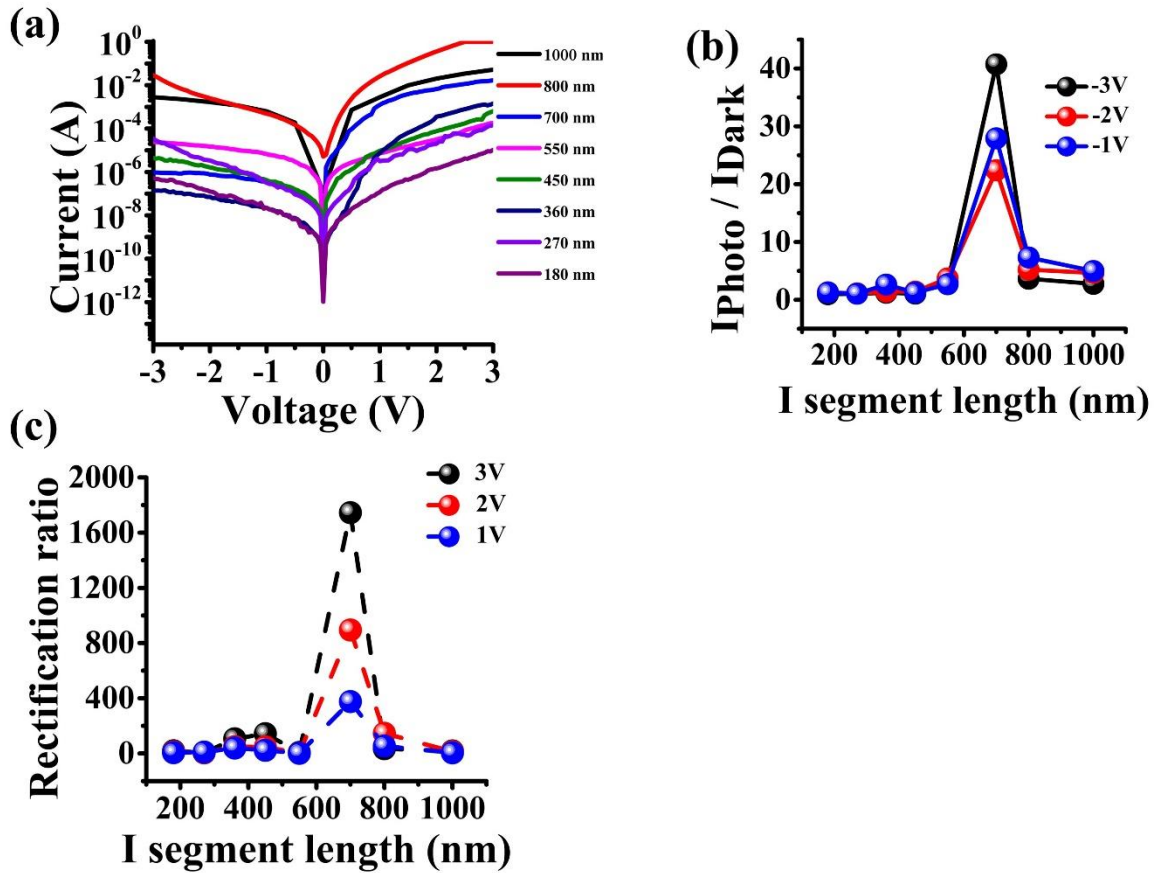


Figure 5.8. Variation of (a) dark current, (b) photocurrent to dark current ratio, and (c) variation of rectification ratio with i- segment length in axial p-i-n NWs.

As demonstrated in figure 5.8a, the i-segment thickness significantly influences both the magnitude and shape of the RT dark IV. The NW sample with a higher i-segment length revealed

the higher dark current might be due to the undepleted region within the intrinsic segment, introducing the diffusion component. In contrast, the sample with a smaller i-segment demonstrated the higher current accompanied by the tunneling-assisted conduction mechanism. The tunneling assisted conduction mechanism in the sample with smaller i-segment thickness is based on the transformation of the dark I-V characteristics from rectifying to symmetrical accompanied by a reduced rectification ratio as suggested in figure 5.8c. Similarly, it was evident that the i-segment thickness greatly influences the photoresponse of the p-i-n NWs. The influence of i-segment thickness on the NW photoresponse is calculated using the photocurrent to dark current ratio referred to as photosensitivity, as demonstrated in figure 5.8b. It is observed that the photosensitivity is compromised at both the longer and smaller i-segment thickness. The reduced photosensitivity at smaller i-segment thickness might be due to the reduced active region area. In contrast, at the higher i-segment thickness, photosensitivity is reduced due to the presence of the undepleted region.

Similarly, p-segment thickness is also crucial to enhance the photoresponse of the axial p-i-n NWs. The p-segment is required to suppress the substrate contribution on the NW performance. Suppose there is no p-segment in the axial p-i-n NWs. In that case, the photogenerated carriers from the substrate might migrate to the i-segment, compromising the photoresponse of the NWs. In addition, the p-segment thickness should not be larger indefinitely because of the waveguiding effects; the light reflected from the substrate might be absorbed in the p-segment. From careful investigation, the p-segment thickness of ~ 280 nm is established as an optimized thickness to achieve high-performance axial p-i-n NWs slightly longer than the diffusion length of the photocarriers in the GaAsSb material system.

5.7.3 Minimization of reservoir effect and radial overgrowth. The axial p-i-n NWs suffer from the infamous reservoir effect due to the definite solubility value of the growth species on the catalyst droplet. In the p-i-n NW growth, the growth is initiated with the p segment growth. After completing p-segment growth, the supply of p-type dopant, Be, is stopped, and i-segment growth is initiated. Although the supply of Be is blocked from the source, the Ga droplet acts as a source of Be with a tendency to diffuse into the i-segment making it more p-type, which is undesirable. To address this issue, we have adopted three different approaches, first pulsing Be for the last 30 sec of the p-segment growth at an interval of 5 sec. The second approach was to stop the Be supply in the last 1 minute of the p-segment such that the p-segment growth continues with the Be atoms that are dissolved in the melt. The third and final approach was to reduce the growth temperature by 5 °C after the p-segment growth, as the droplet supersaturation increases with the decreased temperature. The growth interruption for 1 min further facilitates the Be precipitation. Among three approaches, lowering the substrate temperature during the growth interruption was established as a practical approach to reducing the Be migration to the i-segment. The reduced unintentional doping concentration in the i-segment of the NW sample employing the third approach suggests that decreasing the substrate temperature during the growth interruption might be an effective approach to reduce the diffusion of Be from p-segment to the i-segment. Similarly, the suppressed dark current and enhanced photocurrent in the NW sample employing the third approach also establish that decreasing the substrate temperature during the growth interruption suppresses the reservoir effect.

Similarly, radial overgrowth is another challenge in the growth of axial p-i-n NWs. It stems from the competition between the axial and the radial growth. The complete selection of one mode

and the rejection of the other mode is rare. Thus, this radial overgrowth provides an additional pathway for parasitic conduction. This parasitic conduction path gives the shunt resistance in the NWs. In the NWs, there are two resistances, namely series and shunt resistance. The series resistance corresponds to the intrinsic resistance of the NWs, and the shunt resistance comes into the picture due to the parallel parasitic conduction path. The high-quality NWs are characterized by the minimum series resistance and maximum shunt resistance. As the radial overgrowth corresponds to the shunt resistance, the extent of radial overgrowth in the p-i-n NWs can be correlated qualitatively to the magnitude of shunt resistance. The schematic of ideal axial p-i-n NWs and the NW with radial overgrowth is depicted in Figures 5.9a and 5.9b, respectively. Similarly, the NWs can be modeled electrically as a current source with a diode and shunt resistance connected in parallel, followed by series resistance, as shown in figure 5.9c. To suppress the radial overgrowth, we have adopted three different approaches. The first approach was to carry out the growth of successive segments at a higher As/Sb ratio such that the axial growth rate is enhanced with the increased As/Sb ratio. The design of the experiment was to increase the As/Sb ratio from 9 in p-segment, 10 in i-segment, and 11 in n-segment (Sample A). The second approach was high temperature annealing of each segment after the growth to evaporate the radial overgrowth (Sample B). The third and final approach was increasing the consecutive segment growth temperature as the VS radial overgrowth is favorable at the lower growth temperature (Sample C). The efficacy of these approaches is assessed by calculating the value of corresponding shunt resistance of the NWs, and the increased magnitude of series resistance hints to the efficient approach.

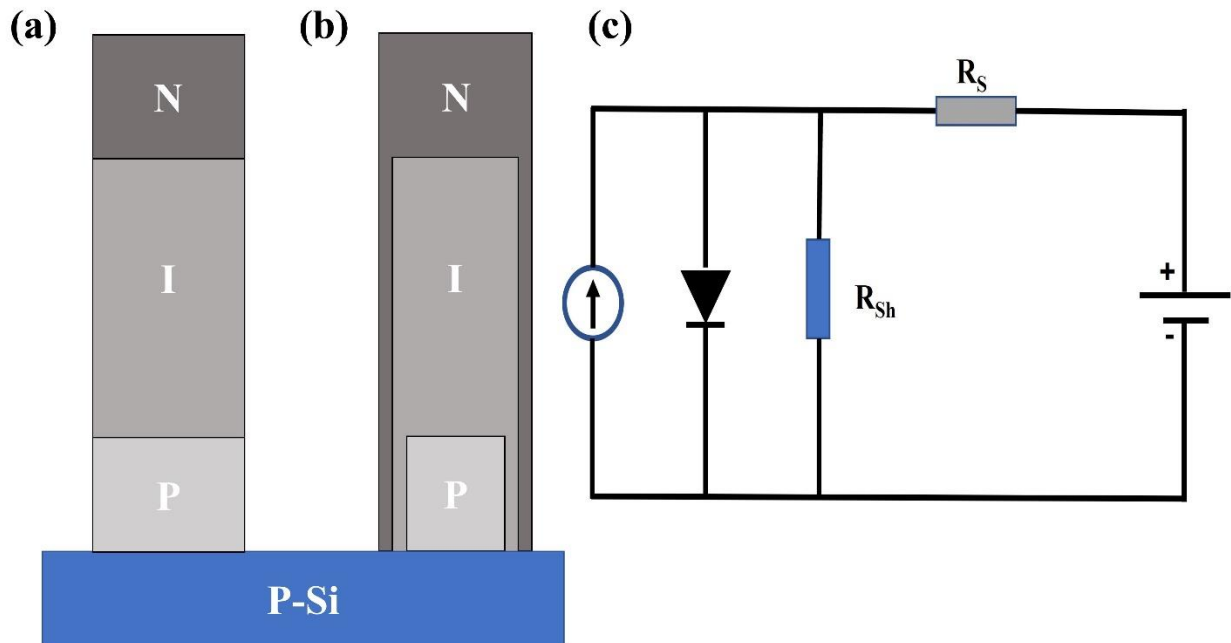


Figure 5.9. Schematic of axial p-i-n NWs demonstrating (a) ideal growth, (b) axial NW with radial overgrowth, and (c) electrical modeling of NWs.

The shunt resistance value is calculated by linear fitting the low forward bias I-V characteristics. The best fit of the experimental dark I-V characteristics against the linear equation and the slope's inverse gives the shunt resistance magnitude. Finally, axial p-i-n NWs grown employing the above approaches are assessed against the dark current and the magnitude of shunt resistance. The variation of dark current and the shunt resistance with the different approaches are mentioned in the figure below:

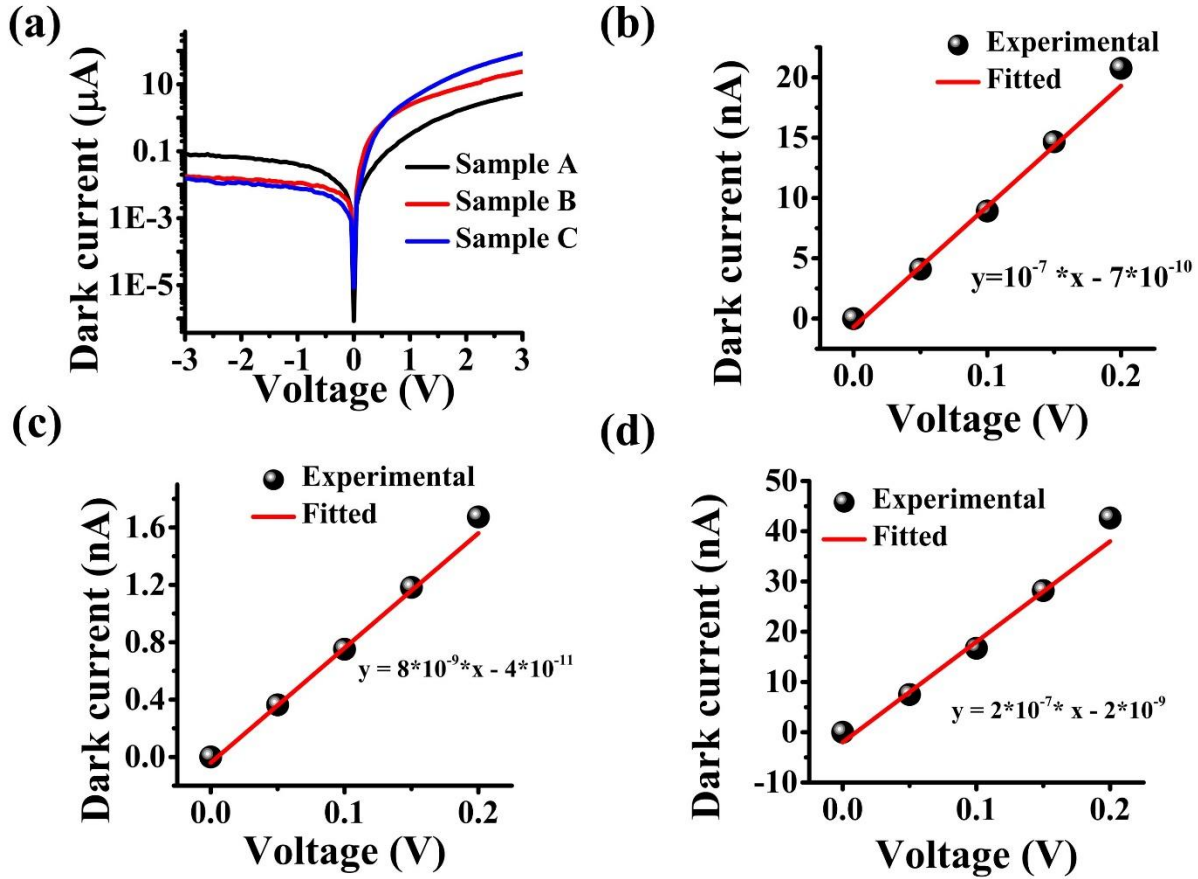


Figure 5.10. (a) Variation of RT dark current, (b), (c), and (d) linear fitting of experimental dark I - V characteristics for shunt resistance calculation employing different approaches,

As shown in figure 5.10a, the dark current value is significantly suppressed in samples B and C compared to sample A (in reverse bias). Similarly, the best fit of forward bias dark current in samples A, B, and C, as demonstrated in figures 5.10b, c, and d, suggested that shunt resistance's value increased from $1 \text{ M } \Omega$ in sample A to $125 \text{ M } \Omega$ in sample B. The shunt resistance value was calculated as $0.2 \text{ M } \Omega$ in the as-grown NW sample.

5.7.3 Growth interruption. Similarly, during the growth of p-i-n GaAsSb NWs in the axial configuration, growth interruption was established as a fundamental approach for attaining high-quality vertical NWs. However, the NW sample without interruption exhibited tilted structure, as shown in figure 5.11a, whereas the vertical NWs were achieved with interruption as depicted in figure 5.11b. Therefore, the bending of the NWs sample without interruption might be due to the stress accumulation at the interface. But with interruption, the NWs have the flexibility for interface reconstruction reducing the density of dangling bonds minimizing the interface stress. Similarly, the failure to obtain the RT PL spectra in the NW sample without growth interruption suggests the defective NWs with poor optical properties.

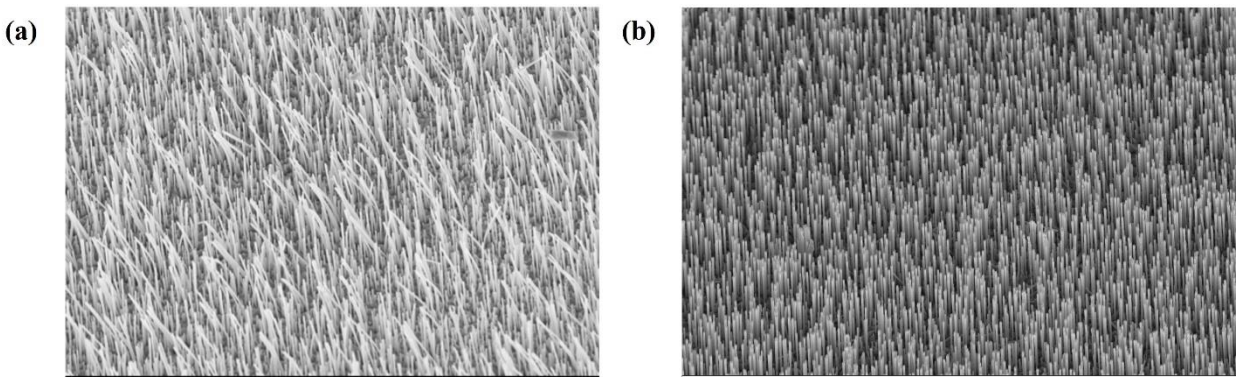


Figure 1.11. SEM images of GaAsSb p-i-n NWs (a) without and (b) with growth interruption

5.7.3 Approaches to suppress the dark current. Various efforts have been made in the literature to suppress the magnitude of the dark current in the p-i-n axial heterostructured NWs. As the dark current masks the photoresponse and introduces the noise in the device, minimal dark current is one of the stringent requirements in optoelectronic device applications. Formation of heterostructure might be one approach to suppress the dark current because the band bending at the heterointerface might add potential that needs to be overcome by the thermal carriers during conduction and might help suppress the dark current in the heterostructured NWs. In addition, instead of abrupt transition from higher bandgap p-segment to low bandgap i-segment, the graded

transition, i.e., continual change in the As and Sb flux during the i-segment growth, might be an appropriate approach to suppress the dark current, as the formation of the interface in the high bandgap material is an effective approach to reduce the dark current. The Te doping in the n-segment was initiated at lower GaTe cell temperature and was increased towards the top. The initiation of n-segment growth at the lower doping suppresses the magnitude of dark current by forming the interface at the higher bandgap. Higher doping is required at the top for ohmic contact formation with the Ag NWs.

Based on the optimization approaches discussed above, the axial p-i-n NWs were fabricated. The properties of the optimized axial GaAsSb p-i-n NWs will be discussed in the following section.

5.8 Optimized heterostructured axial p-i-n NWs

The optimized GaAsSb p-i-n NWs were grown in the axial configuration to realize NW ensemble PD. Structural properties of these NWs were investigated using the SEM images as demonstrated in figure 5.12a, displaying high-density vertical NWs with an average length of $\sim 1.5 \pm 0.1 \mu\text{m}$ and a diameter of $\sim 148 \pm 8 \text{ nm}$ with minimal diameter variation along the NW axis. The existence of the catalyst droplet at the NW tip suggests that the VLS growth ceases only during the passivation shell growth suggesting the uninterrupted growth of each segment. The inset in figure 1a demonstrates the schematic of heterostructure axial p-i-n NWs.

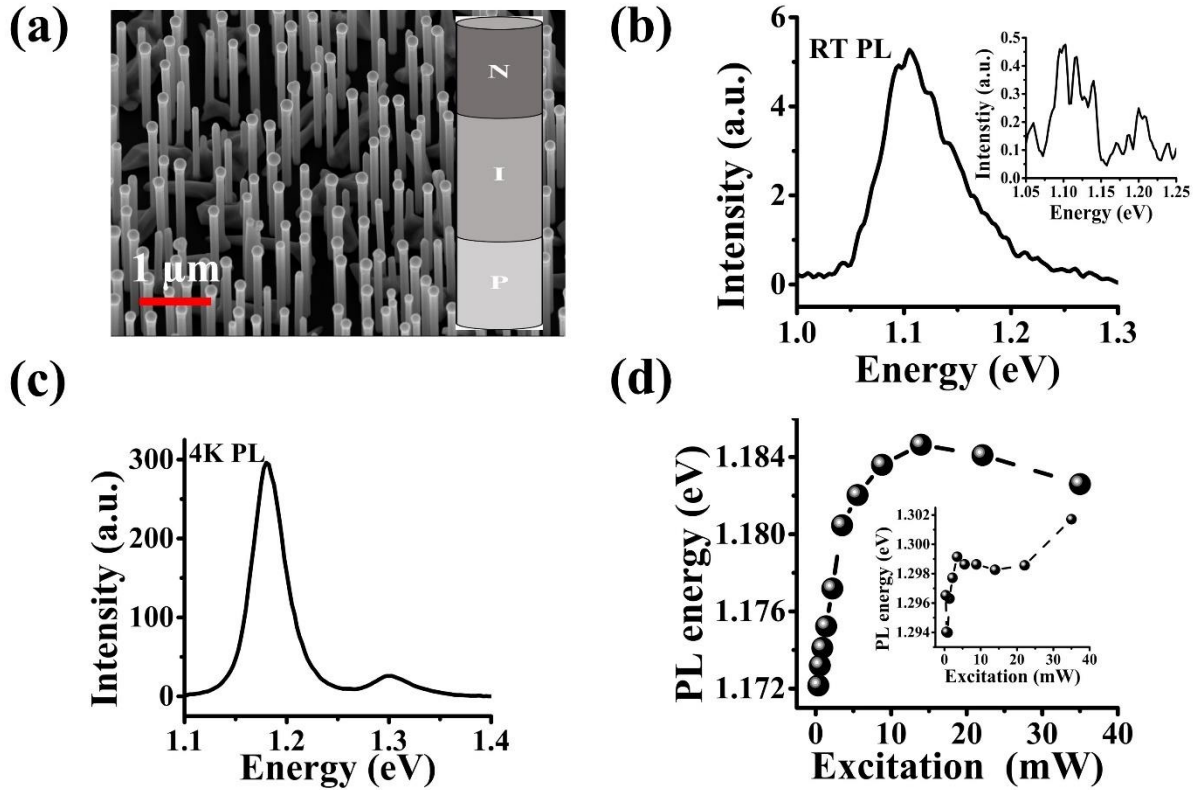


Figure 5.12. (a) SEM images (inset shows the schematic), (b) low temperature (4K) PL spectra, (c) excitation dependent PL emission energy variation, and (d) excitation dependent PL intensity variation of axial GaAsSb p-i-n heterostructure nanowires at 4K (inset corresponds to the higher energy peak).

Similarly, the optical properties were assessed employing room temperature (RT) and low temperature (4K) PL spectroscopy. Attainment of the RT PL peak suggests the successful realization of high-quality NWs, as several reports in the literature struggle to achieve the RT PL peak. The heterostructure axial p-i-n NW demonstrated a single asymmetrical peak at ~ 1.2 eV with a long exponential decay tail on the higher energy side, which might be due to the convolution of the emission from n-segment with the emission from i-segment. However, at the lower excitation intensity, the single asymmetric peak is deconvoluted into two distinct peaks positioned at ~ 1.12 eV and ~ 1.2 eV, respectively, as demonstrated in the inset of figure 5.12b. The splitting

of a single PL peak into two distinct peaks at lower excitation intensity because at higher excitation, the maximum number of higher energy photons were able to reach the i-segment region and contribute to the conduction from i-segment and due to the suppressed emission from the n-segment, the longer exponential decay tail occurs on the higher energy side. At the lower excitation power, the penetration depth of the incident photon is reduced, and the photons are absorbed almost equally on both the n and i-segment, as suggested by the distinct PL peak under reduced illumination power. However, the deconvolution of the PL peak is more prominent in the 4K as shown in figure 5.12 c with a significantly higher PL emission intensity suggesting the high-quality axial p-i-n NWs. The higher intensity of PL peak positioned at ~ 1.2 eV indicates that the minimum photons are absorbed in the top n-segment. Similarly, the excitation-dependent 4K PL emission is depicted in figure 5.9d, where the inset corresponds to the excitation-dependent PL spectra of the higher energy peak. At lower excitation, the PL peak demonstrated the blueshift due to the band filling effect that resulted from the increased photocarrier concentration. Further, increasing the excitation power, the PL peak is redshifted, which might be due to the local heating of the semiconductor NWs at higher excitation and the semiconductor bandgap usually decreases at the higher temperature. In contrast, the higher energy peak demonstrated the blue-red-blue shift of the PL energy with excitation, as demonstrated in the inset of figure 5.12d due to the competition between the local heating and band filling effects.

To study the extent of band bending at the interface in the p-i-n NWs, we grew the different n and i-segment. The PL emission from the individual n and i-segment were 1.22 eV and 1.15 eV, respectively. This variation of the PL emission energy in the heterostructured p-i-n NWs might be attributed to the band bending at the heterointerface. The heterostructure caused the band bending of 0.2 eV on the heterointerface. The PL intensity and the position were invariant with the number

of scans, suggesting that the NWs can withstand the laser illumination, implying higher NW burnout resistance, repeatability, and reliability.

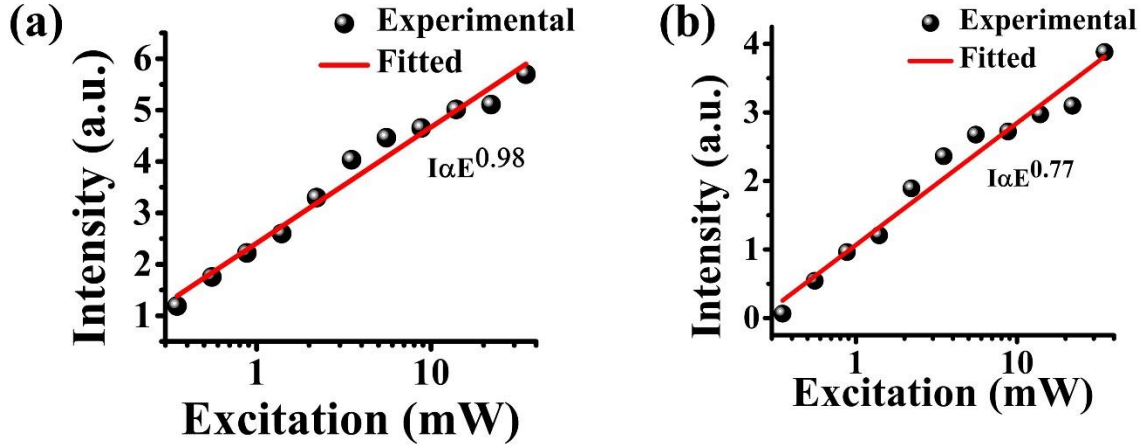


Figure 5.13. The power-law dependence of the excitation intensity on (a) lower energy and (b) higher energy 4K PL spectra

Similarly, the excitation-dependent 4K PL peak intensity for both the lower and higher energy peaks is demonstrated in Figures 5.13a and 5.13b, respectively. The heterojunction's lower and higher energy 4K PL peaks showed the different power-law dependence on the excitation intensity. The power-law dependence of PL intensity with excitation can be expressed mathematically by the following relation:

$$I = E^{\alpha} \quad (23)$$

Where I is the PL intensity, E is the excitation intensity, and α is the exponent of the excitation power. As demonstrated in the supplementary information, the value of α is 0.98 in the lower energy peak, whereas that is 0.77 in the higher energy peak. The lower energy PL peak intensity demonstrated almost a linear dependence of the intensity with excitation, whereas the higher energy peak demonstrated the sublinear dependence. This sublinear dependence is attributed to the Auger recombination present within the semiconductor material.

5.9 Heterojunction p-i-n NW photodetector

The ensemble NW PD was fabricated, capitalizing the optimized, high-quality vertical heterostructured p-i-n axial NWs. The heterojunction NWs were realized using the higher bandgap n and p-segment and lower bandgap i-segment. Heterojunction PD is preferred over the homojunction as the former has the advantage of increased photoabsorption in the active region, as discussed in the previous section of this chapter. The performance of NW PD was assessed using various characterization techniques. Heterostructured NW PD fabricated employing the variety of optimization techniques discussed in this chapter demonstrated rectifying dark I-V characteristics suggesting the realization of high-quality i-segment accompanied by the significant photoresponse as depicted in 5.14a. The superimposed photo and dark current characteristics observed the photocurrent enhancement by 3 orders of magnitude. Similarly, the rectification ratio decreases with illumination, which might be due to the lower photocurrent enhancement under the forward bias than in the reverse biased condition. The lower photocurrent enhancement in the forward bias is because the photocurrent and the diffusion current are opposite.

In contrast, both have the same direction in the reverse biased condition. Similarly, to further investigate the photosensitivity of ensemble NW PD, the voltage-dependent spectral response (I - λ - V) was measured as depicted in 5.14b, demonstrating the bandpass characteristics with the lower wavelength cutoff at $\sim 0.6 \mu\text{m}$ and the higher wavelength cutoff at $\sim 1.1 \mu\text{m}$. The lower wavelength is cutoff is dictated by the thermalization loss, enhanced surface absorption, and the screening of the photogenerated carriers. In contrast, the higher wavelength cutoff corresponds to the material bandgap. The higher wavelength cutoff is at $\sim 1100 \text{ nm}$, which is consistent with the value of the RT PL peak. Furthermore, the cutoff wavelength value is independent of voltage, suggesting the minimized density of the energy states within the forbidden energy gap.

A C-V measurement is also a practical approach to developing insight into the material property. The frequency-dependent capacitance (C-V-f) spectra in figure 5.14c revealed that the capacitance is independent of frequency in the reverse-biased and decreases with increasing frequency in the forward biased. This can be explained by considering a p-i-n NW as a parallel plate capacitor. The bias independent C-V characteristics under the reverse biased condition suggest a complete depletion of the i-segment. It indicates that the doping in the neutral region is adequate to deplete the i-segment completely, leading to the depletion region independent of the reverse bias. At the same time, frequency-independent C-V characteristics point towards the high-quality i-segment with reduced defect density. A decrease in defect density significantly reduces the generation-recombination (g-r) centers capable of generating charge carriers responding to the change in frequency. In addition, a high-quality depletion region is further attested by a significantly lower ideality factor of 2.45.

Furthermore, the decreased capacitance with frequency in forward bias indicates that fewer carriers can respond to the perturbation at a higher frequency. Along the same line, the exponential increase in capacitance beyond the knee voltage suggests the effective diffusion of the charge carriers from the neutral region to the depletion region, increasing the carrier concentration. Similarly, the conductance of the NW PD was frequency independent both under the forward and the reverse biased condition, as depicted in 5.14d. The frequency-independent conductance in both conditions might be attributed to the high-quality depletion region due to the reduced defect-assisted carrier generation capable of responding to the perturbation. On the other hand, the conductance is voltage-independent at all frequencies in the reverse biased condition suggesting the complete depletion of the i-segment. The sharp increase in the conductance occurs ~ 1.45 V, suggesting that the built-in potential of 1.45 V is present in the p-i-n NWs. The experimental I-V

curve also demonstrated the sharp increase in the forward bias current at around 1.5 V of forward bias, suggesting the value of built-in potential is approximately 1.5 V. Similarly, from the $1/C^2$ vs V plot as demonstrated in 5.14e, the i-segment doping was achieved to be $3.26 \times 10^{15} \text{ cm}^{-3}$ employing equation 20. When the experimental data is fitted linearly against equation 20, the slope of the curve gives the unintentional doping in the i-segment.

The depletion region of ensemble NW PD was calculated employing equation 19. The depletion region width is $\sim 730 \text{ nm}$ without a bias voltage. The i-segment thickness in the axial p-i-n NWs is 700 nm referring to the complete depletion of the i-segment. Similarly, the voltage dependent LFN spectroscopy is depicted in figure 5.14f. The noise level increases with the increased reversed biased voltage due to the increased stochastic behavior with increased voltage. Similarly, the NW PD demonstrated the G-R noise as a dominant noise source with a corner frequency of $\sim 20 \text{ Hz}$ at all the voltages. With the increase in the reverse-biased voltage, the noise becomes slightly dependent on the frequency; this might be attributed to the increased randomness of the thermal carriers with high reverse-bias voltage in the axial p-i-n NW PD. Thus, from this observation, the doping in the neutral region is sufficient to completely deplete the intrinsic segment of the NWs, resulting in the suppressed dark current, significantly higher rectification ratio, voltage-independent capacitance, conductance, and substantially lower noise level.

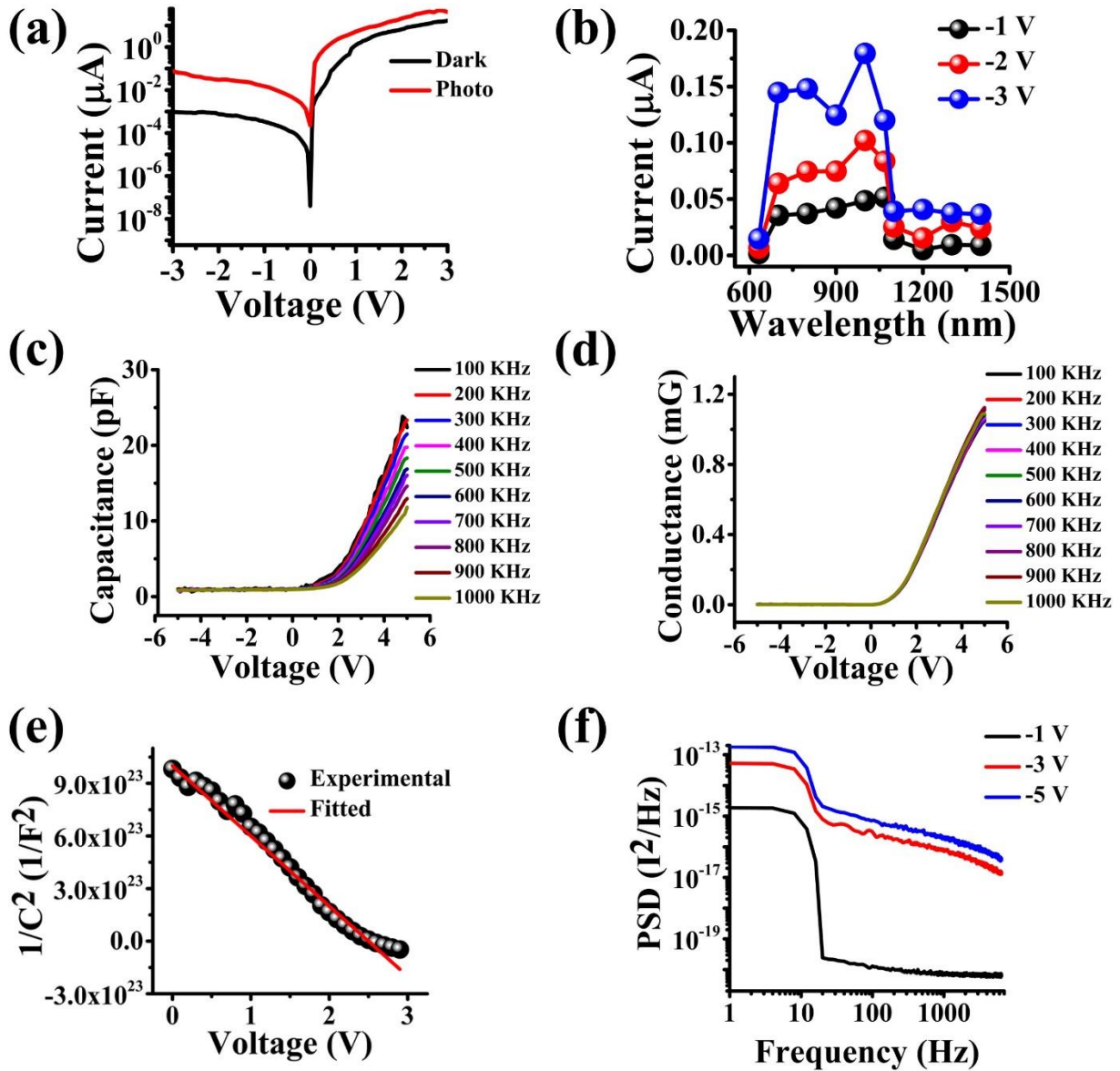


Figure 5.14. Superimposed dark and photocurrent, (b) spectral response, (c) C-V measurement, (d) G-V measurement, (e) linear fitting of experimental C-V curve to calculate the unintentional doping in i-segment, and (f) LFN spectroscopy of the ensemble axial heterostructure p-i-n NW photodetector

The PD figure of merit value was calculated utilizing the ensemble PD's electrical response.

The responsivity value was calculated to be 120 A/W, whereas the detectivity was estimated to be

1.31×10^{13} Jones. Recently, Mauthe et al. designed high-speed InGaAs NW PD with a spectral response from 1200-1700 nm and responsivity of 0.68 AW^{-1} [28]

CHAPTER 6

Summary and future scope

6.1 Summary

This dissertation discusses the realization of axial GaAsSb p-i-n NW PD operating in the NIR region (i.e., 1.1 μm). This work focuses on examining the existing challenges of the growth of axial GaAsSb p-i-n NWs and developing appropriate approaches to address those challenges. High-quality axial p-i-n heterostructure NWs were grown using optimized growth methods, and high-performance ensemble NW PD was demonstrated. In the following section, the achievement of this dissertation will be discussed in detail.

6.6.1 Optimization of Ga catalyst seed droplet consumption and the post-growth in-situ annealing approach in Te-doped GaAs NWs. A systematic investigation of the amount of As flux employed during the seed droplet consumption showed that the droplet consumption approach dictates the density of stacking faults present at the NW tip. In addition, the in-situ post-growth annealing of Te doped NWs was found to engender acceptor level complex, as attested by an additional lower energy PL peak, a transformation of dark I-V characteristics from rectifying to leaky, and negative photoconductivity accompanied by increased activation energy compared to as-grown NW counterparts. Thus, the as-grown NWs using the same amount of As flux during the seed droplet consumption as that used during the growth are established as an optimized growth recipe for the growth of Te-doped GaAs NWs. **(The manuscript is in preparation for submission to the journal)**

6.1.2 Te-doping optimization of GaAsSb NW and Schottky diode ensemble NW PD realization. In the literature, there is a considerable amount of work on the Te doping of GaAs NWs, but this is the first work discussing the optimization of Te-doping of the GaAsSb NWs using

the captive GaTe source. The Te doping of GaAsSb NWs is tricky due to the interplay of two surfactants changing the droplet energy. The extent of doping in the NWs was varied by changing the dopant cell temperature. The dopant source temperature of 550 °C was established as an optimized Te source temperature for the optimum dopant incorporation within the NW crystal lattice using various characterization techniques as a feedback mechanism. Similarly, the field emission was identified as a dominant current conduction mechanism in the n-GaAsSb NWs doped to the concentration of $\sim 5 \times 10^{15} \text{ cm}^{-3}$. The ensemble NW PD fabricated with optimized n-GaAsSb NWs demonstrated significant photosensitivity with the bandpass spectral response up to $\sim 1.2 \mu\text{m}$, the responsivity of $\sim 620 \text{ A/W}$, EQE of $7 \times 10^4 \%$ and the detectivity of $\sim 1.2 \times 10^{12} \text{ Jones}$. (This work was published in **Nanotechnology** journal in 2020.)

6.1.3. Compensation of GaAsSb i-segment. We established an approach of Te compensation (i.e., n-type) of the i-segment, which is intrinsically p-type. The intermittent supply of Te for 2 secs of every 2 mins i-segment growth was found to be an efficient compensation approach as confirmed from increased PL emission with reduced FWHM, increased photosensitivity, and decreased dark current followed by the reduction in overall residual carrier concentration in the devices. **This work is the first report on the compensation of the p nature of the intrinsic GaAsSb segment, and the manuscript is under preparation**

6.1.4 Growth interruption. Achieving a clean interface between the different segments of the p-i-n NWs is crucial to achieving a high-performance device. Therefore, we developed a unique approach of growth interruption to grow a clean interface. In this approach, the overall NW growth is paused for 60 seconds by closing the shutters after each segment growth to facilitate the surface reconstruction at the interface. Opening of Ga shutter for 2 sec before the initiation of the growth

of another segment was enough to replenish the seed droplet and keep the VLS growth mechanism intact.

6.1.5 Suppression of reservoir effect. The droplet reservoir effect deteriorates the optical and electrical properties of the axial p-i-n NWs. This becomes an issue in our axial p-i-n NW configuration, particularly for p-dopants. As a result, the Be from the Ga droplet tends to diffusion to the i-segment, increasing the residual p-type concentration. This was minimized by decreasing the NW growth temperature to precipitate the Be. The minimization of the reservoir effect was confirmed by the reduced magnitude of dark current, increased dark current rectification ratio, and decreased overall residual concentration of the i-segment.

6.1.6 Suppression of the radial overgrowth. In the axial configuration, p-i-n NWs suffer from the radial overgrowth detrimental to NW optical and electrical properties. Radial overgrowth arises due to the lack of growth mode selectivity, i.e., the complete selection of either growth mode is impossible. Radial overgrowth is undesirable in the axial p-i-n NWs, as it introduces a parallel parasitic conduction path, eventually increasing the overall dark current. To minimize the influence of the radial overgrowth on the NW characteristics, we developed an approach of high-temperature UHV in-situ segment annealing. The efficacy of this approach is verified by the decreased dark current, increased rectification ratio, and increased NW shunt resistance.

6.1.7 Realization of high-performance Schottky barrier and p-i-n ensemble NW PDs.

A high-performance Schottky diode ensemble NW PD was fabricated exploiting the optimized n-GaAsSb NWs. The NW PD on Si demonstrated excellent photosensitivity accompanied by the bandpass spectral response with a higher wavelength cutoff at $\sim 1.2 \mu\text{m}$. With high figure of merits, namely responsivity of $\sim 620 \text{ A/W}$ and the detectivity of $\sim 1.2 \times 10^{12} \text{ Jones}$, these PDs have proven to be promising candidates for the NIR photodetection applications.

Similarly, an ensemble p-i-n NW PD fabricated employing the optimized heterostructured axial p-i-n NW operating at $\sim 1.1 \mu\text{m}$ demonstrated a responsivity of $\sim 120 \text{ A/W}$ and a much higher detectivity of $\sim 1.3 \times 10^{13} \text{ Jones}$.

6.2 Future works

The optimized axial p-i-n NWs grown utilizing the growth recipe discussed in this dissertation operating in $1.1 \mu\text{m}$ has the potential to be used in the variety of next-generation future applications listed below:

6.2.1 Self-powered axial ensemble p-i-n NW PD. As the p-i-n NWs operate in the photovoltaic mode, these optimized axial NWs can be used for self-powered applications. Furthermore, as the self-powered devices function by capitalizing on the built-in potential obviating a need for external bias, these NWs can be used as a building block for low-power nanostructured devices.

6.2.2 Patterned axial ensemble p-i-n NW PD. The finding of this work can also be extended to patterned GaAsSb axial p-i-n NW growth. The growth of axial p-i-n NWs in the patterned configuration enables us to control the NW diameter and the fill factor. As a result, the light-NW interaction can be enhanced, widening the scope of high-performance axial p-i-n NWs and the ensemble PD.

6.2.3 Fabrication of axial ensemble p-i-n NW PD operating in the low loss telecommunication wavelength region. The bandgap of a PD material strictly dictates its ability to detect the incoming optical signal. To realize GaAsSb NW material capable of detecting the $1.3 \mu\text{m}$ radiation, the bandgap can be tuned by increasing the Sb incorporation within the NW crystal lattice. But the growth of NWs with higher Sb incorporation is challenging due to the surfactant nature of Sb [20] capable of altering the Ga droplet energy and the contact angle and making the

NW growth relatively tricky. Furthermore, due to the alteration in the surface energy of the droplet, the droplet bulges out. Instead of the droplet getting supersaturated and precipitated as NWs, the 2D growth is promoted, which is not desirable. So, to address those challenges, we can adopt a few approaches as listed below.

6.2.3.1 Approach to the growth of higher Sb NW segment. To address the challenges in the growth of NWs with a higher Sb composition to encompass telecommunication wavelength, we will be discussing four different approaches that might facilitate the NW growth. First, increasing the Sb flux used in the growth is a straightforward way of increasing the Sb incorporation in the NWs. Second, using the same Sb flux but decreasing the As flux, i.e., reducing the overall BEP ratio such that the axial growth rate of the NWs will be suppressed. As a result, the incorporated Sb will be distributed over the smaller volume, thus increasing the overall Sb incorporation in the NWs. However, this approach comes with an increased NW growth duration. Similarly, the third approach is decreasing the NW growth temperature as the Sb incorporation is enhanced at a lower growth temperature. In addition to that, the fourth approach might be the pulsing of As during the higher Sb segment growth.

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