# DESIGN AND FABRICATION OF A GALLIUM PHOSPHIDE NANOWIRE BETAVOLTAIC DEVICE

### DESIGN AND FABRICATION OF A GALLIUM PHOSPHIDE NANOWIRE BETAVOLTAIC DEVICE

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A Thesis Submitted to The School of Graduate Studies in Partial Fulfillment

of the Requirements for

The Degree Doctor of Philosophy

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McMaster University DOCTOR OF PHILOSOPHY (2025) Hamilton, Ontario, Canada (Engineering Physics)

TITLE:	Design and Fabrication of a Gallium Phosphide Nanowire Be-
	tavoltaic Device
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NUMBER OF PAGES: xxxviii, 189

#### Lay Abstract

Betavoltaic (BV) devices generate electricity from beta radiation (energetic electrons) and have the potential to provide long-lasting power for applications where replacing batteries is impractical. Despite decades of research, these devices remain underdeveloped, particularly in designs using nanoscale materials like III-V semiconductor nanowires (NWs). This thesis explores how the shape and structure of BV devices influence their performance, addressing challenges that limit efficiency in conventional designs. By studying the interaction between material properties and device geometry, this research provides new insights into optimizing BV energy conversion at the nanoscale. This work also demonstrates advanced techniques for fabricating gallium phosphide (GaP) NW-based BV generators, offering a promising approach to improving power output and efficiency. The findings contribute to both the theoretical understanding and practical development of BV devices, paving the way for future innovations in compact, long-lasting power sources for space, medical, and remote sensing applications.

#### Abstract

Betavoltaic (BV) devices, which convert beta particle radiation into electrical power, represent a promising solution for long-term energy generation in environments where traditional low power sources are impractical. While BV technology has been studied for over fifty years, its development has been limited, particularly in the emerging field of III-V semiconductor nanowire (NW) implementations. This dissertation advances both the theoretical understanding and practical development of gallium phosphide (GaP) NW-based BV generators, with a specific focus on overcoming geometric constraints that impact device performance.

Through comprehensive modeling and experimental validation, this work establishes fundamental relationships between NW architecture, material properties, and energy conversion efficiency. The research presents novel insights into optimizing carrier transport and radiation absorption through precise control of NW geometry and material interactions. New processing techniques for fabricating tailored GaP NW arrays are developed and demonstrated, enabling enhanced BV performance through improved charge collection efficiency.

The findings bridge critical gaps in current understanding of radiation-driven energy conversion in nanostructured materials, while providing practical solutions to long-standing

challenges in BV device design. This work establishes a foundation for developing highefficiency BV power sources, with potential applications in space exploration, medical implants, and remote sensing systems. The theoretical framework and fabrication methodologies presented here open new pathways for advancing BV technology toward practical implementation.

To my parents for their unwavering love and support through every stage of my life.

#### Acknowledgements

First, I'd like to thank my research supervisor Dr. Ray LaPierre for providing the opportunity to pursue this endeavour, and putting his faith in me to see it through to the end. Ray's encouragement and guidance have taught me about what it means to be a good researcher and collaborator. I am grateful for the many practical learning and networking opportunities in the form of training programs, conferences and workshops, afforded to me through Ray's support. I would also like to thank my advisory committee members, Dr. Ryan Lewis and Dr. Dave Novog for their challenging questions and insight. Thank you for pushing me to go beyond what I thought I was capable of. In the process, I have learned more about myself than I ever expected.

Many thanks to the past and present LaPierre group members who helped me progress over the years. When I began, Simon McNamee equipped me with much of the knowledge needed to get started on the project. I am deeply grateful to Mitchell Robson who took the time to teach me the entire device fabrication and electrical characterization process even after he completed his studies. None of this would have been possible without his patience and willingness to help me. Thank you to Ara Ghukasyan and Paige Wilson for training and helpful discussions. Special thanks to Devan Wagner, for helping me get started with device modeling. To my current fellow group members Ethan Diak and Linh Lam, thank you for the many laughs, friendship and encouragement. Working alongside both of you has been an absolute pleasure.

A tremendous thank you is owed to the Centre for Emerging Device Technology (CEDT) staff at McMaster. First and foremost, thank you to Nebile Isik Goktas for not only training me in everything from wafer preparation to device processing, but for also providing invaluable knowledge of MBE and nanowire growth. I am incredibly grateful for the patience you showed me when I first joined the group. Thank you to Doris Stevanovic for all of the technical support and processing knowledge, and for always being a friendly face in the department. Thank you to Shahram Ghanad-Tavakoli for performing all of the MBE growths. I am grateful to the Canadian Centre for Electron Microscopy (CCEM) staff at McMaster University, Chris Butcher and Jhoynner Martinez for SEM training and troubleshooting, as well as Carmen Andrei for performing TEM. I would also like to acknowledge Alex Tsukernik of the Toronto Nanofabrication Centre (TNFC) at the University of Toronto for his assistance with EBL.

I am grateful for funding from the Natural Sciences and Engineering Research Council (NSERC) CREATE TOP-SET program, Ontario Graduate Scholarships and the Department of Engineering Physics, which enabled this research.

To my family and friends, although I can't list you all, thank you for staying the course with me. This thesis stands as a testament to the incredible community of individuals who have supported me throughout this journey. To my parents, thank you for always being in my corner and supporting me in every endeavour. Had it not been for you fostering my curiosity and love of learning, I would have never gone down this path. To my brother Mathieu, thank you for being an infinite source of laughter and positivity in my life. To my grandma, thank you for being there to cheer me on no matter the activity. Thanks to you I have always known a life filled with love. To Neil and Dianna, your unwavering love and belief in me strengthened my resolve when I needed it most. To Paige and Jared, thank you both for the many nights spent laughing into the early hours of the morning whenever I needed an outlet.

Lastly, and most importantly, thank you to my partner, best friend, and love of my life, Kevin. There aren't enough words to express my gratitude for your unconditional love and support over the past nearly 11 years. You've shown such grace and selflessness throughout this process. Thank you for enduring this journey with me and for never wavering, even when I felt lost. Through it all, you always found a way to make me laugh. This accomplishment is as much yours as it is mine. I can't wait to see where life takes us next.

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## Abbreviations, Symbols, and Definitions

#### Abbreviations

2D	two-dimensional
3D	three-dimensional
AFM	atomic force microscopy
AlGaP	aluminum gallium phosphide
ВСВ	bisbenzocyclobutene
BHF	buffered hydrofluoric
BSE	backscattered electron
BV	betavoltaic
ССЕМ	Canadian Centre for Electron Microscopy
CEDT	Centre for Emerging Device Technologies
CL	cathodoluminescence

CVD	chemical vapor deposition
DC	direct current
DI	deionized
E-beam	electron beam
EBL	electron beam lithography
ECR	electron cyclotron resonance
ЕНР	electron-hole pair
FEG	field-emission gun
GaP	gallium phosphide
GS-MBE	gas-source molecular beam epitaxy
HF	hydrofluoric
HRTEM	high-resolution transmission electron microscopy
ICP	inductively-coupled plasma
юТ	internet of things
IPA	isopropyl alcohol
ІТО	indium tin oxide
IV	current-voltage
JV	current density-voltage

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LMA	Levenberg-Marquardt algorithm
MBE	molecular beam epitaxy
MFP	mean free path
ML	monolayer
MOCVD	metal-organic chemical vapor deposition
MSE	mean square error
NIL	nano-imprint lithography
NW	nanowire
PECVD	plasma-enhanced chemical vapor deposition
PE	primary electron
PH <sub>3</sub>	phosphine
PL	photoluminescence
PR	photoresist
PS	porous silicon
PVD	physical vapor deposition
PV	photovoltaic
QNR	quasi-neutral region
RF	radio-frequency

RHEED	reflection high-energy electron diffraction
RIE	reactive ion etching
RTA	rapid thermal annealing
SA-VLS	self-assisted vapor liquid solid
SAE	selective-area epitaxy
SCR	space-charge region
SEM	scanning electron microscopy
SE	secondary electron
SiO <sub>2</sub>	silicon dioxide
SiO <sub>x</sub>	silicon oxide
SRV	surface recombination velocity
STEM	scanning transmission electron microscopy
TEM	transmission electron microscopy
TRF	trust region reflective
TNFC	Toronto Nanofabrication Centre
UHV	ultra-high vacuum
UV	ultraviolet
VASE	variable angle spectroscopic ellipsometry

VLS	vapor-liquid-solid
VS	vapor-solid
XPS	X-ray photoelectron spectroscopy

### **Definitions and Symbols**

$(R_i, C_j)$	nanowire pad row and column position in the nanowire pad matrix
$A_{\rm cell}^{\rm NW}$	cross-sectional area of nanowires within the nanowire array unit cell
$A_s$	radioisotope source activity
A <sub>cell</sub>	nanowire array unit cell cross-sectional area
В	radiative recombination coefficient
$C_n$	minority electron Auger recombination coefficient
$C_p$	minority hole Auger recombination coefficient
D	nanowire diameter
$D_n$	minority electron diffusion constant
$D_p$	minority hole diffusion constant
E	electric field
Ē	beta spectrum mean energy
$E_F$	Fermi energy (or chemical potential)

$E_T$	trap state energy
E <sub>c</sub>	conduction band energy
$E_{g}$	bandgap energy
E <sub>i</sub>	intrinsic Fermi level
$E_{v}$	valence band energy
$E_{dep}$	average beta particle energy deposited in an absorber medium
E <sub>max</sub>	beta spectrum maximum energy
FF	fill factor
G	beta electron-hole pair generation rate
$G(r,\xi)$	Green's function
$G_p$	shunt conductance
Ι	current
I <sub>0</sub>	saturation current
$I_v$	modified Bessel function of the first kind of order $v$
$J_{dark}^{\Delta n}$	excess minority electron diffusion current density in the quasi-neutral
	region
$J_{ m sc}^{\Delta n}$	excess minority electron short-circuit current density in the quasi-neutral

$J_{ m sc}^{ m dep}$	depletion region generation current density
$J_{dark}^{\Delta p}$	excess minority hole diffusion current density in the quasi-neutral region
$J_{ m sc}^{\Delta p}$	excess minority hole short-circuit current density in the quasi-neutral re-
	gion
J <sub>0</sub>	saturation current density
$J_{dark}$	diode dark current density
$J_{mp}$	maximum power point current density
J <sub>sc</sub>	short-circuit current density
K <sub>v</sub>	modified Bessel function of the second kind of order $v$
L	nanowire length
L <sub>c</sub>	characteristic collection length
$L_n$	minority electron diffusion length
$L_p$	minority hole diffusion length
$N_D^+$	ionized donor dopant concentration
$N_A^-$	ionized acceptor dopant concentration
N <sub>A</sub>	acceptor dopant concentration
N <sub>B</sub>	nominal background dopant concentration
N <sub>D</sub>	donor dopant concentration

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$N_T$	trap state concentration
<i>N</i> <sub><i>A</i></sub> ,	effective acceptor dopant concentration
$N_{D'}$	effective donor dopant concentration
N <sub>c</sub>	conduction effective density of states
$N_{v}$	valence effective density of states
P <sub>in</sub>	input power density
$P_{mp}$	maximum power point
R	nanowire radius
Ŕ	average beta particle range
RR	rectification ratio
R <sub>p</sub>	nanowire p-doped core radius
R <sub>sh</sub>	shunt resistance
R <sub>s</sub>	series resistance
S(E)	stopping power
$S_p$	minority hole surface recombination velocity
Т	temperature
$U_{Auger}^{\max}$	maximum Auger recombination rate
$U_{SRH}^{\max}$	maximum Shockley-Read-Hall recombination rate

U <sub>Auger</sub>	Auger recombination rate
U <sub>SRH</sub>	Shockley-Read-Hall recombination rate
U <sub>rec</sub>	depletion region recombination rate
U <sub>rad</sub>	Radiative recombination rate
V	voltage
Vs	radioisotope source volume
Va	external bias voltage
V <sub>bi</sub>	built-in junction potential
V <sub>mp</sub>	maximum power point voltage
Voc	open-circuit voltage
$W\left[u_{<},u_{>} ight]$	Wronskian
$\Delta E_g$	bandgap energy narrowing
$\Delta n$	steady-state excess minority electron concentration
$\Delta p$	steady-state excess minority hole concentration
Γ	incomplete gamma function
$\Phi^{AM1.5G}_i$	AM1.5G solar spectral irradiance
Ψ	electrostatic potential
$\Psi_{n_0}$	electrostatic potential in the n-type quasi-neutral region

$\Psi_{p_0}$	electrostatic potential in the p-type quasi-neutral region
η	conversion efficiency
$\eta_{eta}^{ t 2D}$	3D source geometry beta capture efficiency
$\eta_eta^{ extsf{3D}}$	2D source geometry beta capture efficiency
$\eta_{eta}$	beta capture efficiency
$\eta_{pp}$	electron-hole pair production efficiency
λ	wavelength
$\mu_n$	minority electron mobility
$\mu_p$	minority hole mobility
$\phi^E_i$	photon flux per unit energy
ρ	electrostatic charge density
$ ho_s$	radioisotope source density
$\sigma_n$	minority electron capture cross-section
$\sigma_p$	minority hole capture cross-section
$ au_{n_0}$	minority electron lifetime in the depletion region
$ au_n$	minority electron lifetime in the quasi-neutral region
$ au_{p_0}$	minority hole lifetime in the depletion region
$ au_p$	minority hole lifetime in the quasi-neutral region
θ	azimuthal angle
---------------------------------	--
ε	electric permittivity
$\mathcal{E}_{_{\mathrm{EHP}}}$	mean energy required to generate an electron-hole pair in an absorber medium
Er	relative permittivity
d:p	nanowire array diameter-pitch ratio
$d_p$	nanowire p-doped core diameter
$d_{ss}$	source-to-substrate distance
f <sub>sa</sub>	radioisotope source self-absorption loss factor
h	Planck's constant
ħ	reduced Planck's constant
k <sub>B</sub>	Boltzmann constant
$m_0$	electron rest mass
n	electron carrier concentration
$n_0$	equilibrium minority electron concentration
n <sub>ieff</sub>	effective intrinsic carrier concentration
n <sub>i</sub>	intrinsic carrier concentration
p	hole carrier concentration

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p	nanowire array pitch
$p_0$	equilibrium minority hole concentration
q	elementary charge
r	radial position
$r^*$	point of maximum recombination in the depletion region
$r_1$	radial position of the nanowire p-core/intrinsic shell interface
<i>r</i> <sub>2</sub>	radial position of the nanowire intrinsic shell/n-shell interface
$r_n$	edge of the depletion region in the n-doped nanowire shell
$r_p$	edge of the depletion region in the p-doped nanowire core
t	radioisotope source thickness
t <sub>i</sub>	nanowire intrinsic shell thickness
$t_n$	nanowire n-doped shell thickness
$v_{th}$	thermal velocity
W	depletion region width
Wi	intrinsic shell depletion region width
W <sub>n</sub>	n-shell depletion region width
Wp	p-core depletion region width
W <sub>src</sub>	radioisotope source width

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- z axial position
- Z atomic number

# **Declaration of Academic Achievement**

This thesis contains material that was previously published in academic journals. I, Amanda Thomas, declare that the work presented in this thesis, titled Design and Fabrication of a Gallium Phosphide Nanowire Betavoltaic Device, is solely my work, completed under the supervision of Dr. Ray LaPierre. Any references to other works within this document are clearly cited and credited. I acknowledge the contributions of the following contributors. Their efforts were essential to the completion of this thesis.

Former CEDT technician Shahram Ghanad-Tavakoli operated the molecular beam epitaxy reactor and oversaw the nanowire growths in Chapter 4. TNFC technician Alex Tsukernik operated the electron beam lithography (EBL) system. Simon McNamee designed the EBL pattern. Earlier PV and BV radial NW device physics models developed by Dr. Brendan Kayes and Devan Wagner, respectively, were the inspiration for the model in Chapter 2. Dave Novog is acknowledged for providing access to the <sup>63</sup>Ni source for BV device testing.

# **Chapter 1**

# Introduction

# **1.1 Background of Betavoltaics**

Betavoltaic devices (BV) operate analogously to photovoltaic (PV) devices. However, instead of relying on a photon flux source for the generation of electron-hole pairs, in a BV device, the continual spontaneous decay of the radioisotope's unstable nucleus results in the emission of a flux of electrons which carry large amounts of kinetic energy (on the order of keV). These highly energetic electrons are known as  $\beta$  particles. The  $\beta$  particles transfer their energy to the electrons of the semiconductor target material via Coulomb scattering and Bremsstrahlung emission<sup>1</sup>, triggering a series of impact ionization events, spurring the generation of electron-hole pairs (EHPs). The EHPs are separated by the semiconductor pn junction and collected into the contacts resulting in the generation of electrical power. A single scattering interaction can trigger thousands of impact ionization events. However, since the flux of the  $\beta$  particles is extremely low, BV devices generate very small current densities on the order of  $\mu$ A cm<sup>-2</sup> to nA cm<sup>-2</sup>. As a result, BV devices are most suitable for  $\mu$ W to nW applications<sup>2</sup> requiring extended periods of uninterrupted power output. Despite their low power densities, BV devices offer numerous advantages stemming from their small device footprint. BV devices occupy a compact spatial footprint, typically less than a cubic centimetre, resulting in very high energy densities ( $1 \text{ MJ cm}^{-3}$  to  $1000 \text{ MJ cm}^{-3}$ ), approximately  $10 \text{ to } 1 \times 10^4$  times higher than to their lithium-ion counterparts<sup>2,3</sup>, whereas the miniaturization of chemical batteries is restricted by their low energy density<sup>3</sup>. Because of the low decay rate (i.e. long half-life) of the radioisotopes used (1 to100 years), BV devices have the potential to supply power for many years beyond the limitations of conventional lithium-chemistry batteries. BV devices are also highly pressureand temperature-insensitive; as such, they are capable of operating in a variety of extreme environments that render conventional battery technology inoperable. With these considerations in mind, the goal of nuclear batteries is not to replace chemical batteries in high power output applications, but instead to provide power generation in low power applications where chemical batteries are not a feasible solution. Additionally, BV devices can be integrated with rechargeable chemical batteries and supercapacitors to provide continuous trickle charging<sup>3</sup>.

When designing a betavoltaic device, key considerations consisting of source material selection, semiconductor material selection and device geometry must be made. Based on the intended BV device applications, a radioisotope with a suitable decay rate should be chosen to meet operational lifetime requirements. In addition to half-life, the characteristic energy spectrum (specifically the average and maximum  $\beta$  decay energies) of the  $\beta$  source must also be considered. The  $\beta$  decay energy determines the overall power density of the BV device. Therefore, the  $\beta$  source should be chosen such that the emitted  $\beta$  flux maximizes the number of impact ionization event-generated EHPs per scattering

event within the semiconductor material without damaging the semiconductor lattice. Radioisotopes with decay energies below 100 keV are below the semiconductor lattice damage threshold, which is estimated to be between 100 keV to 200 keV<sup>4</sup>. Such radioisotopes are also easily shielded and safe for human use<sup>5</sup>.

The value of a semiconductor material's effective ionization energy has been shown to be independent of the nature of the ionizing particle<sup>6</sup>. Ionization is instead dependent on the type of ionizing particle or its energy. Given the ionization energy associated with a semiconductor, the radioisotope should be chosen such that the  $\beta$  particles, on average, will possess sufficient kinetic decay energy to trigger ionization upon impact with the semiconductor material. In addition to the half-life and characteristic energy considerations, the safety, availability and cost of the  $\beta$  source must also be considered. Limited availability of a given radioisotope can ultimately limit BV device commercialization scalability<sup>7</sup>. For applications involving human or animal interaction, such as biomedical implants, or use in IoT devices, source material safety is of the utmost concern. Sufficient shielding must be provided with all BV devices to avoid unintended interactions with the emitted ionizing radiation. The process of adequately shielding BV devices incurs additional manufacturing complexity and cost. As a result, high-purity sources with no secondary reactions are most suited for BV devices. Based on these requirements, <sup>3</sup>H, <sup>63</sup>Ni, and <sup>147</sup>Pm have emerged as the most commonly used radioisotopes in BV devices<sup>1,7,8</sup>.

The power conversion efficiency of a BV device is determined by the combination of the source material properties, semiconductor material properties, and device geometry. Each of these properties will be discussed in greater in detail in subsequent chapters. Many of the device performance metrics that govern PV devices, such as carrier collection efficiency, bandgap energy, recombination mechanisms, short-circuit current, open-circuit voltage, and fill factor, also govern BV device performance. As a result, BV device power conversion efficiency relies heavily on the semiconductor material's ability to both excite and extract EHPs. For an ideal BV device, the power conversion efficiency has been shown to be directly proportional the semiconductor bandgap energy, and inversely proportional to the effective ionization energy<sup>6</sup>. Higher open-circuit voltages are possible with wider bandgap materials, leading to higher power conversion efficiencies. In general, materials with longer minority carrier diffusion lengths possess higher carrier collection efficiencies<sup>9</sup>, owing to the fact that the minority carriers are able to diffuse a larger distance across the semiconductor junction towards the contacts (where collection occurs) before a recombination event occurs, thus contributing to the overall device current. Recombination outside of the collection areas within the device can be detrimental to device performance, as carrier collection effciency is reduced. Therefore, the growth of defect-free semiconductor materials in BV devices can significantly reduce the non-radiative recombination rate within a device. Given these limiting factors, the semiconductor material systems chosen must prioritize wide bandgap materials, the maximization of carrier collection efficiency, and the minimization of recombination outside of the collection areas within the BV device. Si, Ge, SiC, and GaN are common choices for BV devices<sup>10</sup>.

Finally, BV device geometry must be carefully considered. Traditional BV devices employ a two-dimensional (2D) planar device geometry in which planarized layers of radioisotope are deposited on a semiconductor substrate<sup>2</sup>. Due to the isotropic  $\beta$ -emission profile of radioisotopes, approximately half of the emitted  $\beta$  particles are not captured by the semiconductor material, thus limiting the practical efficiency of planar BV devices to the available surface area for source material deposition within range of the semiconductor junction. In a planar BV device, as more source material is deposited, a limiting thickness is reached where  $\beta$  particles emitted from the furthest point from the junction will be blocked by intermediate source material, resulting in what is known as self-shielding<sup>4</sup>. Self-shielding limits the total amount of  $\beta$  particles captured by the semiconductor junction, and thus the total  $\beta$  energy that reaches the semiconductor. A commonly proposed structuring solution to enhance  $\beta$  particle capture efficiency has been to adopt an interpenetrating device structure, in which the planarized radioisotope layer is embedded between two semiconductor layers. Such a configuration serves to promote the interaction of more  $\beta$  particles with the semiconductor and radioisotope source<sup>11</sup>. Although the  $\beta$  particle capture efficiency the additional cost incurred to grow a sufficiently thick capping layer of absorbing semiconductor material, or capping with another substrate, greatly limits the scalability of such a fabrication process. Furthermore, to achieve a compact device form factor whilst maintaining a high energy capacity requires a more complex BV device design than the conventional 2D planar device<sup>4</sup>.

# 1.2 III-V Nanowires

III-V semiconductor material systems have received a great deal of attention over the last fifty years for use in a variety of optoelectronic devices due to the wide array of alloy systems and associated material properties that exist<sup>2,12,13</sup>. Vertical III-V NW arrays can be used to overcome many of the limitations of planar BV device technology. Monte Carlo simulations by Wagner et al.<sup>14</sup> have shown that utilizing vertical NWs instead of thin films or bulk semiconductors should result in significant energy output and device performance improvements compared to traditional BV cells. Nanowire geometry simultaneously provides a larger volume for source material deposition as well as a larger volume of available absorbing semiconductor material. By vertically filling the space between the NWs, a greater volume of source material can be deposited in NW-based betavoltaic devices compared to planar devices. The increased interfacial area between the NWs and the  $\beta$ emitter source, results in improved energy coupling from the source to the semiconductor absorber. Using molecular beam epitaxy (MBE) and the vapor-liquid-solid (VLS) growth method, custom patterned vertical NW arrays that spatially confine charge carriers within the semiconductor on the nanometre scale can be synthesized, allowing for the mitigation of the aforementioned performance-limiting factors.

The primary limitation of planar III-V thin film device technologies is the limited number of material systems that can be grown directly on silicon substrates. Lattice constant mismatch between the substrate and epitaxially grown material dictates whether a film can be grown directly on the substrate. Unlike conventional thin film planar BV devices, NWbased device material systems are not limited by the lattice mismatch constraint. In NWs, lattice mismatch-induced strain can be relaxed elastically at the NW free surface without the formation of dislocations<sup>2</sup>, allowing for greater accommodation of lattice mismatchinduced strain within the NWs. As a result, NW heterostructures can be readily grown on inexpensive silicon substrates, offering increased flexibility in materials system choice at reduced manufacturing costs.

## **1.3** Literature Review

In 1953, Radio Corporation of America (RCA) pioneered the development of the first betavoltaic device<sup>4</sup>, comprised of a silicon p-n junction and a 50 mCi <sup>90</sup>Sr-<sup>90</sup>Y radioactive source. The silicon-based RCA device initially achieved a 0.4% conversion efficiency<sup>4</sup>. However, severe degradation of device performance was observed over the duration of one week, resulting in a final efficiency of 0.2%<sup>7</sup>. In general, semiconductors are susceptible to both displacement and ionization damage from incident radation. The decay of <sup>90</sup>Sr to <sup>90</sup>Y, followed by the decay of <sup>90</sup>Y, generated a flux of  $\beta$  particles of relatively large average energies ranging from 0.5 MeV to 2.3 MeV, exceeding the semiconductor lattice radiation damage threshold for silicon. During scattering interactions, the  $\beta$  particles of the <sup>90</sup>Sr-<sup>90</sup>Y source possessed sufficient kinetic energy to displace the atoms within the Si crystal lattice, leading to the observed rapid degradation of device performance. The work done by RCA highlighted the impact of the radioisotope's characteristic energy spectrum on device performance, motivating research into the use of alternative lower energy  $\beta$  emitter source materials.

In 1974, a group at Donald W. Douglas Laboratories, a subsidiary of the McDonnell Douglas Corp., led by Dr. L. C. Olsen developed the first commercialized betavoltaic device using a promethium <sup>147</sup>Pm source in the form of  $Pm_2O_3$  to avoid radiation damage within the semiconductor lattice. The device consisted of stacked layers of silicon cells coupled to the promethium source. The Donald W. Douglas Laboratories device was licensed for commercial use in cardiac pacemakers under the product name Betacel, with over 100 people receiving pacemakers powered by Betacel devices before the eventual termination of the Betacel project. The Betacel battery achieved an output power of up to 400  $\mu$ W and an efficiency of 4 %, with a reported lifetime of up to 10 years<sup>7</sup>. Despite the substantial progress made in the development of betavoltaic device commercialization, the Betacel devices suffered from high fabrication cost and a limited availability of <sup>147</sup>Pm. Due to the

presence of <sup>146</sup>Pm, a contaminant generated by the decay of the <sup>147</sup>Pm source<sup>7</sup>, additional shielding was required within the device to prevent the escape of harmful gamma radiation, resulting in increased device volume and production cost.

In 2005, using standard semiconductor device fabrication techniques, Sun and colleagues reported the fabrication of a novel betavoltaic device consisting of a tritium (<sup>3</sup>H) source and a three-dimensional (3D) porous silicon diode structure (see Fig. 1.1), demonstrating an order of magnitude improvement of betavoltaic power-generation efficiency compared to reported efficiencies of planar devices<sup>8</sup>. A 3D network of pores of varying sizes, classified as microporous ( $\leq 2$  nm), mesoporous (2 nm to 50 nm), or macroporous (> 50 nm), was formed between a depth of 40 µm to 50 µm along the surface of the Si substrate via electrochemical anodization. Following the formation of the porous network, p-n junctions were introduced on all accessible surfaces of the pores via solid-source diffusion<sup>8</sup>.



Figure 1.1: Representation of the porous silicon 3D device structure. The continuous p-n junction in neighboring pores is shown. Modified from Ref. 8.

Using a 3D porous morphology, the majority of the device characteristics associated with conventional 2D planar geometries were maintained within the pores due to the large internal surface areas observed within the pores. The prevalence of this phenomenon was shown to increase with pore size<sup>8</sup>. For the porous channels of the 3D BV device, Sun et

al. demonstrated an energy conversion efficiency ratio  $\eta_{3D}/\eta_{2D}$  of 9.9 ± 2.2. The observed device performance improvements were attributed to the geometry increase from two dimensions to three dimensions, suggesting that nearly every emitted  $\beta$  particle (~84%) entered a nearby porous silicon BV junction as a result<sup>8</sup>.

In the years following the Betacel project, progress in BV technology development waned primarily as a result of improved performance and safety of lithium-chemistry batteries, as well as significant manufacturing cost reductions. Combined with the rise of lithium-chemistry batteries, increased public concerns over the safety of radioactive materials contributed to the steep decline in research efforts towards betavoltaic device development.

In the early to mid 2000s, research into wide bandgap semiconductors and high-purity radioisotope sources resulted in a small succession of efforts to develop commercially viable betavoltaic devices. There presently exists a handful of active commercial betavoltaic device manufacturers. The devices produced by these companies demonstrate output powers ranging from 5  $\mu$ W to 100  $\mu$ W using <sup>3</sup>H or <sup>63</sup>Ni-based sources. Building on the work by Sun et al, BetaBatt has employed a 3D diode geometry within their trademarked *BetaBattery* device design to develop devices whose performance exceeds current planar BV devices. BetaBatt is currently developing a betavoltaic device consisting of tritiated 3D silicon diodes to serve as micro-power unit sources for a variety of applications. Performance metrics for current commercially available BV batteries are listed in Table 1.1.

Company/Device	Source	Activity	Power	SC Material	Geometry
City Labs - NanoTritium	<sup>3</sup> H	100 mCi	100 µW	Si compound	2D
Widetronix - Firefli-N	<sup>63</sup> Ni	5 to 500 mCi	5 to 500 nW	SiC	2D
Widetronix - Firefli-T	<sup>3</sup> Н	25 mCi to 2.5 Ci	10 to 1000 nW	SiC	2D
BetaBatt - BetaBattery	Tritiated Butyl	8 Ci	25 μW	Porous Si (PS)	3D

Table 1.1: Device specifications for current commercially available BV devices. It should be noted that the BetaBattery is currently in development.

In 2018, McNamee developed a prototype NW betavoltaic device in which a solgel containing <sup>63</sup>Ni was deposited in the volume between the NWs via a spin-coating process<sup>4</sup>. The prototypical device consisted of p-i-n core-shell morphology GaP NWs with an Al<sub>0.3</sub>Ga<sub>0.7</sub>P passivating shell. The p-type and n-type regions were doped with Be and Te concentrations of  $5 \times 10^{18}$  cm<sup>-3</sup> and  $10^{19}$  cm<sup>-3</sup>, respectively. A  $\beta$  current on the order of a few tenths of a  $\mu$ A was observed, confirming the existence of the betavoltaic effect in the NW-based device as well as the applicability of the fabrication methods used to develop the BV device. However, an extremely low power conversion efficiency of less than 0.5 % was reported. The poor device performance observed has been attributed to the semiconductor NW junction design and NW array geometry designs<sup>4</sup>, highlighting numerous avenues for device optimization.

# **1.4 Thesis Overview**

This thesis addresses fundamental challenges in betavoltaic (BV) device technology, with a particular focus on overcoming the geometrical constraints inherent in conventional designs. Despite a half-century history of BV device development, the technology remains relatively unexplored, especially regarding the theoretical and practical limitations of III-V NW-based implementations. The research presented herein examines the intricate relationships between device geometry and material properties, while demonstrating the successful application of advanced NW processing techniques in the fabrication of GaP NW-based BV generators.

The dissertation is structured into six chapters. Chapter 2 establishes the theoretical foundation through the development of an analytical device physics model for NW BV devices, considering both two- and three-dimensional source material geometries. This model enables comprehensive simulation of electrical I-V characteristics across GaP, GaAs, and Si material systems, incorporating various NW morphologies. The analysis encompasses critical efficiency parameters—including short-circuit current density, open-circuit voltage, fill factor, and energy conversion efficiency—while also investigating the impact of array geometries such as pitch spacing.

Chapter 3 explores the synthesis of III-V NWs through vapor-liquid-solid (VLS) growth using molecular beam epitaxy (MBE). This chapter details the development and optimization of MBE growth protocols for core-shell GaP NW arrays, alongside comprehensive experimental preparation procedures. The subsequent chapter outlines the device fabrication methodology, encompassing polymer planarization and back-etching, photolithographic top contact patterning, magnetron sputter deposition, and rapid thermal annealing processes.

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Experimental electrical characterization of the NW BV device is presented in Chapter 5, where device performance is evaluated through electrical measurements under exposure to an external solid <sup>63</sup>Ni source using a four-point probe configuration. The dissertation concludes with Chapter 6, which not only addresses the processing challenges encountered during device fabrication, but also proposes potential solutions and identifies promising directions for future advancement in III-V NW-based BV technology. Through this systematic investigation, the thesis contributes to both the fundamental understanding and practical implementation of NW-based betavoltaic devices.

# **Chapter 2**

# Analytical Model of a Nanowire-Based Betavoltaic Device

This chapter is reproduced from the publication:

Amanda Thomas, Ray R. LaPierre; Analytical model of a nanowire-based betavoltaic device. J. Appl. Phys. 7 April 2024; 135 (13): 134302. https://doi.org/10.1063/5.0202949

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# 2.1 Introduction

The need for robust and versatile energy sources that surpass the limitations of traditional lithium-based batteries have made betavoltaic (BV) devices a solution with promising potential<sup>7,15–17</sup>. BV devices employ the direct conversion of radioactive decay energy into electrical power through a process analogous to the photovoltaic effect. In a BV device, the energy of the highly energetic electrons ( $\beta$  particles) emitted from a radioisotope source

generates electron-hole pairs (EHPs) within a target semiconductor material through impact ionization events induced by a series of scattering interactions between the betas and the semiconductor target. The separation and collection of the EHPs into the contact regions by the semiconductor p-n junction results in the generation of electrical power.

Given the low flux of  $\beta$  particles from typical radioisotopes, BV devices generate very small current densities on the order of  $\mu$ A/cm<sup>2</sup> to nA/cm<sup>2</sup>.<sup>7,15,18</sup> The half-life of the radioisotope determines the lifetime of the device (up to 100 years from <sup>63</sup>Ni, for example). BV devices are also compact, occupying less than a cubic centimeter of volume. The temperature insensitivity of BV devices allows for continuous operation with minimal fluctuations in device performance in a variety of environmental conditions. The small footprint, long lifetimes, and operational robustness of BV devices make them highly suited for low power applications, particularly those that necessitate minimal or remote access. BV devices have found utility in a diverse range of fields, including health-care, space exploration, deep-sea operations, and military defense/intelligence industries<sup>7,16,17</sup>.

Conventional BV devices employ a planar geometry (the radioisotope is deposited as a thin film on top of the semiconductor), resulting in the loss of nearly half of the isotropically emitted  $\beta$  flux, reducing device conversion efficiency. Planar BV devices are limited by the available surface area for source deposition. Increasing the source thickness results in a saturation of  $\beta$  flux due to self-absorption of the betas by the source material. In 2005, Sun et al. fabricated a tritium (<sup>3</sup>H) source BV device with a porous silicon diode structure, reporting improvement of the BV power-generation efficiency by a factor of 10 compared to planar devices<sup>8</sup>. The observed device performance improvements were attributed to the geometry from 2D to 3D, suggesting nearly every emitted  $\beta$  entered a nearby porous silicon BV junction as a result<sup>8</sup>. Many of the performance-limiting factors of planar BV

devices can be mitigated by adopting a 3D interpenetrating device structure, in which the  $\beta$  emitter source is embedded in the volume between nanowires (NWs). This results in increased source deposition and overall device efficiency.

Unlike thin film BV devices, NW-based device material systems are not limited by the lattice mismatch constraint. In NWs, lattice mismatch-induced strain can be relaxed elastically at the NW free surface without the formation of dislocations<sup>2</sup>, allowing for greater accommodation of lattice mismatch-induced strain within the NWs. As a result, NW heterostructures can be readily grown on inexpensive silicon substrates, offering increased flexibility in materials system choice at reduced manufacturing costs. The limiting efficiency of a betavoltaic device can be approximated by the ratio of the active region bandgap and the effective ionization energy. Gallium phosphide's relatively large bandgap energy of 2.26 eV corresponds to a limiting efficiency of ~25 %<sup>4</sup>, exceeding that of conventional silicon-based BV devices. We present an analytical device physics model that simulates the current-voltage (J-V) characteristics of NW array-based betavoltaic devices for nanostructured and planar source configurations. This model serves as a roadmap to determine the ideal geometry and material properties of p-i-n NW arrays, crucial for the development of a betavoltaic battery.

# 2.2 Model Description

The analytical device physics model presented herein was adapted from the model developed by Kayes et al. for a radial p-n junction NW-array solar cell in Ref. 19 to reflect the carrier transport mechanisms in a NW-based betavoltaic device. Each NW in the array has a core-shell p-i-n junction. Two array source material configurations were investigated: a two-dimensional (planar) source material configuration, in which the radioactive source material is placed on top of the NW arrays where the NWs are oriented with their vertical axis parallel to the direction of absorption of the incident  $\beta$  particle flux, and a three-dimensional source material configuration in which the source material is embedded within the array, occupying the volume between the NWs as shown in Fig. 2.1. The energy conversion efficiencies of both configurations were compared to evaluate the implications of geometry on the various aspects of device performance.



Figure 2.1: a) Nano-structured betavoltaic device schematic. The radioisotope source material occupies the volume between the NWs. In the planar source configuration, the volume between the NWs is instead filled with a planarizing electrically insulating polymer and the source material is deposited atop the NW tips. *L* is the NW length, *d* is the NW diameter and *p* is the pitch (separation) between NWs. b) NW p-i-n junction radial crosssection.  $R_p$  is the p-core radius,  $t_i$  is the intrinsic shell thickness, and  $t_n$  is the n-shell thickness. Carrier separation occurs along the radial direction. The anode and cathode electrodes are deposited on back of the p-type substrate and on the nanowire n-shell, respectively.

The model was constructed by solving the minority carrier drift-diffusion transport equations, as well as Poisson's equation, in the cylindrical geometry (shown in Fig. 2.1) for a set of boundary conditions within each respective region of the junction. Combining the solutions for each component of the device current density, the total device current density can be expressed as a function of the bias voltage, referred to as the device J-V characteristic, J(V). The short-circuit current density  $J_{sc}$ , open-circuit voltage  $V_{oc}$ , fill factor FFand energy conversion efficiency  $\eta$  were subsequently determined from the resulting J-V characteristic. The core-shell geometry was used as the primary parameter optimization search space. The input parameter space was constructed from the set of p-doped core diameter and n-doped shell, from which the unintentionally doped shell thickness was implicitly determined<sup>1</sup>. The conversion efficiencies of each simulated J-V characteristic were computed and plotted as a function of the core-diameter  $d_p(=2R_p)$  and n-shell thickness  $t_n$ . The derivations of Poisson's equation and the minority carrier transport equations are provided in Appendices I. and II.

## 2.2.1 Dark Conditions

In the absence of an incident  $\beta$  flux, the excess minority carrier generation rate vanishes and the solutions to the steady-state excess minority carrier continuity equations are the solutions to the homogeneous continuity equations. The boundary conditions under dark conditions within the p-type and n-type quasi-neutral region (QNR) are given by Eq. (A45) and Eq. (A46) of the Appendix, respectively,

$$\begin{cases} \lim_{r \to 0} |\Delta n(r)| < \infty \\ \\ \Delta n(r) \Big|_{r=r_p} = n_0 \left( e^{\frac{qV}{k_B T}} - 1 \right) \end{cases}$$
(2.2.1)

<sup>&</sup>lt;sup>1</sup>The intrinsic shell thickness was assumed to occupy the remainder of the NW diameter for a given p-core diameter and n-shell thickness  $(d_p, t_n)$ .

$$\begin{cases} \Delta p(r) \Big|_{r=r_n} = p_0 \left( e^{\frac{qV}{k_B T}} - 1 \right) \\ \\ S_p \Delta p(r) \Big|_{r=R} = -D_p \frac{\partial \Delta p}{\partial r} \Big|_{r=R} \end{cases}$$
(2.2.2)

where  $S_p$  is the surface recombination velocity (SRV) of the minority holes at the external NW surface<sup>19</sup>, *V* is the bias voltage, *q* is the elementary charge,  $k_B$  is the Boltzmann constant, *T* is the temperature,  $r_p$  is the edge of the depletion region in the p-doped core, and  $r_n$  is the edge of the depletion region in the n-shell. Surface recombination velocities were selected assuming passivation of the exterior NW shell surface (Table A7 in Appendix VI.). In these operating conditions the minority carrier injection and recombination currents constitute the device current.

#### 2.2.2 Short-circuit Conditions

The short-circuit current density of the junction corresponds to the  $\beta$ -current generated in the absence of any external bias voltage  $J_{sc} = J(V = 0)$ . The boundary conditions under short-circuit conditions within the p-type and n-type QNRs are given by Eq. (A47) and Eq. (A48), respectively,

$$\begin{cases} \lim_{r \to 0} |\Delta n(r, z)| < \infty \\ \\ \Delta n(r, z) \Big|_{r=r_p} = 0 \end{cases}$$
(2.2.3)

$$\begin{cases} \Delta p(r,z) \Big|_{r=r_n} = 0 \\ \\ S_p \Delta p(r,z) \Big|_{r=R} = -D_p \frac{\partial \Delta p}{\partial r} \Big|_{r=R} \end{cases}$$
(2.2.4)

The total output current density within the QNRs was computed by summing the individual current contributions of each radial cross-section of the NW over its length.

## 2.2.3 Electron-Hole Pair Generation

Impinging  $\beta$  particles deposit their kinetic energy in the semiconductor via a sequence of elastic and inelastic scattering interactions until they either escape the host material, or deposit the entirety of their kinetic energy, at which point they reach thermal equilibrium with the host<sup>20,21</sup>. The inelastic collisions stimulate the generation of carriers within the absorbing medium via the absorption of the  $\beta$  electron energy during collisions, or via ionization due to the displacement of host atoms<sup>20</sup>.

Stopping power S(E) describes the rate of energy loss per unit path length (*s*) of charged particles travelling through a material. The Bethe-Bloch equations<sup>22</sup> describe the stopping power of a material for incident charged particles of a given energy using the continuous energy loss approximation<sup>21</sup>,

$$S(E) = -\frac{1}{\rho} \frac{\mathrm{d}E}{\mathrm{d}s} \tag{2.2.5}$$

where  $\rho$  is the material mass density. Absorber media with similar atomic composition as well as density-normalized thickness values are expected to possess similar mass stopping powers<sup>23</sup> because stopping power depends primarily on the density and atomic composition of the material, both of which are related to the material's electron density. Materials with higher atomic number Z and density typically have higher stopping powers as they contain more electrons per unit volume for the  $\beta$  particle to interact with, which can greatly influence the  $\beta$  particle's trajectory within the host material. Moreover, materials with similar atomic composition will have broadly similar stopping powers as the similar underlying mixture of elements will yield broadly similar electronic configurations.

The electron-hole pair generation rate within the semiconductor is proportional to the rate of energy dissipation by the impinging  $\beta$  electrons<sup>24</sup>. The incident  $\beta$  electron energy can be replaced by the  $\beta$  electron range<sup>24</sup> in Eq. (2.2.6). The total average energy dissipated by a  $\beta$  particle within an absorber material at a given penetration depth x is described by the  $\beta$  particle's energy deposition profile  $E_{dep}$ . It is determined from the material's stopping power by integrating the product of the stopping power and the  $\beta$  particle energy probability distribution P over the  $\beta$  energy spectrum<sup>25</sup>.

$$E_{dep} = \int_0^x dR' S(R') P(R')$$
 (2.2.6)

Electronic (mass) stopping power data tables from the NIST *ESTAR* database<sup>26</sup> were used for each of the materials. P was obtained from Ref. 27. Radioisotope material properties are listed in Table A8 in Appendix VII.

The incident  $\beta$  particle energy is related to the  $\beta$  particle range  $\bar{R}$ , which corresponds to the maximum average distance travelled by an incident  $\beta$  particle with kinetic energy E within a given target material before depositing the entirety of its kinetic energy. Alternatively,  $\bar{R}$  can be interpreted as the minimum absorber thickness required to stop an incident  $\beta$  particle with average energy E. The average  $\beta$  range — expressed in terms of the density-normalized absorber thickness — for mono-energetic  $\beta$  particles is described by the semi-empirical single range-energy equation in Eq. (2.2.7) determined by Katz and Penfold<sup>28</sup>:

$$\bar{R} = \begin{cases} 412E^{(1.265 - 0.0954 \ln E)}, & 0.01 < E < 2.56 \text{ MeV} \\ 530E - 0.106, & 2.56 < E < 20 \text{ MeV} \end{cases}$$
(2.2.7)

where *E* is the incident  $\beta$  electron energy in MeV, and  $\overline{R}$  (mg cm<sup>-2</sup>) is the corresponding density-normalized range. Equation (2.2.7) was used to determine the  $\beta$  particle range for a given incident  $\beta$  particle energy. The upper-bound limit of integration of the  $\beta$  particle penetration depth in Eq. (2.2.6) was computed from Eq. (2.2.7) assuming the maximum  $\beta$  particle energy  $E_{max}$ .

The EHP generation rate is given by:

$$G = A_{s}\rho_{s}f_{sa}\eta_{\beta}\eta_{pp}$$
  
=  $A_{s}\rho_{s}f_{sa}\eta_{\beta} \times \frac{E_{dep}}{\varepsilon_{_{EHP}}}$   
=  $A_{s}\rho_{s}f_{sa}\eta_{\beta} \times \frac{E_{dep}}{2.8E_{g} + 0.5}$  (2.2.8)

where  $\eta_{\beta}$  ( $\beta$  capture efficiency) is the fraction of emitted  $\beta$  particles directed towards a pi-n junction within the unit cell (Fig. 2.2),  $f_{sa}$  is the radioisotope self-absorption loss factor,  $\rho_s$  is the source density,  $A_s$  is the source activity, and  $\eta_{pp}$  is the EHP production efficiency. The EHP production efficiency quantifies the semiconductor's utilization of the absorbed  $\beta$  particle's kinetic energy towards EHP generation. It is the ratio of the  $\beta$  particle energy deposited in the semiconductor to the mean energy required to generate an EHP in the absorber medium,  $E_{dep}$  and  $\varepsilon_{_{EHP}}$ , respectively.

The semi-empirical relationship of  $\varepsilon_{\rm FHP}$  in the denominator of Eq. (2.2.8) describes EHP

production in semiconductor materials due to incident  $\beta$  radiation, and was presented by Klein in Ref. 29. As the impinging  $\beta$  particle penetrates the converter volume, its kinetic energy is transferred to the converter volume's crystal lattice, resulting in a cascade of EHP production events. On average, approximately 1.8  $E_g$  of the incident  $\beta$  energy deposited in the converter volume is lost to acoustic phonon generation and ~0.5 eV is lost to optical phonon generation<sup>15</sup> during a pair production event. The remainder of the incident  $\beta$ energy stimulates the production of the EHP. Thermalization reduces the semiconductor efficiency of the BV device, thus reducing the overall conversion efficiency.

The  $\beta$  capture efficiency  $\eta_{\beta}$  consists of losses derived from both the source and NW geometries. For a slab source placed above the NWs, at most 50% of emitted  $\beta$  particles will be transmitted towards the converter volumes. Embedding the source material between the NWs mitigates these directional source losses by increasing the number of directions along which emitted  $\beta$  particles are likely to encounter a converter volume. In practice, the slab source efficiency is significantly lower than 50% due to other prevalent loss mechanisms such as self-absorption and backscattering losses.

The directional source losses associated with the source geometry were modelled by the  $\beta$  capture efficiency in Eq. (2.2.9). The geometric form factor corresponding to the  $\beta$  capture efficiency is given by the ratio of the total contribution of source surface area elements within the unit cell whose emitted  $\beta$  particles are directed towards a nearby NW to the total source surface area within the unit cell. The NWs are arranged in the hexagonal lattice shown in Fig. 2.2. A rectangular non-primitive unit cell was selected, with each unit cell containing 2 NWs. The  $\beta$  capture efficiency for the 2D geometry (radioisotope source slab on top of the NWs) and the 3D geometry (source between the NWs) is given, respectively, by

$$\begin{cases} \eta_{\beta}^{2\mathsf{D}} = \frac{\sqrt{3}p^{2}}{2pt + 2\sqrt{3}pt + 2\sqrt{3}p^{2}} \times \left(\frac{A_{cell}^{NW}}{A}\right) \\ \\ \eta_{\beta}^{3\mathsf{D}} = \frac{2\pi dt + 2(p-d)t + 2\left(\sqrt{3}p - d\right)t}{2\pi dt + 2(p-d)t + 2\left(\sqrt{3}p - d\right)t + 2\left(\sqrt{3}p^{2} - \frac{\pi d^{2}}{2}\right)} \times (\mathsf{F} - \mathsf{ratio}) \end{cases}$$
(2.2.9)

where (Fig. 2.2) p is the separation (pitch) between NWs, t is the radioisotope source slab thickness, A is the area of the array unit cell,  $A_{cell}^{NW}$  is the cross-sectional area of the NWs within the unit cell, and F-ratio is defined below for the 3D geometry. In the 3D geometry, the source thickness t is given by the NW length.

When the source material is placed on top of the NWs,  $\beta$  capture losses can be incurred from the empty spaces between the wires. The  $\beta$  particles that are emitted downwards towards the empty regions between the NWs will not be captured, and thus do not contribute to the device current, assuming negligible scattering towards the NWs. The ratio of the NWs cross-sectional area to the unit cell cross-sectional area represents the packing fraction of the NWs within the unit cell. Maximizing NW packing in the array maximizes the capture of available betas. Similarly for a 3D source geometry, a filling ratio (F – ratio) is defined for the source volume. The filling ratio accounts for the variations in the apparent source activity owing to modulation of the source volume. The source activity is proportional to the source volume. Thus, increasing the source volume yields larger source power densities in the absence of self-absorption effects. The filling ratio is quantified by the fraction of the unit cell area occupied by the source material<sup>2</sup>:

F - ratio = 
$$\frac{\sqrt{3}p^2 - \frac{\pi d^2}{2}}{\sqrt{3}p^2} = 1 - \frac{\pi}{2\sqrt{3}} \left(\frac{d}{p}\right)^2$$
 (2.2.10)

-



Figure 2.2: a) NW array hexagonal lattice, with periodic NW spacing (pitch) p and diameter d. The NW positions are depicted by the circles. b) Rectangular non-primitive unit cell used to determine the simulated source and converter volumes. c) Simulated radioisotope cross-sectional area within the unit cell.



Figure 2.3: Simulated nano-structured source volume.  $w_{src} \equiv (p - d)$  is the source width and t is the vertical source thickness.  $\beta$  particles (green sphere) emit uniformly in all directions.

<sup>&</sup>lt;sup>2</sup>The filling ratio is unity for the planar case in which the radioisotope sits atop the NWs since the source material covers the entire unit cell area.

By Eq. (2.2.11), self-absorption losses become more pronounced as the source thickness *t* increases;  $\mu$  is the radioisotope's linear attenuation coefficient. The vertical source thickness of the 2D planar source was scaled to yield a power input density equivalent to that of the 3D configuration, allowing for the direct comparison between the 2D and 3D source geometries.

$$f_{sa} = \frac{1 - e^{-\mu t}}{\mu t} \tag{2.2.11}$$

<sup>63</sup>Ni was chosen as the radioisotope for all cases. Two source material configurations were examined to assess the impact of employing nano-structuring techniques on the device performance: a thin-film source placed on top of the NWs, and a (3D) configuration in which the source material occupies the volume between the NWs within the array — the proposed device schematic is shown in Figs. 2.1 and 2.3. When the source material is placed atop the NWs the generation rate of excess carriers within the NW due to the absorption of incident *β* particles decays exponentially along the NW's vertical axis. The EHP generation rate along the NWs can be approximated by a stretched exponential function as shown in Ref. 30:

$$G(z) = G_0 \exp\left(-\left(\alpha z\right)^{\nu}\right) \tag{2.2.12}$$

where  $\alpha$ ,  $G_0$ , and v correspond to the absorption coefficient, maximum EHP generation rate, and stretching factor, respectively. The absorption coefficient describes the decay of excess EHPs generated by impinging  $\beta$  particles within the semiconductor<sup>31</sup>.

For the 3D source configuration in which the source material occupies the volume surrounding the NWs, the EHP generation rate along the radial direction of the NWs can be approximated by a Gaussian function ( $v \approx 2$ )<sup>32,33</sup>. However, due to the slowly varying nature of the Gaussian, the EHP generation rate varies very little (<1%) over the NW's diameter length scale (10s - 100s of nm). A constant EHP generation rate was therefore assumed for the 3D source configuration.

$$G \simeq G_0 \tag{2.2.13}$$

For example, the EHP generation rate in GaP is shown in Fig. A3 of Appendix VII. The absorption coefficient, maximum EHP generation rate, and stretch factor in Eq. (2.2.13) were determined from fits to the EHP generation rate. A stretching factor of 2.3 was obtained for the fit to Eq. (2.2.12), closely approximating a Gaussian line-shape. For 3D source geometry configurations, all of the external NW surface area along the length of the NWs contacts the source material, and is readily available for absorption of the impinging betas.

#### 2.2.4 Total Device Current Density

The total device output current density J(V) is the superposition of the  $\beta$ -generated and recombination current densities in the QNR and depletion regions:

$$J(V) = J_{dark}(V) - J_{sc}$$
(2.2.14)

where  $J_{\text{dark}}$  consists of the injection and recombination current densities.  $J_{\text{sc}}$  is the shortcircuit current density due to the flux of incident  $\beta$  particles. The recombination current density in the depletion region consists of recombination due to radiative, Auger, and Shockley-Read-Hall (SRH) recombination, discussed in Section 2.2.5. Solutions for J(V)are presented in Eqs. (A36) to (A59).

#### 2.2.5 Carrier Recombination

Carrier recombination in the depletion region is attributed to Shockley-Read-Hall, Auger, and radiative recombination mechanisms. In general, the recombination current densities are computed by integrating the recombination rates over the volume:

$$J_{\rm rec} = \frac{q}{\pi R^2} \iiint dV U_{\rm rec} = \frac{2q}{R^2} \iint r dr dz U_{\rm rec}$$
(2.2.15)

The minority carrier lifetimes in the depletion region ( $\tau_{n_0,p_0}$ ) were computed as a function of the trap state density  $N_T$  and the capture cross-sections  $\sigma_{n,p}$  from Eq. (A76) in the Appendix. As a result, the minority carrier lifetimes in the depletion regions of Si and GaAs were set to ~1 µs. A depletion region minority carrier lifetime of ~2 ns was selected for GaP. The minority carrier lifetimes within the QNRs were computed as functions of the acceptor and donor dopant concentrations according to semi-empirical models from literature. Details of the carrier recombination rate derivations and material parameters are discussed in Appendices III. to VI.

#### 2.2.6 J-V Characteristics

The input source power density  $P_{in}$  is defined by,

$$P_{\rm in} = \frac{A_s \rho_s V_s E}{A} \tag{2.2.16}$$

where  $A_s$  is the specific activity of the source,  $V_s$  is the source volume,  $\overline{E}$  is the mean energy of the  $\beta$  spectrum, A is the source area within the simulated unit cell, and  $\rho_s$  is the source density. Slab source device simulations were configured to match the input power density of the 3D devices to allow for the direct comparison between planar and 3D source geometries. For <sup>63</sup>Ni,  $\bar{E} = 17.45$  keV.

The device conversion efficiency  $\eta$  is given by,

$$\eta = \frac{J_{\rm sc}V_{\rm oc}FF}{P_{\rm in}} \tag{2.2.17}$$

The fill factor (FF) is a measure of the device's rectification and is thus considered to be a measure of the p-i-n quality<sup>34</sup>. It is the ratio of the maximum device output power density to the maximum theoretically achievable output power density. The fill factor can also be interpreted graphically as the squareness of the J-V curve<sup>35</sup>

$$FF = \frac{J_{mp}V_{mp}}{J_{sc}V_{oc}}$$
(2.2.18)

where  $J_{mp}$  and  $V_{mp}$  are the current density and voltage, respectively, at the maximum power point. Solutions to the minority carrier drift-diffusion equations are presented in Appendix II.

## 2.3 Results and Discussion

Device performance predictions ( $J_{sc}$ ,  $V_{oc}$ , FF,  $\eta$ ) were obtained for GaP, GaAs, and Si for various NW lengths (L = 1, 3, 5, 7.5, 9 and 10 µm) and NW diameters (D = 200, 260, 300, 400, 500, 550, 600, 700, 800 and 900 nm). The diameter-pitch ratio was varied from 0.1 to 0.95. The acceptor and donor concentrations were varied ( $N_A = 5 \times 10^{18}$  and  $10^{19}$  cm<sup>-3</sup> and  $N_D = 10^{17}, 5 \times 10^{18}$  and  $10^{19}$  cm<sup>-3</sup>). The best efficiencies for 2D and 3D source geometries are summarized in Table 2.1 and Fig. 2.4 for GaP, GaAs and Si. The best GaP results in

Table 2.1 were determined from the Figs. 2.5 and 2.6 surface plots. Optimum results for Si and GaAs are available in Figs. A5 to A8.

Of the semiconductor materials selected, GaP devices outperformed their counterparts for both 3D and 2D planar source geometries. Improvement factors of ~7.9, 7.8 and 8.7 were observed for GaP, GaAs and Si, respectively, for 3D source configurations compared to using a planar thin film source. These results demonstrate the substantial gains in device performance that can be realized by careful engineering of the source and converter geometry.

Table 2.1: Best device efficiency results across all simulated devices for GaP, GaAs, and Si planar (2D) and 3D source configurations.

		N <sub>A</sub>	$N_D$	$(d_p, t_n, t_i)$	(d:p)	D	L	$J_{\rm sc}$	V <sub>oc</sub>	FF	η	Improvement Factor
		cm <sup>-3</sup>	cm⁻³	nm		nm	μm	µAcm <sup>-2</sup>	V		%	
GaP	2D	10 <sup>19</sup>	5 × 10 <sup>18</sup>	(459, 49.5, 171)	0.95	900	1	0.0328	0.997	0.806	1.02	7.9
	3D	10 <sup>19</sup>	$5 \times 10^{18}$	(24, 29.4, 58.6)	0.4	200	10	2.34	1.096	0.809	8.05	
Calle	2D	10 <sup>19</sup>	$5 \times 10^{18}$	(468, 207, 9)	0.95	900	1	0.057	0.55	0.802	0.961	7.6
GdAS	3D	10 <sup>19</sup>	$5 \times 10^{18}$	(24, 46, 42)	0.4	200	10	4.05	0.58	0.807	7.32	7.6
Si	2D	10 <sup>19</sup>	10 <sup>19</sup>	(458, 220.5, 17)	0.95	900	1	0.066	0.24	0.627	0.382	0.7
	3D	$5 \times 10^{18}$	10 <sup>19</sup>	(86, 47, 10)	0.4	200	10	4.67	0.29	0.623	3.34	0.7



Figure 2.4: Best efficiencies of the simulated devices for 3D and 2D  $^{63}$ Ni source configurations. The NW diameter was varied from D = 200, 260, 300, 400, 500, 550, 600, 700, 800 and 900 nm. For each diameter, devices were simulated for NW lengths varying from <math>L = 1, 3, 5, 7.5, 9 and 10 µm. In order to investigate the effects of the device geometry for each NW diameter the NW array pitch was set such that the ratio of the NW diameter to the array pitch (d : p) was varied from 0.1 to 0.95.



Figure 2.5: Simulated GaP betavoltaic devices for a 3D source configuration with properties a)  $J_{sc}$  b)  $V_{oc}$ , c) FF, d) efficiency.  $N_A = 10^{19} \text{ cm}^{-3}$ ,  $N_D = 5 \times 10^{18} \text{ cm}^{-3}$ , D = 200 nm,  $L = 10 \,\mu\text{m}$ , (d:p) = 0.4.



Figure 2.6: Simulated GaP betavoltaic devices for a 2D source configuration with properties a)  $J_{sc}$  b)  $V_{oc}$ , c) FF, d) efficiency.  $N_A = 1 \times 10^{19} \text{ cm}^{-3}$ ,  $N_D = 5 \times 10^{18} \text{ cm}^{-3}$ , D = 900 nm, L = 1 µm, d : p = 0.95

#### 2.3.1 General Trends

#### 2.3.1.1 Nanowire Length

A linear correlation was observed between the NW length and the energy conversion efficiency when a 3D source geometry was used (see Fig. 2.7). The optimum conversion efficiency increased from 6.62 % to 8.05 % when the NW length was varied from 1  $\mu$ m to 10  $\mu$ m, respectively, and the NW diameter was held constant at 200 nm in Fig. 2.7. Longer NWs yielded higher efficiencies for each of the materials examined. The strong positive correlation stems from the high source loading that can be achieved with tall NWs. The distance between adjacent NWs ( $w_{src}$ ; see Fig. 2.3) remains constant as the NW length scales. Provided the source width remains on the order of 10s to a few 100 nm, then selfabsorption losses will be mitigated as the beta particle escape probability remains very high. Larger source volumes increase the radioisotope's activity, raising the total number of beta particles emitted towards the NWs. This enhanced the EHP generation rates within the surrounding NWs as the beta source deposited more power into the NWs. The input power density rose from  $2.58 \,\mu$ W/cm<sup>2</sup> to  $25.83 \,\mu$ W/cm<sup>2</sup> when the NW length was increased from  $1 \,\mu$ m to  $10 \,\mu$ m. The short-circuit current increased as more excess carriers were generated within the depletion regions of the p-i-n junctions, and subsequently separated and collected.



Figure 2.7: Efficiency as a function of the NW p-core diameter and n-shell thickness for simulated 3D source geometry GaP betavoltaic devices. The NW length was varied from a) 1 µm b) 5 µm c) 10 µm, while the NW diameter, dopant concentrations, and diameter-pitch ratio were fixed at D = 200 nm,  $N_A = 10^{19}$  cm<sup>-3</sup>,  $N_D = 5 \times 10^{18}$  cm<sup>-3</sup>, and d : p = 0.4, respectively.

Conversely, predicted device performance degraded as the source width became comparable to the beta particle range. This is because, on average, emitted beta particles no longer possessed sufficient energy to escape the source material and penetrate a nearby NW. The emitted betas instead deposited their energy into the surrounding radioisotope
material and were re-absorbed. A higher source activity most strongly influences the shortcircuit current density. Increasing the NW length leads to larger short-circuit current density gains compared to the open circuit voltage ( $J_{sc}^{max}$  : 0.195 µA/cm<sup>2</sup> to 2.34 µA/cm<sup>2</sup>,  $V_{oc}^{max}$  : 1.087 V to 1.096 V). Variations in the short-circuit current density were therefore shown to be the dominant parameter determining device performance when the NW length was varied. The trends in Fig. 2.7 are supported by Eqs. (A51) to (A52) and Eqs. (A57) to (A59) in the Appendix, which confirm a linear dependence on NW length for both the short-circuit QNR and space-charge region current densities, as well as the dark current densities within the QNRs.

Shorter NWs proved to be more advantageous for the planar source geometry placed on top of the NWs. The optimum conversion efficiency decreased by an order of magnitude from 1.02 % to 0.015 % when the NW length was increased from 1 µm to 10 µm, respectively, and the NW diameter was held constant at 900 nm for the GaP devices in Fig. A9 (see Appendix IX.). The drastic reduction in performance stemmed from shortcircuit current density losses. The optimum short-circuit current density was reduced by 80.4 %, from 32.9 nA/cm<sup>2</sup> to 6.42 nA/cm<sup>2</sup>. In contrast, the optimum open-circuit voltage loss was approximately 19.7 % ( $V_{oc}^{max}$  : 0.997 V to 0.801 V). The fill factor decreased by less than 3 %.

In general, device performance is expected to improve in the 2D source geometry with increasing NW length, which enables the absorption of more beta particles along the NW's vertical axis, thereby increasing the short-circuit current density. However, the observed negative correlation was attributed to our approach to match the planar source's power density to that of the 3D source configuration for a given NW length, diameter, and diameter-pitch ratio. Doing so incurred self-absorption losses (Eq. (2.2.11)) for the

planar source as the vertical source thickness was increased. In the planar source configuration the radioisotope source's power grows with the source thickness up to a limiting thickness, after which self-absorption losses begin to dominate. Once the source thickness approaches the beta particle range, the beta particle's escape probability drastically decreases, as the beta particles will on average lack sufficient energy to escape the radioisotope material. We can therefore conclude that for the 2D source geometry used in Fig. A9, the NWs should be packed together as closely as possible, and the NW length should be comparable to the beta particle range. A higher source activity can be achieved via the use of radioisotope source engineering techniques such as the inclusion of beta particle reflector surfaces in Ref. 36 to recycle backscattered beta electrons.

#### 2.3.1.2 Nanowire Diameter

A negative correlation between the efficiency and the NW diameter was observed for the 3D source geometry in Fig. 2.8. The optimum conversion efficiency decreased from 8.05 % to 4.51 % ( $\Delta \eta \simeq -44$  %) when the NW diameter was increased from 200 nm to 900 nm, respectively, and the NW length was held constant at 10 µm in Fig. 2.8. The short-circuit current density (not shown) was responsible for this observation. The optimum open-circuit voltage decreased marginally from 1.09 V to 1.07 V.



Figure 2.8: Efficiency as a function of the NW p-core diameter and n-shell thickness for simulated 3D source geometry GaP betavoltaic devices. The NW diameter was varied from a) 200 nm b) 450 nm c) 900 nm, while the NW length, dopant concentrations, and diameter-pitch ratio were fixed at  $L = 10 \,\mu$ m,  $N_A = 10^{19} \,\mathrm{cm}^{-3}$ ,  $N_D = 5 \times 10^{18} \,\mathrm{cm}^{-3}$ , and d : p = 0.4, respectively.

Thinner NWs can accommodate more radioisotope source material between the NWs, resulting in greater beta particle flux directed toward the NWs. The current density therefore rises as the input power density scales with source activity. The beta particle energy deposition rate is also largest at the semiconductor surface, where the beta particle will typically deposit most of its kinetic energy within the first few hundred nanometres of the semiconductor. The observed decrease in the optimum short-circuit current density from  $2.34 \,\mu\text{A/cm}^2$  to  $1.34 \,\mu\text{A/cm}^2$  as the NW diameter was changed from 200 nm to 900 nm was attributed to the onset of self-absorption, which reduced the source activity at the larger NW diameters examined. Although a relatively high F-ratio of ~ 85.5 % was maintained at each NW diameter in Fig. 2.8,  $w_{\text{src}}$  increased by an order of magnitude from 300 nm to 1.35  $\mu$ m (the diameter-pitch ratio was held constant at 0.4). When the NW diameter was 900 nm the latter source width exceeded the beta particle range of electrons in GaP ( $R_0 = 1.24 \,\mu$ m) with average energy of 17.45 keV. The self-absorption factor decreased from 0.856 to 0.53 when the diameter was increased from 200 nm to 900 nm, respectively, effectively reducing the source activity by 32.6 %. We can therefore ascribe the primary

loss mechanism in Fig. 2.8 to self-absorption. These results highlight the limitations of the 3D source geometry, in that, self-absorption can only be mitigated so long as the source width is not comparable to the beta particle range (i.e.  $w_{src} \ll R_0$ ).

 $\eta$  was more sensitive to n-shell thickness variations compared to p-core diameter variations. The efficiency generally fell with increasing  $t_n$  for each of the NW diameters in Fig. 2.8.

In general, excess minority holes in the n-QNR suffered from shorter diffusion lengths and lower mobility than excess minority electrons in the p-QNR ( $L_n = 476$  nm,  $L_p =$ 113 nm in Fig. 2.8). The collection of excess minority holes in the n-QNR is enhanced when  $t_n \leq L_p$ , ensuring excess minority holes generated within a diffusion length of the junction were collected. A broader range of p-core diameters can therefore be accommodated with little fluctuation in device performance as seen in Fig. 2.8. In contrast, thicker NWs proved to be preferable when a 2D source geometry was used. Broader NWs improved the beta capture efficiency (Eq. (2.2.9)) by expanding the proportion of the unit cell's surface area that was covered by NWs. Consequently, better surface coverage increased the likelihood of betas emitted from the bottom surface of the source material being captured by a p-i-n junction.

#### 2.3.1.3 Doping

The results in Table 2.1 and Fig. 2.9 indicate that in general higher conversion efficiencies favoured moderately high doping levels. The doping profile determined many of the material properties governing carrier transport within the semiconductor junction. The minority carrier diffusion lengths  $L_{n,p}$ , mobilities  $\mu_{n,p}$ , lifetimes  $\tau_{n,p}$ , diffusion constants  $D_{n,p}$ , equilibrium carrier concentrations  $(n_0, p_0)$ , as well as the bandgap energies in each region of the junction  $E_{g_{n,i,p}}$  were computed as a function of the net dopant concentrations according to Eqs. (A61) to (A68) and the data in Tables A1 to A8 in the Appendix.

The minority electron and hole mobility decrease with increasing doping concentration according to Refs. 37–42. Minority carriers experience higher rates of scattering in the presence of high impurity concentrations. The minority electron diffusion length in the p-QNR decreased from  $L_n = 871$  nm to 476 nm when  $N_A$  was increased from  $5 \times 10^{18}$  cm<sup>-3</sup> to  $10^{19}$  cm<sup>-3</sup>. Similarly, in the n-QNR,  $L_p$  was  $3.72 \,\mu$ m, 113 nm and 24 nm when  $N_D$  was  $10^{17}$  cm<sup>-3</sup>,  $5 \times 10^{18}$  cm<sup>-3</sup> and  $10^{19}$  cm<sup>-3</sup>, respectively. Similar trends were observed for  $D_{n,p}$ ,  $\mu_{n,p}$  and  $\tau_{n,p}$  in the QNRs, each of which decreased as the corresponding dopant concentration was increased.



Figure 2.9: Efficiency as a function of the NW p-core diameter and n-shell thickness for simulated 3D source geometry GaP betavoltaic devices. The acceptor and donor dopant concentrations were varied from a)  $N_A = 1 \times 10^{19} \text{ cm}^{-3}$ ,  $N_D = 5 \times 10^{18} \text{ cm}^{-3}$  b)  $N_A = 10^{19} \text{ cm}^{-3}$ ,  $N_D = 10^{19} \text{ cm}^{-3}$  c)  $N_A = 5 \times 10^{18} \text{ cm}^{-3}$ ,  $N_D = 1 \times 10^{17} \text{ cm}^{-3}$  d)  $N_A = N_D = 5 \times 10^{18} \text{ cm}^{-3}$ ,  $N_D = 1 \times 10^{17} \text{ cm}^{-3}$  d)  $N_A = N_D = 5 \times 10^{18} \text{ cm}^{-3}$ ,  $N_D = 1 \times 10^{19} \text{ cm}^{-3}$ . The NW length, diameter, and diameter-pitch ratio were held constant at  $L = 10 \,\mu\text{m}$ ,  $D = 550 \,\text{nm}$  and d : p = 0.4, respectively.

Shorter minority carrier diffusion lengths and lifetimes are expected to worsen device performance stemming from higher recombination losses and lower collection efficiency.

The efficiency decreased when the NWs were most heavily doped in Fig. 2.9 b) and e). The minority hole lifetime in the n-QNR fell by 4 orders of magnitude from 41.2 ns to 8.3 ps when  $N_D$  was increased from  $10^{17}$  cm<sup>-3</sup> to  $10^{19}$  cm<sup>-3</sup> in Fig. 2.9 c) to e). The highest efficiency occurred when the p-core was heavily doped and the n-shell was moderately doped in Fig. 2.9 a). Even though the optimum  $J_{sc}$  decreased slightly from 1.77  $\mu$ A/cm<sup>2</sup> to 1.76  $\mu$ A/cm<sup>2</sup> going from Fig. 2.9 d) to a), a larger open-circuit voltage (1.084 V vs. 1.078 V) was achieved at the optimum configuration in Fig. 2.9 a) due to the larger built-in potential.

SRH recombination was the dominant recombination mechanism in the depletion region for each of the materials examined. Auger recombination was negligible at the carrier concentrations in Fig. 2.9. Radiative recombination was negligible in GaP and Si. The SRH recombination current density was primarily determined by the minority carrier lifetimes within the depletion region ( $\tau_{n_0}$ ,  $\tau_{p_0}$ ), as well as the thickness of the NW's intrinsic shell and doping ( $N_A$ ,  $N_D$ ). The minority carrier lifetimes in the depletion region (see Eq. (A76) in Appendix VI.) were determined by the trap density  $N_T$ .

Increasing the n-shell thickness  $t_n$  reduced the total short circuit current density because doing so reduced the intrinsic region and depletion region thickness.  $\eta$  was therefore more sensitive to  $t_n$  in Figs. 2.9 a), b), d) and e).

In contrast,  $\eta$  was less sensitive to  $t_n$  and more sensitive to  $d_p$  in Fig. 2.9 c). Reducing the dopant concentrations increase the depletion region thickness and reduces the internal electric field. The intrinsic region facilitates the establishment of the built-in potential across the junction which is impeded by the low dopant concentration. A thin p-core in Fig. 2.9 c) increases the intrinsic region thickness which is needed to support the larger depletion region.

#### **2.3.1.4** Short-Circuit Current Density $-J_{sc}$

The most effective strategy to enhance the short-circuit current density in GaP with a 3D source geometry involved increasing the p-core diameter whilst keeping the n-shell as thin as possible without fully depleting the n-shell. The largest short-circuit current density (2.39  $\mu$ A/cm<sup>2</sup>) in Fig. 2.5 a) was achieved when the p-core diameter and n-shell thickness  $(d_p, t_n)$  were 104 nm and 17 nm, respectively. The positive correlation between the short-circuit current density and the p-core diameter occurred primarily as a consequence of Eq. (A57), which shows the excess minority electron short-circuit current density in the p-QNR to be proportional to the square of the p-QNR's width ( $J_{sc}^{\Delta n} \propto r_p^2$ ). Varying ( $d_p, t_n$ ) from 104 nm and 16.9 nm to 24 nm and 46 nm, respectively, in Fig. 2.5 reduced the p-QNR width from 46.6 nm to 2.72 nm ( $\Delta r_p \simeq -94$ %). As a result,  $J_{sc}^{\Delta n}$  fell by 2 orders of magnitude from 0.53  $\mu$ A/cm<sup>2</sup> to 1.8 nA/cm<sup>2</sup>.

Since excess carriers generated within the depletion region have a high collection probability, it is beneficial to ensure that absorption occurs predominantly in the depletion region. Therefore, increasing the n-shell thickness reduces the short-circuit current density because doing so reduces the achievable thicknesses of the p-core and intrinsic shell.

## 2.3.1.5 Open-Circuit Voltage – V<sub>oc</sub>

The open-circuit voltage in Fig. 2.5 b) was maximized when the intrinsic shell was made as thin as possible (10s of nm). The maximum open-circuit voltage in Fig. 2.5 b) (1.135 V) was achieved when the intrinsic shell thickness was set to 6.44 nm.  $V_{oc}$  decreased from 1.135 V to 1.071 V when  $(d_p, t_n)$  were varied from 95 nm to 24 nm and 46 nm to 8.6 nm, respectively, corresponding to increasing  $t_i$  from 6.4 nm to 79.4 nm. Increasing  $t_i$  enlarged the depletion region width w, but reduced the junction's internal electric field, and thus the open-circuit voltage.

Wider bandgap materials are well-suited for BV applications as they naturally yield larger built-in potentials, which raises the upper bound limit of the open-circuit voltage, thereby increasing the device's maximum achievable power output. Larger built-in potentials can also be achieved by heavily doping the p and n-regions of the junction.

The highest open-circuit voltages in Table 2.1 were achieved with GaP for both the 2D and 3D source geometries for GaP due to its wide bandgap energy compared to both Si and GaAs.

#### 2.3.1.6 Fill Factor — FF

The fill factor was maximized by balancing the competing optimum junction morphologies for the short-circuit current density and open-circuit voltage. Little variation in the fill factor was observed when the NW p-core diameter and n-shell thickness were varied in each of the best devices in Table 2.1 and Figs. 2.5 and 2.6. In general, the optimum fill factor was achieved when the device output power was maximized.

#### **2.3.1.7** Conversion Efficiency – $\eta$

The results in Table 2.1 conclude that the 3D source geometry yields a nearly 8-fold improvement in conversion efficiency compared to the 2D source geometry. NWs should be grown as tall as possible while maintaining thin diameters (on the order of ~ 200 nm) and moderate diameter-pitch ratios of approximately 0.4. Efficiency was maximized as a trade-off between  $J_{sc}$  and  $V_{oc}$ . NW p-i-n junctions offer no significant benefit over thin film junctions for the 2D source geometry. In such a case, the NW lengths should be on

the order of the beta particle range, and they should be made to be very wide. Additionally, NW packing should be maximized for the 2D source to ensure maximum beta capture efficiency.

#### 2.3.1.8 Array Geometry

The primary challenge of BV device design is the maximization of the deposited beta emitter energy over what is typically a very narrow region (i.e. the depletion region) compared to the range of the beta particle. In an ideal BV device, the entirety of the incident beta electron's energy would be deposited within the depletion region to maximize carrier separation and collection<sup>10</sup>.

The optimum diameter-pitch ratios for the 3D source geometry in Fig. 2.10 indicated the existence of a trade-off between the radioisotope volume and the converter volume. While maximizing the volume of source material surrounding the NWs enhanced the flux of incident beta particles, thereby increasing beta-generated current, it concurrently reduced the density of NWs within the array. Hence, achieving optimal device performance necessitated a balance between the volumes of the source and converter to maximize the absorption of incident beta particles and the available power input. Previous simulations in Ref. 27 have also reported the existence of optimal diameter-pitch ratios for various radioisotope sources; however, these predictions have not been confirmed experimentally.



Figure 2.10: Efficiency vs. diameter-pitch ratio for the optimum performant simulated nanostructured betavoltaic devices using a <sup>63</sup>Ni radioisotope source a) GaP (circles) D = 200 nm,  $N_A = 10^{19} \text{ cm}^{-3}$ ,  $N_D = 5 \times 10^{18} \text{ cm}^{-3}$  b) GaAs (squares) D = 200 nm,  $N_A = 10^{19} \text{ cm}^{-3}$ ,  $N_D = 5 \times 10^{18} \text{ cm}^{-3}$  b) GaAs (squares) D = 200 nm,  $N_A = 10^{19} \text{ cm}^{-3}$ ,  $N_D = 5 \times 10^{18} \text{ cm}^{-3}$ , and c) Si (triangles) D = 200 nm,  $N_A = 5 \times 10^{18} \text{ cm}^{-3}$ ,  $N_D = 10^{19} \text{ cm}^{-3}$ , for L = 1, 5 and 10 µm. Gaussian fits to each simulated data set were computed using a Levenberg-Marquardt least-squares algorithm<sup>43</sup>.

Shorter broader NWs performed best when the planar source configuration was used. Device performance for the planar source geometry was severely inhibited by source losses. Directional and self-absorption losses decimated the power input delivered to the NWs. At most, 50 % of the emitted beta particles were directed towards the NWs located below the radioisotope source. Of the available beta flux, the fraction of the incident flux that reached the NWs was heavily influenced by NW density within the array. The optimum diameter-pitch ratio approached unity for devices with a 2D source geometry, as  $\eta_{\beta}$  was maximized. A diameter-pitch ratio of unity maximized the NW packing factor, thereby minimizing the empty volume between the NWs where beta particles would not be captured.

NWs approaching 1  $\mu$ m in both length and diameter resulted in the highest conversion efficiencies for the 2D source in Table 2.1 and Fig. 2.11. The NW lengths of these devices were reasonably close to the average beta particle range within each of the respective materials —  $R_0 = 1.24$ , 0.966 and 2.2  $\mu$ m for GaP, GaAs, and Si, respectively when  $\bar{E} =$  17.45 keV. Ideally, matching the NW length to the incident beta range ensures that incident beta particles will on average deposit all of their kinetic energy within the NWs.



Figure 2.11: Efficiency vs. diameter-pitch ratio for the optimum performant simulated betavoltaic devices employing a planar <sup>63</sup>Ni radioisotope source a) GaP (circles) D = 900 nm,  $N_A = 10^{19}$  cm<sup>-3</sup>,  $N_D = 5 \times 10^{18}$  cm<sup>-3</sup>, b) GaAs (squares) D = 900 nm,  $N_A = 10^{19}$  cm<sup>-3</sup>,  $N_D = 5 \times 10^{18}$  cm<sup>-3</sup>, and c) Si (triangles) D = 900 nm,  $N_A = N_D = 10^{19}$  cm<sup>-3</sup>. Quadratic fits to each simulated data set were computed using a Levenberg-Marquardt least-squares algorithm<sup>43</sup>.

Bandgap narrowing had a negligible effect on device performance for both the 2D and 3D source geometries. The optimum conversion efficiency decreased by 0.07 % and 0.01 % (absolute), when bandgap narrowing was omitted for the 3D and 2D source geometries, respectively. Omitting bandgap narrowing lowered conversion efficiencies slightly but did not affect trends in efficiency versus diameter-pitch ratio for both source geometries.

# 2.4 Conclusion

The model presented offers an approach to NW betavoltaic device design, allowing for detailed investigation of the underlying physical phenomena contributing to the predicted device electrical characteristics. Analytical expressions describing excess minority carrier charge transport within radial p-i-n junctions were derived by solving Poisson's equation and the excess minority carrier continuity equations in a cylindrical coordinate system. The model predicted optimal NW core-shell junction configurations for GaP, GaAs, and Si materials, along with optimal donor and acceptor dopant concentrations for each material. The results indicated that the performance of these devices is significantly influenced by source and array geometries. The dependence on the NW diameter-pitch ratio revealed a trade-off between maximizing source volume and absorber volume.

Experimental validation is needed to assess the model's accuracy and limitations. Future research may explore other radioisotope source materials, such as tritium (<sup>3</sup>H) and promethium-147 (<sup>147</sup>Pm), as well as popular betavoltaic converter materials like SiC, diamond, and GaN, to further validate and assess the model. The model provides a transparent approach to NW betavoltaic device design, enabling a detailed exploration of the underlying physical processes that influence device electrical characteristics. Enhancements to the model's robustness could involve more accurate modeling of beta electron-hole generation rates that accounts for the stochastic path of scattered betas. Experimental results to validate the parameter dependence of our model are not available in the literature, and could be a topic of future study.

# **Chapter 3**

# **Nanowire Growth and Characterization**

# 3.1 Introduction

This chapter presents the essential processes and equipment used in NW sample preparation and growth. An overview of molecular beam epitaxy (MBE) and self-assisted vaporliquid-solid (VLS) growth provides the foundational understanding needed to comprehend the epitaxial growth process and physical mechanisms underlying vertical NW array synthesis. Additional technical details regarding sample preparation processes are provided in Appendix X.

Shahram Ghanad-Tavakoli is acknowledged for the growth of the NWs. Alex Tsukernik is acknowledged for performing EBL.

# 3.2 Background

## 3.2.1 Molecular Beam Epitaxy (MBE)

MBE is a physical vapor deposition (PVD) epitaxial growth technique used to produce microand nano-scale semiconductor structures such as thin films and NWs. MBE emerged in 1968 from the work of Alfred Cho and John Arthur at Bell Labs in the interest of developing more sophisticated device structures with smaller dimensions<sup>44</sup>. MBE research has since matured significantly, evolving into a widely adopted growth method for both academic studies and commercial industrial applications.

The MBE growth process is based on the reaction of thermal molecular (and atomic) beams with a heated substrate surface under ultra-high vacuum (UHV) conditions<sup>44</sup>. In traditional MBE, mass transport of the growth species to the substrate is facilitated by thermal evaporation of source material using effusion cells. The evaporant beam fluxes are directed towards the substrate positioned on a heated rotating stage. The substrate is heated to ensure condensation of the impinging flux leading to epitaxial growth. Substrate rotation ensures uniformity of the flux distribution and conformal coverage of the substrate surface during deposition. The impinging particles deposit on the substrate surface in a mixture ratio determined by the flux rates and their individual sticking probabilities<sup>45</sup>, characterized by sticking coefficients. The sticking coefficient described process to occur, an UHV environment with pressures below  $1 \times 10^{-9}$  Torr is required. At such pressures, the mean free path (MFP) of the beam molecules greatly exceeds the distance they must travel from the source (effusion cell) to the substrate, also known as the source-to-substrate distance. Under these conditions, molecular gas flow is achieved, resulting in effectively

no collisions between the molecules in the impinging beam flux. MBE requires an ultraclean deposition environment, maintained by a liquid nitrogen-cooled shroud that acts as a cryogenic pump to prevent water vapor and other volatile contaminants from reaching the substrate surface.



Figure 3.1: Schematic of the principal elements of a MBE reactor (from Ref. 46).

Molecular beam epitaxy (MBE) is fundamentally a kinetically controlled process governed by the dynamic interplay of evaporation, adsorption, desorption, surface diffusion, and incorporation of elemental constituents<sup>45</sup>. Operating at deposition rates as low as 0.1 monolayers (ML) per second, MBE enables the growth of exceptionally pure films in an ultra-clean environment<sup>45</sup>. The precise control of material deposition is achieved through effusion cell temperatures and mechanical shutters, which regulate source fluxes by opening and closing in front of the effusion cells. This mechanism enables the formation of heterostructures with atomically sharp interfaces and precisely controlled doping profiles, allowing for both abrupt transitions in dopant concentration and type. While this level of precision permits the achievement of monolayer-thick films, MBE faces practical limitations in industrial applications due to its slow growth rate, high operational costs, and inability to process multiple samples simultaneously.

## **3.2.2** Electron Beam Lithography (EBL)

Lithography is the process of transferring patterns from one medium to another<sup>47</sup>. Electron beam lithography (EBL) has been most widely implemented for patterning mesoscopic structures or systems in electron-sensitive films with unique advantages of high resolution in feature size, high reliability in processing, high accuracy in positioning/alignment, and high flexibility in custom pattern replication<sup>48</sup>. EBL is analogous to photolithography, which is commonly used to pattern larger micron-scale features. In EBL, a focused beam of electrons, produced by a high-voltage source and an electron-emitting filament, is used to trace a predefined two-dimensional pattern onto an electron-sensitive resist. The pattern is defined by a 2D digital map divided into individual pixels<sup>49</sup>. Magnetic fields focus the beam, ensuring precise patterning. EBL is performed under high vacuum to minimize scattering of the electron beam during its transit to the sample surface.

Different areas of the resist become soluble in a developer solvent depending on the type of resist used. Positive resists become soluble to the developer solvent upon exposure to the electron beam, as shown in Fig. 3.2. The impinging beam electrons break the cross-linking bonds between the polymers of the resist, making them more soluble in the developer<sup>45</sup>. When immersed in the developer solution, the exposed (developer-soluble) regions of a positive resist dissolve, exposing the surface beneath the resist. In negative resists, exposure to the electron beam strengthens the polymer bonds by cross-linking, making them less soluble to the developer solution. After development, the exposed areas of the negative resist remain. The lithograpically-generated patterns can be transferred

to the substrate material under the resist using a variety of methods such as etching or deposition.



Figure 3.2: EBL patterning process.

A typical EBL system system consists of a scanning electron microscope (SEM), a precision stage, and a computer control system that precisely directs the electron beam's shape and position. The stage achieves nanometre-scale positioning accuracy in all three dimensions through a laser-interferometric system combined with servo-motors and piezoelectric actuators<sup>45</sup>. To minimize beam spreading, the system operates at high acceleration voltages of 100 kV<sup>50</sup>.

Photolithography's resolution is fundamentally limited by the wavelength of the exposing photons ( $\approx$ 400 nm). EBL overcomes this limitation by utilizing electrons instead of photons, achieving a maximum resolution determined by the electrons' de Broglie wavelength. The electron wavelength depends on beam energy according to Eq. (3.2.1), where *E* is expressed in keV<sup>49</sup>. This enables the fabrication of features smaller than 10 nm<sup>45</sup>.

$$\lambda_e = \frac{1.266}{E^{0.5} [1 + 0.9979E - 6E]^{0.5}} \text{ (nm)}$$
(3.2.1)

EBL offers the flexibility to draw an extremely wide range of custom patterns, eliminating the need for physical masks required in photolithography. However, this advantage comes with drawbacks. In EBL, each pixel in the pattern must be sequentially exposed to the electron beam, resulting in relatively long write times on the order of tens of minutes to hours, making it a relatively costly process. These limitations restrict the manufacturing scale at which EBL can be applied efficiently. For industrial applications at larger scales, techniques such as nano-imprint lithography (NIL) are more suitable due to their lower cost and high throughput<sup>51</sup>.

## 3.2.3 Plasma-Enhanced Chemical Vapor Deposition (PECVD)

Chemical vapor deposition (CVD) is the process of chemically reacting a volatile compound of a material to be deposited, with other gases, to produce a nonvolatile solid that deposits atomistically on a suitably placed substrate<sup>52</sup>. The deposited film's thickness, uniformity and stoichiometry depend on the reactants supplied to the substrate surface. CVD growth is characterized by (i) gas transport into the chamber and to the substrate, (ii) interface chemical reactions to form the film, and (iii) purging of reaction byproducts from the chamber. Figure 3.3 shows a typical PECVD reactor configuration.

High-temperature CVD processes for producing thin films and coatings have found increasing applications in diverse technologies ranging from the fabrication of solid-state electronic devices to the production of rocket engine and nuclear reactor components<sup>52</sup>. Low-temperature deposition of insulating and passivating films has been a strong driving force behind the development and adoption of CVD processing methods<sup>52</sup>. Plasmaenhanced chemical vapor deposition (PECVD) is an adaptation of traditional chemical vapor deposition. It is primarily used for the deposition of dielectric and passivating films.



Figure 3.3: Diagram of the fundamental components of a typical ECR-PECVD system.

The use of plasma primarily serves to lower the temperatures at which deposition can occur. The necessary energy for the chemical reaction is provided by the plasma, thus enhancing the chemical reaction rates of the precursor gases<sup>53</sup> and lowering the temperature at which deposition can occur. In PECVD, the plasma is typically excited via the injection of process gases into the reaction chamber where a radio frequency discharge between two electrodes, situated at the top and bottom of the chamber, is generated. Irrespective of the plasma excitation method, to generate a plasma an equilibrium must be struck between the ionization and recombination processes in the bulk plasma<sup>54,55</sup>. In the PECVD system used to prepare the wafers Sections 3.5 and 3.6, a microwave frequency signal was generated instead of a radio frequency signal. This method of plasma excitation can achieve a high ion density at relatively low chamber pressures, on the order of a few mTorr to a few Torr, allowing for the use of low energy ions<sup>49</sup>. In the growth of SiO<sub>x</sub> films, the low energy ions are ideal for the removal of hydrogen from the actively growing film without causing damage<sup>56</sup>.

At the relatively low pressures in PECVD, the electrons, owing to their extremely small

mass, can attain high velocities before the polarity of the RF (or microwave) field reverses. The heavier ions of the plasma, however, cannot achieve a high velocity before the RF field polarity reverses. The electrons can be maintained at very high equivalent temperatures, while the heavier ions remain at ambient temperatures<sup>45</sup>. The temperature difference allows the high-energy electrons to dissociate precursor molecules and generate relatively large quantities of free radicals, processes that are highly improbable at low temperatures<sup>45</sup>.

Compared to MBE, PECVD growth offers a more conformal nature and relatively lower operational and equipment costs, making it more scalable for depositions below one micron<sup>57</sup>. Line-of-sight to the substrate surface(s) is unnecessary, allowing PECVD deposition to be carried out in parallel on multiple substrate surfaces.

## 3.2.4 Wet Etching

Wet etching is a chemical process in which solid materials are immersed in a corrosive solution to selectively remove specific regions of the material. The etchant reacts chemically with the exposed surfaces, dissolving the targeted areas and leaving behind the desired structure<sup>45</sup>. During the process, light agitation is necessary to ensure uniform material removal. Agitation promotes consistent contact between the etchant and the material while preventing the accumulation of waste byproducts, which can obstruct the reaction<sup>45</sup>. Most wet etch processes are isotropic, removing material at an equal rate in all directions. While isotropy is beneficial for certain applications, it often leads to undercutting — where the material beneath masking or etchant-resistant layers is unintentionally removed. This characteristic makes wet etching unsuitable for applications requiring anisotropic etching, where material removal must be restricted to specific directions. Undercutting, a key limitation of isotropic wet etching, is illustrated in Fig. 3.4.



Figure 3.4: Illustration of the process of wet-etching a thin film deposited on a substrate. A masking layer is used to define a pattern. Isotropic etching causes undesirable lateral undercuts, shown in orange.

The solubility of etch reaction products in the etchant solution is critical for maintaining etch rate and profile uniformity<sup>58</sup>. Insoluble reaction products can accumulate on the material surface, hindering the reaction by blocking fresh reactants from accessing the reaction site. The etch rate in wet etching primarily depends on the concentration of the etchant, which is influenced by both the bulk concentration and the replenishment rate of fresh etchant<sup>58</sup>. Additional factors, such as temperature and the efficiency of waste removal from the reaction zone also significantly impact the etch rate. Wet etching is characterized by high selectivity and repeatability, enabling reasonable control over the material removal process. Moreover, its scalability facilitates simultaneous processing of multiple substrates or large areas, making it particularly suitable for industrial fabrication pipelines. This combination of high selectivity, scalability, and repeatability underscores its utility in large-scale semiconductor manufacturing.

# 3.3 Characterization Methods

## 3.3.1 Scanning Electron Microscopy (SEM)

SEM is a microscopy technique in which the surface of a specimen is imaged using an electron beam. In SEM, electrons generated via thermionic or field emission from an electron gun cathode are focused down to a tight beam of just a few nm in width, using magnetic condenser lenses. Using scanning coils, the electron beam is scanned, or rastered, across the sample surface, mapping each pixel in a two-dimensional grid to construct an image.

SEM operates under high vacuum, ensuring low contamination within the electron column and specimen chamber. This increases the mean free path of the primary beam electrons (PEs) by minimizing scattering before they reach the sample surface. Impinging electrons from the primary beam interact with the sample surface through elastic and inelastic scattering mechanisms, as illustrated in Fig. 3.5. A series of detectors collects the scattered electrons, constructing a three-dimensional image of the sample surface. Typical beam electron energies can range from 100 eV to 30 keV depending on the SEM resolution and operating mode—either backscattered-electron (BSE) or secondary electron (SE) detection mode<sup>45</sup>. Depending on the operational mode, SEM can also provide information about sample topography, material composition, and crystal structure. For example, BSEs can be used to construct electron diffraction images, from which crystal orientation is determined.



Figure 3.5: Types of primary beam electron-specimen scattering interactions: (i) inelastic scattering ionizes the surface atoms of the specimen, releasing secondary electrons, (ii) PEs are elastically scattered by the atomic nuclei of the sample and are deflected backwards out of the sample, (iii) tightly bound inner (K) shell electrons can be ejected from the specimen when they scatter PEs. Higher energy electrons fill the vacancy in the electronic shell, releasing energy in the form of characteristic X-rays from the specimen in the process. Slight deflections of the PEs from inelastic scattering cause broadening of the beam within the specimen.

SEM requires a sufficiently thick sample, such that the PEs deposit their energy through scattering interactions over a finite (interaction) volume within the specimen. Otherwise, the incident electrons would instead pass through the sample never reaching the detectors. As the electron beam probes the specimen, the beam electrons may undergo elastic scattering through large angles (> 90 °) in which they are reflected backwards out of the interaction volume, known as backscattering, or inelastic scattering through small angles, which ejects loosely bound outer shell electrons of the surface atoms (i.e. SEs). Heavy elements, due to their higher atomic number (Z), and therefore greater number of electrons, yield a larger fractions of BSEs. This is attributed to the increased repulsion between the incident beam electrons and the bound electrons in the heavier atoms, which enhances scattering. Electron scattering is responsible for the variation in pixel brightness (i.e. contrast) across the scanned area. Electrons scattered by heavier elements retain more kinetic energy compared to those scattered by lighter elements, striking the BSE detector with greater energy, thus producing brighter images. Scattering depends strongly on the specimen's properties, including material composition, crystal structure, and sample topography. To maximize detection, BSE detectors are typically positioned to encircle the primary beam, allowing them to capture BSEs regardless of their scattering direction<sup>45</sup>.

Secondary electrons (SEs) possess low kinetic energies ( $\approx 10 \text{ eV}^{59}$ ) as they are ejected from the outermost electronic shell of the surface atoms, limiting their mean free path. Only SEs generated within the first few nm of the specimen are able to escape the sample. As a result, SEs must be accelerated towards the SE detector to ensure they can be detected. This is accomplished by applying a positive bias of approximately 400 V to a collector grid, which attracts the electrons. They are then further accelerated towards a phosphor screen or scintillator biased at several kV<sup>45</sup>. Upon striking the detector, the accelerated electrons generate a sufficiently bright flash for detection. SE emission is heavily dependent on the specimen surface conditions<sup>59</sup>.

Figure 3.6 shows the fundamental components of a SEM. A basic SEM consists of an

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electron gun, anode, electromagnetic lenses, scanning coils and electron detectors. Electron gun assemblies consist of either thermionic or field-emissions guns (FEGs). Within the electron gun assembly, the electron motion is controlled only by electrostatic fields. Electrostatic lenses are formed when positive and negative electric fields are placed near each other<sup>60</sup>, such as the electron gun and anode within the electron column. A thermionic electron gun supplies electrons by sufficiently heating a conductive metal filament, such as tungsten, until the electrons posses enough thermal energy to overcome the material's work function and escape the filament. The filament temperature is modulated by applying a current to the filament. Increasing the filament current increases the number of generated electrons up to a saturation point, beyond which no increase in electron generation is observed<sup>60</sup>.



Figure 3.6: Diagram of the principal elements of a scanning electron microscope.

FEGs are typically made by sharpening a metal filament such as single crystal tungsten down to a ~100 nm radius tip, and applying a large negative bias, on the order of several kV to the sharpened tip. Thermionic electron gun sources are less expensive than FEGs, but produce less coherent electron beams. The anode plate is held at a positive charge, creating a strong potential difference between the filament tip and the anode, capable of overcoming the metal's thermionic energy barrier. The potential gradient rips electrons off of the filament, and accelerates them down the electron column towards the condenser lens. In this way, emission is preferentially stimulated from the metal tip. FEG systems require cleaner low pressure environments, as any debris stuck to the filament tip reduces emission. However, they produce much smaller emitted beam diameters (thus better resolution)<sup>60</sup>. Moreover, FEGs generally have a longer filament life than thermionic electron guns since they emit electrons without requiring high temperatures<sup>60</sup>.

The brightness of an electron gun is a critical parameter, as it directly impacts image quality. It quantifies the total electron current that can be focused onto the sample surface and represents the total number of electrons that can be concentrated at a specific point on the specimen per second<sup>59</sup>. In general, a FEG provides higher electron source brightness than a thermionic electron gun.

Electromagnetic lenses shape the electron beam within the SEM column by leveraging the Lorentz force (Eq. (3.3.1)) to control the electron trajectories, causing them to spiral and converge toward a focal point. The Lorentz force **F** describes the force an electron travelling with velocity **v** experiences in the presence of a magnetic field **B**,

$$\mathbf{F} = -e\mathbf{v} \times \mathbf{B} \tag{3.3.1}$$

where e is the elementary charge. The magnetic condenser lens is a tightly wound copper

coil encircling a cylindrically symmetric soft iron core with a central bore. Passing a current through the coil generates an axially symmetric magnetic field<sup>61</sup> along the axis of the bore. The iron core enhances and shapes the magnetic field. Beam electrons travelling parallel to the optical axis are unaffected by the magnetic field. However, beam electrons travelling along off-axis trajectories are deflected along a helical path down towards the focal point by the radial component of the magnetic field <sup>59</sup>. Varying the coil current adjusts the lens' focal length. Since the magnetic field is strongest near the edge of the lens (i.e. bore of the iron core) and weaker near the optical axis, electrons farther from the optical axis experience a stronger deflecting force than those closer to it. Off-axis beam electrons may converge prematurely before diverging again, resulting in a blurred spot rather than a precise focal point. Distortions arising from variations in the electron path radius within the beam are referred to as spherical aberration. Placing a small aperture after the lens blocks off-axis electrons, reducing their influence on image formation while decreasing the beam convergence angle and minimizing spherical aberration<sup>59</sup>, but at the cost of reduced beam brightness, which can impact image contrast.

For a given accelerating voltage (e.g. 15 kV), the beam electrons exhibit a narrow energy distribution around a mean value (e.g. 15 keV). Consequently, electrons with slightly different energies are focused at varying focal lengths along the optical axis, converging in a disc rather than a single point, thus increasing the probe size and reducing image sharpness. Beam electron energy spread is inversely proportional to the accelerating voltage<sup>59</sup>, causing its impact to be more pronounced at lower voltages. This type of image degradation caused by differences in beam electron energies is referred to as chromatic aberration. Fluctuations in the accelerating voltage as well as the magnetic lens current

can lead to chromatic aberration<sup>59</sup>. In reality, unavoidable spherical and chromatic aberrations prevent electromagnetic lenses from ever focusing electrons to a perfect point.

After passing through the condenser lens, radially opposing magnetic (scanning) coils deflect the electron beam in both the x and y-directions<sup>60</sup>, rastering the beam across the sample surface. The raster pattern starts at the top-left corner of the viewing window and moves horizontally to the right until it reaches the edge of the scan area. The beam then shifts down one line, and returns to the left side, repeating this process until the entire window is scanned. Finally, the objective lens (another magnetic lens) focuses the electron beam onto the sample. Emitted BSEs and SEs are collected by their respective detectors, whose signals are amplified and sent to a video display system to generate the final SEM image.

A JEOL-7000F and a FEI Magellan 400 SEM were used to image the NWs discussed in Section 3.6.

### 3.3.2 Ellipsometry

Ellipsometry is a widely utilized and non-destructive optical measurement technique for characterizing thin film thickness, optical constants and material properties. This technique operates by analyzing changes in the polarization of light caused by reflections within the material<sup>62</sup>. The precision of the determined parameters depends on the accuracy of the fitted model. For well-defined samples, thicknesses can be precisely measured within a few Å<sup>50</sup>.

In an ellipsometric measurement, a reference beam of light with a known polarization state is directed obliquely onto the sample surface. Upon interaction with the sample, the

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incident light undergoes reflection or transmission, resulting in a change in its polarization. The altered polarization is then measured, and the relative change in polarization, along with the phase difference, is calculated. To determine the optical constants and film properties, a model of the sample is constructed based on the measured data, and regression analysis is applied to optimize the fit parameters by minimizing the mean square error (MSE)<sup>63</sup>. A basic ellipsometer is illustrated in Fig. 3.7.



Figure 3.7: Illustration of the general principal of ellipsometry and the components of a basic ellipsometer.

A J.A. Woollam M-2000 Variable Angle Spectroscopic Ellipsometer (VASE) was used to confirm the oxide film thickness in Section 3.5.

## 3.4 Fundamentals of Nanowire Growth

NWs are typically synthesized by either top-down (subtractive) or bottom-up (additive) techniques. Top-down approaches employ the selective removal of material from thin film layers, often via etching, to define the NW structure. With this method, the NW dimensions and morphology can be controlled with a high degree of repeatability and uniformity.

Top-down approaches also tend to scale quite well, allowing for a high NW growth throughput. However, understanding and managing strain energy is crucial for successful thin film growth. During deposition strain develops in thin films through two key mechanisms: lattice parameter mismatch at hetero-interfaces and mechanical stress from the progressive stacking of layers. Above a critical film thickness, accumulated strain energy can only be relieved through the formation of dislocations. These strain-related challenges make thin film growth a significant constraint in top-down synthesis, where both the substrate-NW material system compatibility and critical film thickness ultimately dictate which types of NWs can be successfully synthesized. In contrast, bottom-up epitaxial NW growth bypasses these limitations, as strain is relieved along the free NW sidewall surfaces<sup>2</sup>. As a result, NWs can tolerate identical lattice mismatches without forming defects due to their high surface-to-volume ratio<sup>50</sup>. Various epitaxial methods can be used for bottom-up NW growth. This chapter focuses specifically on selective-area epitaxy (SAE) vapor-solid (VS) and vapor-liquid-solid (VLS) NW growth, as these techniques were used to synthesize the NWs in Section 3.6.

In SAE, a patterned oxide layer is typically used as a template/mask to deterministically control the NW location and size. The oxide layer promotes the preferential nucleation of NWs on the exposed substrate in the mask openings while inhibiting nucleation on the oxide surface. Utilizing an oxide layer also minimizes parasitic thin film/crystallite growth on the surface between the NWs. In VLS growth a liquid metal catalyst droplet "seed particle" mediates NW nucleation by collecting impinging adatoms supplied by vapor fluxes. Historically, Au nano-particles were a common metal catalyst <sup>64–66</sup>. However, in recent years, self-assisted VLS growth has become a favored approach. In self-assisted growth, the seed particle is a constituent of the NW so as to eliminate the risk of contamination from the

catalyst, which can lead to the development of deep level defects within the NWs<sup>67</sup>. Thus, group III metals, with their low melting temperatures, typically serve as seed particles for the nucleation of III-V NWs<sup>68</sup>. Lithographic techniques such as electron beam lithography (EBL) can be used to pattern holes into the SiO<sub>x</sub> layer.

VLS droplet formation is critical for the nucleation of self-assisted VLS NWs. At the NW growth temperature, the group V species vapor pressure exceeds that of the group III species. Under these conditions, liquid group III droplet formation is naturally favorable at the growth temperature as the group V species is favoured to remain in the vapor phase, and the group III species in the liquid phase<sup>69</sup>. At elevated growth temperatures, group III adatom diffusivity is increased, resulting is longer diffusion lengths. During nucleation the group III adatoms diffuse across the oxide surface in a thermally activated random walk process<sup>70</sup>, where they undergo collisions and accumulate within the oxide mask holes, forming liquid group III droplets. In contrast, lower growth temperatures reduce group III adatom diffusivity, causing a smaller fraction of the impinging adatoms to reach the holes. As a result, rather than accumulating within the holes, the group III adatoms condense on the oxide surface. Group III liquid droplet formation can be further enhanced by establishing group III-rich conditions at the substrate surface. The introduction of a group III flux prior to the initiation of the group V flux, commonly referred to as a "pre-deposition", supplies a large group III flux to the substrate surface, forming liquid group III droplets which act as reservoirs for the collection of impinging growth species. Pre-deposition steps have been used to promote sufficient filling of oxide mask holes for improved vertical III-V NW yield under appropriate growth conditions  $^{71-75}$ . In sub-optimal growth conditions, the large group III flux supplied to the oxide surface during pre-deposition can be deleterious to vertical NW yield, instead increasing the population of parasitic crystallites within the

oxide holes and on the oxide surface.

NW growth is believed to be nucleated by three main pathways, illustrated in Fig. 3.8: (i) direct impingement of the adatoms on the droplet, (ii) direct impingement on the NW sidewalls, and (iii) surface diffusion or secondary flux due to desorption of the adatoms after impingement on the substrate or NW sidewalls<sup>67,76,77</sup>. Group III adatoms may diffuse on the NW sidewalls, while group V diffusion is considered negligible due to the high vapor pressure of group V species<sup>2</sup>. The phase transitions from vapor to solid are driven by the chemical potential gradient between the vapor, liquid, and solid phases ( $\mu_v > \mu_l > \mu_s$ )<sup>68,78</sup>. Crystal growth continues through precipitation from the supersaturated liquid droplet as long as this chemical potential hierarchy is maintained<sup>50,67</sup>.



Figure 3.8: VLS growth nucleation pathways: (i) direct impingement of the adatoms on the droplet, (ii) diffusion of the group III (purple) adatoms along the sidewalls, and (iii) surface diffusion of the adatoms after impingement on the substrate or NW sidewalls.

Various NW properties including length, diameter, doping, composition and position can all be controlled by the SAE-VLS process growth conditions. VLS growth conditions include substrate temperature, source impingement rates, and flux ratios. The impingement rate of the growth species is the number of particles per unit time per unit area that strike the substrate surface; and hence greatly influences the NW growth rates. The substrate temperature is controlled to ensure condensation of the incident flux. For the growth of III-V NWs, the ratio of the incident group V to group III flux is given by the V/III flux ratio. Variations in V/III flux ratio can induce changes in growth rate and NW morphology. The angle the droplet makes with the NW top facet and the sidewalls (i.e. the contact angle)  $\beta$  is strongly correlated with the NW crystal phase. While bulk III-V semiconductors typically form a cubic zinc-blende (ZB) crystal structure, they can instead adopt a wurtzite (WZ) structure when grown as NWs under specific conditions. Namely, very small contact angles (generally below 100°) and very large contact angles (generally above 125°) yield the ZB crystal structure, otherwise the NW adopts a WZ crystal structure<sup>79</sup>. Modulation of the droplet size and shape can therefore be used to precisely control the NW crystal phase and hence the optoelectronic properties of the NWs.

NW growth preferentially along the axial growth direction arises primarily from the direct impingement of incoming flux on the droplet. Previous studies have demonstrated that the vertical growth rate of III-V NWs is constrained by the availability of group V adatoms to the group III droplet, due to the large reservoir of group III atoms present in the droplet<sup>80,68</sup>. Consequently, increasing the supply of group V material to the droplet increases the NW length. The NW diameter is strongly correlated to the droplet size<sup>78</sup>. Initially, the droplet volume is determined by the size of the holes within the mask. However, as NW growth progresses, the droplet volume is influenced by numerous factors such as the impingement rates of the group III and V fluxes, the V/III flux ratio, substrate temperature and surface energies at the liquid-solid interface of the NW, which can in turn alter the resulting NW diameter. Since the droplet size controls both axial and radial growth modes, and is strongly influenced by the V/III flux ratio<sup>77</sup>, the growth rates can be regulated by adjusting this ratio. Low V/III flux ratios correspond to increased group III fluxes, which yield larger droplets. At low V/III flux ratios, the increased arrival rate of the group III species leads to increased scattering from the oxide surface and direct deposition on the droplet. Because the liquid droplet acts as preferential sink for the group III species<sup>79</sup>, the re-emitted group III material and the group III material directly impinging on the droplet are absorbed by the droplet, thereby increasing the droplet size and NW diameter as a result.

Surface diffusion of the group III and V adatoms is heavily mediated by temperature. At elevated growth temperatures the group III adatom diffusivity is sufficient for the group III adatoms to diffuse along the NW sidewalls and reach the droplet at the top of the NW<sup>2</sup>, thereby contributing to axial NW growth. However, at low growth temperatures (~ 500 °C for MBE) the suppression of group III adatom diffusivity favors radial growth modes, leading to nucleation predominantly on the NW sidewalls<sup>2</sup> (i.e. vapor-solid (VS) growth). Shell layers are formed through preferential VS growth on the NW sidewalls. Radial growth modes can alter the NW morphology by widening the NW non-uniformly. In practice, consumption of the group III droplet is used to suppress axial growth and encourage radial growth. Introducing a large group V flux (i.e. high V/III ratio) encourages the precipitation of solid III-V material, thus consuming the surplus of group III adatoms within the droplet. Under these conditions, the group III adatom diffusivity is suppressed<sup>2</sup>, resulting in nucleation predominantly on the NW sidewalls for subsequent growth.

# 3.5 Sample Preparation

Arrays of GaP p-i-n junction NWs were grown at McMaster University by gas source molecular beam epitaxy (GS-MBE). The group III (Ga) flux was supplied by thermal evaporation of a solid Ga source and the group V ( $P_2$ ) flux was supplied by a phosphine gas ( $PH_3$ ) source. A gas cracker was used to dissociate the  $PH_3$  predominantly into  $P_2$  and  $H_2$  dimers. The five NW array samples of interest are identified in Table 3.1.

Sample	NW morphology	Junction type	Dopant(s)
А	axial	р	Ве
В	core-shell	p-i	Ве
С	core-shell	p-i	Ве
D	core-shell	p-i-n	Be+Te
E	core-shell	p-i-n	Be+Te

Table 3.1: GaP nanowire sample identification.

Fig. 3.9 outlines the substrate patterning process. NW arrays were grown on 3" (111)  $\pm 0.9^{\circ}$  boron-doped low-resistivity ( $\rho \leq 0.005 \Omega \cdot \text{cm}$ ) p<sup>+</sup>-Si substrates from Virginia Semiconductor Inc. The wafers had a thickness of (275  $\pm$  25) µm and a dopant concentration of  $1 \times 10^{19} \text{ cm}^{-3}$ . The NW arrays were grown using a SAE-VLS growth technique. The positions of the NWs on the substrate were controlled by a silicon oxide (SiO<sub>x</sub>) masking layer. A 30 nm SiO<sub>x</sub> film was deposited across the entire wafer surface using electron cyclotron resonance plasma-enhanced chemical vapor deposition (ECR-PECVD). The average oxide film thickness was confirmed with ellipsometry (J.A. Woollam M-2000 VASE).



Figure 3.9: Substrate patterning process. EBL and RIE are used to define the pattern within square pads in the oxide layer. The mask holes are separated by the array pitch  $\lambda_p$ .

After the oxide deposition, the wafers were transported to the Toronto Nanofabrication Centre (TNFC) at the University of Toronto for EBL. At the TNFC, the wafers were spincoated (6000 rpm for 1 min) with an electron-sensitive positive resist composed of a 1:1 mixture of AR-P 6200.3 and Anisole, and were subsequently soft-baked on a hotplate for 1 min at 150 °C. Hexagonal lattices of ~100 nm diameter circular holes were patterned into 1 mm<sup>2</sup> square pads across the resist using EBL, with each hole serving as a nucleation site for the growth of an individual NW. EBL was chosen due to its capability to resolve nanometre-scale features, which is essential for accurately defining the sub-micron features of the NW array pattern. Following the EBL write process, the wafers were submerged in developer solution (ZED-N50) for 2 min and gently agitated to develop the array holes in the resist. The wafers were subsequently immersed in isopropyl alcohol (IPA) for 30 to 60 s, then dried with N<sub>2</sub> to halt development. Afterwards, the wafers were transported back to McMaster University, where each wafer was cleaved into six pie-shaped pieces depicted in Fig. 3.10.


Figure 3.10: a) Standard wafer pie piece shape and NW pad layout. The sample consists of nine  $1 \text{ mm}^2$  NW square pads, and a larger TEM pad. The row and column position of each pad is specified by a tuple of the form (R<sub>i</sub>, C<sub>j</sub>). Each column contains identical NW pad patterns. Columns 1 to 3 correspond to NW array pitches of 360 nm, 600 nm and 1000 nm, respectively. The TEM pad is typically cleaved and used for NW characterization by TEM; however, other characterization methods can be employed as well. NWs located on the TEM pad have a pitch of 360 nm. b) Schematic of the core-shell p-i-n NW structure.

The NW array patterns were transferred to the  $SiO_x$  mask using a short 75 s reactive ion etch (RIE). A series of ultrasonically agitated baths were used to strip the electron sensitive resist and clean the sample surface of any residue. The sample was sequentially immersed and ultrasonically agitated in 1,3-dioxolane (AR-600-70) electron resist remover (5 min), acetone (3 min), and IPA (3 min), then rinsed with DI water and dried using N<sub>2</sub>.

Immediately before MBE loading, the sample was treated with a 25 s wet etch using a 0.5 % concentration solution of buffered hydrofluoric (BHF) acid and DI water (10:1) to remove any native oxide formed in the mask holes. Once in the MBE chamber, the sample was degassed at 300 °C for 15 min, followed by an inductively-coupled plasma (ICP) cleaning step at 675 °C for 10 min.

## 3.6 Results and Discussion

## 3.6.1 Be-doped Axial GaP NWs

#### 3.6.1.1 Sample A

Table 3.2 specifies the growth protocol for the Be-doped GaP NWs grown in a simple twostage process, consisting of a pre-deposition step followed by the NW growth step. First, Ga droplets were formed in the oxide mask holes using a 250 s Ga pre-deposition at 650 °C with a Ga impingement rate corresponding to a 2D equivalent growth rate of 0.125  $\mu$ m/h. Next, Be-doped NWs with a nearly 100 % yield were grown for 90 min by introducing the P<sub>2</sub> species at a V/III flux ratio of 3. The substrate temperature and Ga impingement rate were identical to the pre-deposition step. The Be dopants were incorporated using a nominal Be flux corresponding to a carrier concentration of 1 × 10<sup>19</sup> cm<sup>-3</sup>. NW growth was terminated by closing the Ga, P<sub>2</sub> and Be fluxes.

Segment	Time	Temperature	Doping	Ga Impingement Rate	V/III Flux Ratio			
		(°C)	(cm <sup>-3</sup> )	(µm/h)				
	Start							
Ga	250 s	650	None	0.125	-			
GaP	90 min	650	Be - 1 × 10 <sup>19</sup>	0.125	3			
End								

Table 3.2: Sample A MBE growth protocol of Be-doped GaP NWs.

SEM was used to evaluate the NW yield and morphology. Fig. 3.11 shows the Be-doped GaP NWs for 360 nm, 600 nm and 1000 nm pitches, respectively. The NW dimensions were determined using ImageJ by counting pixels and converting them to physical lengths based

on the calibrated scale bar in the SEM images. The images in Fig. 3.11b and c were obtained of the two higher pitch NW pads, and at a high magnification, show crystallized droplets clearly visible atop the NWs, supporting the presence of VLS growth. A few parasitic NWs were observed outside of the NW pads, likely stemming from pinholes in the oxide, indicating the growth conditions facilitated sufficiently long Ga diffusion lengths, enabling adatoms to migrate across the substrate surface and accumulate in the mask holes to form Ga droplets.

The NW measurements are summarized in Table 3.3. The NWs exhibited average lengths of  $(3.6 \pm 0.3) \mu m$ ,  $(3.8 \pm 0.3) \mu m$  and  $(3.9 \pm 0.2) \mu m$  for pitches of 360 nm, 600 nm and 1000 nm, respectively. For a 360 nm pitch, the NWs exhibited average bottom and top segment diameters of  $(121 \pm 16)$  nm and  $(106 \pm 20)$  nm, respectively. Similarly, for a 600 nm pitch the NW bottom and top segments measured  $(118 \pm 13)$  nm and  $(101 \pm 7)$  nm, respectively. Finally, for a 1000 nm pitch the NWs exhibited bottom and top diameters of  $(110 \pm 14)$  nm and  $(135 \pm 10)$  nm, respectively.



Figure 3.11: a)-c) SEM images of 30° tilted Be-doped GaP NWs from sample A NW arrays with 360 nm, 600 nm and 1000 nm pitches, respectively. Spherical crystallized catalyst droplets are visible atop the NWs.

Pitch	Average length	Average diameter (top)	Average diameter (base)	Tapering
(nm)	(μm)	(nm)	(nm)	(%)
360	3.6 ± 0.3	106 ± 9	121 ± 8	-0.42
600	3.8 ± 0.3	101 ± 7	118 ± 6	-0.45
1000	3.9 ± 0.2	135 ± 10	110 ± 8	0.65

Table 3.3: Be-doped GaP NW length and diameter measurements for sample A.

As expected, both NW length and diameter increased with pitch (Table 3.5). The formation of complete shell layers is essential for core-shell NW device performance, as incomplete coverage can distort the junction's energy band profile and reduce carrier collection efficiency. In general, the local V/III flux ratio of the fluxes entering the droplet differs from the nominal V/III flux ratio<sup>81</sup>. Preceding studies of GaP NWs have shown that axial and radial growth rates vary with NW pitch, primarily due to beam shadowing and competition for both incident and re-emitted flux among neighboring NWs<sup>80</sup>. This shadowing effect becomes more pronounced in dense NW arrays and with longer NWs, as a larger fraction of the impinging flux is blocked from reaching the NW base. Conversely, in sparser arrays, the collection areas of adjacent NWs are less likely to overlap, hence each NW receives a greater proportion of re-emitted flux, increasing the axial and radial growth rates.

The NWs exhibited uniform lengths and diameters, with minimal tapering between the base and top NW segments for each pitch. The degree of tapering was quantified using Eq. (3.6.1), which calculates the percentage change in NW diameter along its length. The slight positive tapering exhibited for 360 nm and 600 nm pitches suggests slight shrinkage of the Ga droplet during NW growth as Ga was consumed into crystal GaP<sup>79</sup>, resulting in a slight decrease in diameter below the droplet at the end the growth. Conversely, the slight

inverse tapering observed for the 1000 nm pitch arrays suggests a slight expansion in the droplet size during the 90 min NW growth, owing to the accumulation of Ga in the droplet, resulting in slightly larger diameter at the NW tips. Along with reduced beam shadowing and decreased overlap of flux collection areas at the larger pitch, VS deposition of the secondary Ga flux on the NW sidewalls may have also contributed to NW widening. The swelling and shrinking of the Ga droplet volume occurs as the droplet volume tries to reach a stationary state mediated by a stable contact angle<sup>81,78</sup>.

$$\delta_{\text{taper}} = \left(\frac{D_{\text{top}} - D_{\text{base}}}{L}\right) \times 100 \tag{3.6.1}$$

### 3.6.2 Be-doped Core-shell GaP NWs

The growth parameters of the undoped (intrinsic) layer of the core-shell NW junction were investigated in the following two growths (Tables 3.4 and 3.6). Each growth began with an identical Be-doped axial (core) NW growth step as in Table 3.2. However, for both samples B and C, after the first 90 min, the Be effusion cell was immediately shuttered and the undoped GaP shell was grown for 37 min. During the shell growth the substrate temperature was lowered to 520 °C to suppress surface diffusion of the growth species adatoms, thus encouraging greater radial incorporation on the NW sidewalls over growth along the axial direction. The V/III flux ratio was reduced from 3 to 2. Sample B and C are distinguished by the Ga impingement rates of the undoped shell growth step; all other growth parameters were identical between the two growths.

#### 3.6.2.1 Sample B

During the undoped shell growth, the Ga impingement rate was increased to  $1 \mu$ m/h. The complete growth protocol is detailed in Table 3.4, with resulting NW length and diameter measurements summarized in Table 3.5. The NW dimensions exhibited the expected increase with pitch. Compared to Fig. 3.11, Fig. 3.12 reveals a distinct morphological transformation in the core-shell NWs, characterized by prominent hexagonal faceting (particularly for a 1000 nm pitch) after the undoped shell deposition. This hexagonal structure, consisting of {-110} side facets, is characteristic of VS grown NWs on [111] surfaces<sup>50</sup>. The emergence of these hexagonal sidewall facets in Fig. 3.12 suggests that VS deposition becomes the dominant growth mechanism following the Be-doped core segment formation.

Segment	Time	Temperature	Doping	Ga Impingement Rate	V/III Flux Ratio			
		(°C)	(cm <sup>-3</sup> )	(µm/h)				
	Start							
Ga	250 s	650	None	0.125	-			
GaP	90 min	650	Be - 1 × 10 <sup>19</sup>	0.125	3			
GaP	37 min	520	None	1	2			
End								

Table 3.4: Samp	ple B MBE growth	protocol of Be-do	ped (p-i)	GaP core-shell NWs.
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Figure 3.12: a)-c) SEM images of 30 ° tilted Be-doped (p-i) GaP core-shell NWs from sample B NW arrays with 360 nm, 600 nm and 1000 nm pitches, respectively. The Ga impingement rate during shell growth was  $1 \mu m/h$ .

Pitch	Average length	Average diameter (top)	Average diameter (base)	Tapering
(nm)	(µm)	(nm)	(nm)	(%)
360	$4.1 \pm 0.3$	197 ± 10	144 ± 10	1.30
600	4.2 ± 0.3	226 ± 12	160 ± 11	1.57
1000	$4.4 \pm 0.2$	304 ± 9	221 ± 10	1.87

Table 3.5: Be-doped core-shell GaP NW length and diameter measurements for sample B.

The shell thicknesses at the NW base and tips were calculated by comparing the NW diameters measured in Table 3.5 with those recorded in Table 3.3, taking the difference between these measurements. The total NW diameter is given by ( $D = d_{core} + 2t_i + 2t_n$ ), where  $d_{core}$  is the NW core diameter, and  $t_{i,n}$  are the undoped and n-shell thicknesses, respectively. At the NW tips, the average intrinsic shell thickness was 45.5 nm, 62.5 nm and 84.5 nm for a 360 nm, 600 nm and 1000 nm pitch, respectively. Notably, the shell thickness diminished significantly towards the base, measuring 11.5 nm, 21 nm and 55.5 nm for each pitch, respectively, likely owing to beam shadowing and competition between adjacent NWs inhibiting uniform shell deposition along the NW. Smaller pitches and longer

NWs exacerbate these effects. Nevertheless, for 600 nm and 1000 nm pitches, the average intrinsic shell thickness at the NW tips was reasonably close to the predicted nominal thickness of 70 nm. The predicted shell thickness was calculated using,

$$\delta R = \frac{D}{2} \left[ \left[ \frac{4Ft \sin \theta}{D} + 1 \right]^{\frac{1}{2}} - 1 \right]$$
(3.6.2)

from Ref. 82. Here,  $\delta R$  is the shell thickness, F is the 2D equivalent growth rate in nm/s, t is the deposition time,  $\theta$  is the molecular beam angle ( $\theta = 35^\circ$ ), and D is the NW core diameter.

The additional Ga adatom flux increased both the flux delivered to the droplet as well as the flux re-emitted by the oxide surface, leading to higher droplet supersaturation, sustaining axial growth concurrent with lateral growth. Gallium adatoms within one diffusion length of the droplet are preferentially captured for axial growth rather than contributing to radial VS growth<sup>79</sup>. The reduced V/III flux ratio led to accumulation of excess Ga in the droplet, causing its expansion and an increase in the NW's top diameter<sup>68,80</sup>. Meanwhile, the reduced substrate temperature limited surface diffusion of growth species, restricting adatom diffusion along the sidewalls up to the droplet. These growth conditions enhanced VS deposition along the NW sidewalls, causing characteristic widening (i.e. inverse tapering) of the NWs near their tips. Many of the NWs exhibited crystallites or partially formed droplets at their top facet, indicative of complete or partial Ga droplet consumption, respectively.

#### 3.6.2.2 Sample C

In the third growth (Table 3.6), compared to sample B, the undoped shell Ga impingement rate was reduced from 1  $\mu$ m/h to 0.5  $\mu$ m/h. Fig. 3.13 shows SEM images of sample C; they reveal a morphology similar to sample B (Fig. 3.12). The reduced Ga impingement rate produced NWs that were slightly smaller and significantly less tapered compared to sample B. The resulting NW measurements are summarized in Table 3.7. The average tapering factors across all pitches decreased by more than 50 % relative to those in Table 3.5. This reduction in inverse tapering stems from decreased Ga flux to both the droplet and oxide surface, limiting droplet expansion and sidewall incorporation during shell growth. Consequently, the growth exhibits a more balanced distribution between axial and radial modes. Additionally, fewer parasitic NWs were observed outside the NW pads, suggesting a lower density of oxide pinholes. The reduced Ga supply further decreased the likelihood of parasitic growth.

Segment	Time	Temperature	Doping	Ga Impingement Rate	V/III Flux Ratio			
		(°C)	(cm <sup>-3</sup> )	(µm/h)				
	Start							
Ga	250 s	650	None	0.125	-			
GaP	90 min	650	Be - 1 × 10 <sup>19</sup>	0.125	3			
GaP	37 min	520	None	0.5	2			
End								

Tab	le 3.6	: Samp	le C M	BE growt	h protoco	l of Be-c	loped (	p-i)	GaP	core-shell	NWs.
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Figure 3.13: a)-c) SEM images of 30 ° tilted Be-doped (p-i) GaP core-shell NWs from sample B NW arrays with 360 nm, 600 nm and 1000 nm pitches, respectively. The Ga impingement rate during shell growth was 0.5  $\mu$ m/h.

Pitch	Average length	Average diameter (top)	Average diameter (base)	Tapering
(nm)	(μm)	(nm)	(nm)	(%)
360	3.9 ± 0.2	141 ± 14	120 ± 14	0.54
600	4.1 ± 0.2	184 ± 17	145 ± 15	0.95
1000	4.2 ± 0.2	206 ± 24	182 ± 22	0.57

Table 3.7: Be-doped core-shell GaP NW length and diameter measurements for sample C.

For 600 nm and 1000 nm pitches, the average intrinsic shell thickness at the NW tips was 42 nm and 36 nm, respectively, closely matching the predicted thickness of 41 nm. Shadowing is believed to have significantly influenced radial deposition at smaller pitches and at the NW base. At a 360 nm pitch, the NWs exhibited an average intrinsic shell thickness of 18 nm at the tips, with negligible deposition at the base. In contrast, a uniform average shell thickness was observed at both the base and tip for a 1000 nm pitch, further highlighting the strong influence of beam shadowing

## 3.6.3 Be+Te-doped Core-shell GaP NWs

Lastly, the n-type Te-doped shell was grown, completing the core-shell p-i-n junction. Each growth began with identical Ga pre-depositions and Be-doped axial NW core steps. The undoped shells were grown according to either Table 3.4 or Table 3.6. During Te-doped shell growth, the substrate temperature was maintained at 520 °C. The Te flux was introduced for 7 min using a GaTe valved cracker cell operating at 550 °C, corresponding to a nominal flux corresponding to a carrier concentration of  $5 \times 10^{18}$  cm<sup>-3</sup> as confirmed by Hall effect measurements on thin film calibration samples. While the actual incorporation of Te dopants in the GaP NWs remains to be fully characterized, it is expected to be approximately an order of magnitude lower than the nominal value, consistent with observations from other NW doping studies<sup>83</sup>. As in Section 3.6.2, samples D and E are distinguished by the Ga impingement rates during the Te-doped shell growth step.

#### 3.6.3.1 Sample D

Doping can have a dramatic effect on the diffusion and hence the growth process and NW morphology. Under certain growth conditions summarized Table 3.8, the incorporation of a Te-dopant flux resulted in highly unusual NWs exhibiting extreme positive tapering as imaged using SEM (Fig. 3.14). These remarkably tall and thin GaP "nanoantenna", display novel morphology and crystal structure. The GaP NWs containing nanoantenna structures exhibit abrupt transitions from inverse to positive tapering, whereas NWs without antenna structures display only inverse tapering. NW tip diameters as small as 5 nm were observed.

The mean NW diameter decreases linearly with the nanoantenna length. Notably, TEM analysis in Ref. 81 revealed quasi-periodic oscillations in NW diameter along the tapered segments, which were primarily attributed to dynamic fluctuations in the size and shape of

the catalyst droplet at the NW tip. These fluctuations, driven by variations in material supply, consumption, and phase transitions, emerged from the introduction of the Te dopant species under these specific growth conditions. The diameter oscillations correlate with variations in contact angle and crystal phase, where the contact angle fluctuates around a mean value, oscillating between favouring ZB stacking and longer WZ segments<sup>81</sup>. The narrow quasi-periodic segments of sawtooth faceting of the NW sidewalls containing polytypic ZB/WZ structures along the nanoantenna originate from the accumulation of Te on the NW sidewalls, which is believed to modify the surface energetics along the {-110} facets<sup>84</sup>, suppressing Ga adatom impingement and diffusion into the droplet<sup>81</sup>. Te atoms replace Ga atoms in the solid GaP, enhancing Ga desorption from the sidewalls<sup>81</sup>.

Segment	Time	Temperature	Doping	Ga Impingement Rate	V/III Flux Ratio		
		(°C)	(cm <sup>-3</sup> )	(µm/h)			
Start							
Ga	250 s	650	None	0.125	-		
GaP	90 min	650	Be - 1 × 10 <sup>19</sup>	0.125	3		
GaP	37 min	520	None	1	2		
GaP	7 min	520	Te - 5 × 10 <sup>18</sup>	1	2		
End							

Table 3.8: Sample D MB	E growth protocol of E	3e+Te-doped (p-i-n) (	GaP core-shell NWs.



Figure 3.14: a)-c) SEM images of 52.8 ° tilted Be+Te-doped (p-i-n) GaP core-shell NWs from sample D NW arrays with 360 nm, 600 nm and 1000 nm pitches, respectively. d)-f) SEM images of the 30 ° tilted nanoantenna in the 600 nm pitch array with increasing magnification. Hexagonal faceting of the NWs sidewalls is indicative of VS radial growth. The Ga impingement rate during shell growth was  $1 \mu m/h$ .

A complete discussion of the nanoantenna is outside the scope of this thesis. Diak et al. propose a growth model for the Te-doped nanoantenna in Ref. 81. Structural and optical characterization of the ultrathin NWs can be found in Ref. 84. The SEM images of Fig. 3.14 demonstrate that nanoantenna formation is highly dependent on array pitch. The antennas were restricted to the perimeter of the array or sparsely distributed at random throughout the array in Fig. 3.14a and c (360 nm and 1000 nm pitch), respectively, whereas their presence was dominant throughout the array in Fig. 3.14b (600 nm pitch). At smaller pitches, shadowing can significantly restrict the flux delivered to interior NWs within dense arrays, leading to local Ga-rich conditions (V/III ratio < 1)<sup>80</sup>. In contrast, most of the reemitted flux is captured by perimeter NWs, where reduced competition for flux collection effectively increases the local V/III flux ratio, establishing P-rich conditions (V/III > 1)<sup>81</sup>. This elevated V/III ratio at the perimeter promotes rapid axial growth and positive tapering due to accelerated droplet shrinkage in the unshadowed NWs. Antenna formation is therefore more favourable in the absence of shadowing and flux collection competition. However, at large pitches where shadowing is negligible, Ga-rich conditions can arise as the additional supply of Ga adatoms to the droplets reduces the V/III flux ratio below unity<sup>81</sup>.

The NW measurements are summarized in Table 3.9. For NWs without nanoantenna, excessive Ga adatom supply led to increased sidewall deposition, resulting in unexpected widening at both the base and tips. The average Te-doped shell thickness at the NW base was approximately 6 nm, 16 nm and 29 nm for 360 nm, 600 nm and 1000 nm pitches, respectively, closely matching the predicted nominal thickness of 19 nm for the 600 nm pitch arrays. In contrast, the Te-doped n-shell thickness at the NW tips greatly exceeded expectations, measuring 25.5 nm, 60.5 nm and 31 nm for each pitch, respectively. Sample D produced taller NWs (Table 3.9) than those grown under the conditions specified in Table 3.4, highlighting the concurrent progression of axial and radial growth modes.

Table 3.9: Be+Te-doped core-shell GaP NW length and diameter measurements for NWs
without nanoantenna in sample D. The tapered nanoantenna segments were 4.5 $\mu m$ to
5 μm tall.

Pitch	Average length	Average diameter (top)	Average diameter (base)	Tapering
(nm)	(µm)	(nm)	(nm)	(%)
360	$4.4 \pm 0.1$	247 ± 24	156 ± 20	2.10
600	4.5 ± 0.1	347 ± 31	192 ± 37	3.41
1000	$4.6 \pm 0.1$	366 ± 31	279 ± 44	1.90

#### 3.6.3.2 Sample E

The growth protocol for Be+Te-doped GaP NWs is detailed in Table 3.10. The final NW structure incorporated undoped and Te-doped shells, synthesized at a Ga impingement rate of 0.5  $\mu$ m/h. As shown in Fig. 3.15, this protocol successfully suppressed nanoantenna formation across all array pitches, which can be attributed to the reduced effective V/III flux ratio and resulting Ga-rich growth conditions. These findings highlight the critical role of precise growth conditions in controlling nanoantenna formation, demonstrating that such structures emerge only under specific dynamic growth parameters.

Segment	Time	Temperature	Doping	Ga Impingement Rate	V/III Flux Ratio			
		(°C)	(cm <sup>-3</sup> )	(µm/h)				
Start								
Ga	250 s	650	None	0.125	-			
GaP	90 min	650	Be - 1 × 10 <sup>19</sup>	0.125	3			
GaP	37 min	520	None	0.5	2			
GaP	17 min	520	Te - 5 × 10 <sup>18</sup>	0.5	2			
End								

Table 3.10: Sample E MBE growth protocol of Be+Te-doped GaP core-shell NWs.



Figure 3.15: SEM images of 30 ° tilted Be+Te-doped (p-i-n) GaP core-shell NWs from sample E NW arrays with 360 nm, 600 nm and 1000 nm pitches, respectively, at a)-c) low d)-f) high magnifications. The Ga impingement rate during shell growth was 0.5  $\mu$ m/h.

Consistent with the trends documented in Section 3.6.2.2, this protocol resulted in a significant reduction in average tapering factors across all array pitches, showing more than 50% decrease compared to the tapering factors in Table 3.9. The decreased Ga flux re-emitted from the oxide surface and reduced flux into the droplet diminished both radial deposition on the NW sidewalls and Ga droplet expansion, resulting in less NW widening and consequently, reduced inverse-tapering. The Te-doped shell exhibited consistent thickness between the NW base and tips, measuring 9 nm, 16 nm and 19.5 nm for the 360 nm, 600 nm and 1000 nm pitches, respectively. These measured thicknesses aligned well with the predicted n-shell thickness of approximately 10 nm, indicating a more uniform shell deposition under these growth conditions.

Pitch	Average length	Average diameter (top)	Average diameter (base)	Tapering
(nm)	(μm)	(nm)	(nm)	(%)
360	4.3 ± 0.2	170 ± 22	138 ± 25	0.74
600	4.5 ± 0.2	215 ± 18	177 ± 21	0.85
1000	4.6 ± 0.2	253 ± 24	221 ± 23	0.70

Table 3.11: Be+Te-doped core-shell GaP NW length and diameter measurements for sample E.

## 3.7 Conclusions

This investigation has demonstrated the successful development and optimization of Be+Tedoped core-shell GaP NW growth protocols, culminating in the fabrication of NW structures suitable for BV device applications. The optimized growth parameters, detailed in Table 3.10, yielded core-shell GaP p-i-n NWs with precisely controlled dimensions, exhibiting diameters ranging from 138 nm to 253 nm and lengths spanning 4.3 µm to 4.5 µm. These NWs were subsequently integrated into BV devices, with their performance characteristics analyzed in Chapter 5.

Axial NW BV devices also merit investigation, particularly given the superior PV diode performance demonstrated for axial NWs in Ref.85. Motivated by this, efforts were originally undertaken to develop axial GaP NW growth protocols capable of producing sufficiently tall ( $\geq 10 \,\mu$ m) NWs with uniform diameters. Although axial p-i-n GaP NWs 200 nm to 300 nm wide and 7  $\mu$ m to 8  $\mu$ m tall were successfully grown, the resulting morphology was highly undesirable. Severe inverse tapering was observed (not shown), leading to bulbous NWs with tip diameters nearly twice that of the base. As a result, the NWs were

highly prone to breaking during device processing. Moreover, the extended growth times required to achieve such heights via MBE—often exceeding 8 h—render this approach impractical for scalable fabrication in a setting with shared resources. In contrast, these limitations were less pronounced in core-shell GaP NW growths, prompting a shift in focus solely toward the core-shell geometry.

A significant ancillary finding emerged during this investigation: the discovery of novel positive-tapered ultrathin GaP NWs exhibiting fascinating structural characteristics. These NWs, grown under conditions specified in Table 3.8, displayed periodic transitions between ZB and WZ crystal phases that correlated directly with diameter oscillations. While these structures proved suboptimal for betavoltaic applications, their unique dimensional and structural properties suggest promising applications in photonic devices, particularly in single-photon emission and detection systems, as extensively documented by Diak et al. in Refs. 81 and 84.

Several avenues for future investigation have emerged from this work. Primary among these is the need to address parasitic growth between NWs and optimize droplet consumption dynamics during the growth process. Furthermore, comprehensive characterization studies are warranted to elucidate the spatial distribution of dopants within the NW structure, precisely map the crystal phase transitions, and quantify the optical properties of these novel nanostructures. Such investigations would not only enhance our understanding of the growth mechanisms but also facilitate the optimization of these NWs for specific technological applications.

The findings presented in this chapter establish a robust foundation for the controlled synthesis of doped GaP NWs while simultaneously opening new pathways for the development of advanced photonic devices. The demonstrated ability to control NW morphology and composition, coupled with the unexpected discovery of novel structural phenomena, underscores the rich potential of III-V semiconductor NW systems in next-generation electronic and photonic applications.

# **Chapter 4**

# **Device Fabrication**

## 4.1 Introduction

This chapter begins with a technical background and summary of the major device processing techniques, followed by a more detailed description of the procedures used to fabricate the NW device. Additional standard operating procedure (SOP) details for the device processing steps in subsequent subsections are provided in Appendix X.

Figure 4.1 outlines the device processing workflow. To fabricate the device, the NW arrays were first encapsulated within a thermoset spin-on dielectric polymer film. The hardened polymer film provided structural support for the NWs and a planar surface to deposit the top metal contacts. After encapsulation, the polymer film was back-etched by reactive ion etching, leaving only a short segment of the NW tips exposed. Photolithography was used to define the top contact patterns in a photoresist masking layer. Followed by sputter deposition of the metal contact layers to transfer the top contact patterns to the planarized NW arrays. The rear contact was then deposited and device processing was completed with a rapid thermal annealing of the device contacts.



Figure 4.1: Device fabrication process flowchart.

## 4.2 Background

## 4.2.1 Reactive Ion Etching (RIE)

Dry etch processes use reactive gas plasmas to anisotropically etch materials. Reactive ion etching is an ion-assisted, energy-driven, chemical reaction dry etch process<sup>86</sup> commonly used in microelectronic device fabrication. The sample is placed on the bottom electrode plate within the chamber. Ion fluxes generated by a low-pressure plasma are accelerated towards the sample by a DC electric field bias that exists between the top and bottom electrodes in the chamber. The positively charged accelerated ions bombard the sample surface resulting in a combination of physical etching, due to a transfer of momentum between the ions and the sample atoms/molecules, and chemical etching due to the chemical reactions that take place between the chemically active radicals and the sample atoms/molecules.

Inductively-coupled plasma reactive ion etching (ICP-RIE) is an RIE process that allows for independent control of the plasma density without affecting ion energy<sup>45</sup>. In ICP-RIE (see Fig. 4.2), the plasma is generated separately by passing an AC current through a conductive coil wrapped around the chamber within the chamber shroud. The oscillating electric field induces a fluctuating magnetic field, which will in turn induce a circulating electric field at the top of the chamber<sup>45</sup>. The electrons in the chamber are accelerated by the electric field and ionize the gas molecules within the chamber via impact ionization or create reactive radicals. A plasma is excited when the rate at which ions are generated exceeds the rate at which electrons and ions recombine. The existence of the plasma is observed by the glow discharge produced as energy is released by the recombination of the electrons and ions in the chamber.



Figure 4.2: Configuration of a typical RIE system.

The positive ions produced in the plasma are accelerated towards the substrate by the application of a radio frequency (RF) power signal, generated by an RF power supply, to a capacitively coupled electrode at the top of the chamber. In ICP-RIE systems, power is typically supplied at a frequency of 13.56 MHz. Due to their extremely low mass, the electrons are able to achieve a high velocity before the electric field polarity reverses. The heavier ions are unable to build up significant momentum in either direction before the field changes, resulting in only electrons colliding with the bottom electrode<sup>45</sup>. The accumulation of negative charge (electrons) on the bottom electrode establishes a DC electric field between the top and bottom electrodes. The positive ions are accelerated towards

the sample by the DC electric field, resulting in physical etching of the sample surface. The chemically active radicals formed by ionization of the gas molecules are unaffected by the DC field; they reach the sample in a much more isotropic manner<sup>45</sup>. The main disadvantage of RIE is convective heating, which is reduced by placing the wafers on a cooled stage to restrict the temperature<sup>86</sup>.

Etch results are often evaluated using the dimensionless quantities of selectivity and anisotropy, defined in Eqs. (4.2.1) and (4.2.2), respectively. Selectivity describes how much faster one type of material is etched relative to another material. Anisotropy describes the preferential nature of an etch process. It is often defined by the ratio of the lateral etch rate to the vertical etch rate. In RIE, these directions are of primary interest. In practice, a negligible lateral etch rate, as close to zero as possible is desired, resulting in almost exclusive vertical etching. Isotropic etches have a 1:1 lateral to vertical etch rate relationship. Isotropic etching is highly undesirable for many semiconductor fabrication applications.

$$S = \frac{\text{Material 1 Etch Rate}}{\text{Material 2 Etch Rate}}$$
(4.2.1)

$$A = 1 - \frac{\text{Lateral Etch Rate}}{\text{Vertical Etch Rate}}$$
(4.2.2)

### 4.2.2 Photolithography

Photolithography is the process of transferring micron-scale features from a physical mask onto a substrate using light. A photosensitive resist, commonly referred to as a "photoresist", is deposited on the substrate surface via spin-coating. The substrate is then carefully positioned below a chromium shadow mask using a mask aligner and exposed to specific wavelengths of UV light emitted from a mercury arc lamp. Following exposure, the substrate is immersed in a developer solvent to resolve the patterns in the photoresist. The patterning process is illustrated in Fig. 4.3

Photoresist is composed of three primary components: a polymer resin, a sensitizer, and a casting solvent<sup>87</sup>. The polymer resin serves as a binding agent that imparts essential structural and chemical properties to the resist. It ensures strong adhesion to the substrate while forming a structural matrix to encapsulate the photosensitive components. After development, the resin provides the masked regions of the substrate with protection against various chemical and physical etchants and processes.



Figure 4.3: Photolithography patterning process.

The sensitizer in a photoresist contains photoactive compounds that mediate chemical reactions within the polymer matrix<sup>87</sup>. Photochemical reactions alter the chemical structure of the polymer chains within the matrix upon exposure to specific wavelengths of light. The nature of these reactions depends on the resist type, with distinct mechanisms for positive and negative resists, as previously described in Section 3.2.2. Common UV

emission wavelengths employed in this process include h-line (465 nm), g-line (405 nm), and i-line (365 nm)<sup>88</sup>. Furthermore, the type and concentration of the sensitizer significantly influence the photoresist's sensitivity to light, thereby determining the required exposure energy and the resolution of the resulting features.

The solvent in a photoresist fulfills three primary functions. First, it dissolves the photoresist components to produce a uniform, low-viscosity liquid solution necessary for spincoating. Adjusting the solvent concentration enables precise control over the viscosity, allowing for precise control of the film thickness during deposition. Second, the solvent facilitates uniform distribution of the resist across the substrate, ensuring consistent coverage and film quality<sup>87,88</sup>. Finally, during the soft-bake process, the solvent is removed through evaporation, leaving behind a solid, uniform film suitable for subsequent exposure steps.

The relatively fast exposure times used in photolithography coupled with the ability to expose multiple substrates in parallel, make photolithography a highly scalable, highthroughput process. These features, along with its high resolution, have made photolithography a cornerstone of modern microfabrication and semiconductor manufacturing.

#### 4.2.3 Magnetron Sputter Deposition

Sputter deposition, illustrated in Fig. 4.4, often referred to as "sputtering", is a solid-source ion plating physical deposition process<sup>89</sup>. Sputtering uses the kinetic energy of ions from a plasma to eject atoms from a solid source target and propel the ejected particles towards the surface of a substrate, where they condense to form a thin film. It does not rely on heat to melt or evaporate the target material. As a result, materials with very high boiling points, such as tungsten and ceramics for example, can be easily sputtered<sup>90</sup>.



Figure 4.4: Diagram of the magnetron sputtering process. Modified from Ref. 91.

Magnetron sputtering requires a high vacuum environment ( $1 \times 10^{-4}$  Torr to  $1 \times 10^{-6}$  Torr). The chamber is evacuated to remove contaminants such as water vapor, residual gases, oxygen, or hydrocarbons. The low pressure environment also allows for efficient plasma generation. Moreover, reducing the presence of contaminants increases the mean free path of particles in the chamber, creating a more direct pathway to the sputter target, contributing to better overall film uniformity, adhesion and quality. After evacuation, the chamber is back-filled with an inert process gas, such as Ar or Kr, that is used to excite a plasma. The plasma is generated by applying a large negative voltage between the cathode, which is connected to the target, and the anode. The electric potential repels free electrons from the negatively charged cathode, accelerating them away from the target. Magnetron sputtering uses a magnetic field to control the speed and trajectory of the charged particles. The interaction between the magnetic and electric fields confines the electrons along a spiral path in the vicinity of the target surface<sup>92</sup>. This increases the density of ions bombarding the target, resulting in a high sputtering rate<sup>90</sup>. Electrons are

ejected from the valence shell of the gas atoms as they collide with the accelerated free electrons, ionizing the inert process gas within the deposition chamber. Sputtering occurs as the positively charged ions within the plasma are accelerated towards the cathode and bombard the target surface. Restricting the plasma to the target surface also protects the substrate from ion bombardment.

A major side effect of bombarding the target with ions is the build up of heat within the target. Overheating of the target during deposition can result in thermal cracking or uneven erosion of the target, as well as possible damage of the substrate. Therefore, cooling systems for the targets are required. Magnetron sputtering systems typically use water-cooled target mounting plates to efficiently dissipate heat from the target during deposition. The high vacuum environment also limits convective heat transfer within the chamber, allowing for better temperature control of the substrate and other sputtering components within the chamber<sup>90</sup>.

Multiple magnetron sputtering variations exist, including DC, pulsed DC, and RF variations. DC magnetron sputtering requires an electrically conductive target surface. Whereas RF magnetron sputtering does not require the target surface to be electrically conductive. However, RF sputtering requires additional specialized equipment such as impedance matching network controllers, and RF power supplies, making it more expensive than DC variations. The components of a DC/RF magnetron sputtering unit are shown in Fig. 4.5. A Torr International CRC-600 DC/RF magnetron sputtering system (see Fig. 4.5 b) was used to deposit the metal contacts discussed in Section 4.4.

In DC sputtering the power supplied to the target is controlled by a high voltage (HV)

power supply unit, which allows the user to independently set the DC voltage and current. A constant voltage is applied to the cathode. Higher voltages enhance the electric field strength between the anode and cathode, which ionize more gas particles and subsequently accelerate the positively charged gas ions more quickly towards the target, thereby increasing their kinetic energy. Higher energy ions are more likely to eject atoms/molecules from the target, effectively increasing the deposition rate. Increasing the DC current also increases the power. In general, higher powers raise the plasma energy and density.



Figure 4.5: a) Deposition chamber schematic. Modified from Ref. 93. b) Torr International CRC-600 DC/RF magnetron sputtering system (from Ref. 93).

RF sputtering is typically used to deposit insulating/non-conductive materials. Bombarding non-conductive target materials with positive ions causes charge accumulation on the surface of the target. The accumulated positive charges on the target surface repel additional incident positive ions originating from the plasma, thus halting the sputtering process. Charge accumulation can also result in arcing between the target and other components within the deposition chamber, which can damage the system and substrate. In RF magnetron sputtering, a high voltage alternating current (HV/AC) power supply is used to reverse the polarity of the voltage at the cathode (i.e. target surface) at regular intervals<sup>94</sup> to prevent charge build up. An impedance-matching network between the power supply and deposition chamber is required to reduce the reflected power in the circuit<sup>49,95</sup>.

Both the sputter deposition rate and film quality depend on a variety of parameters including chamber pressure, gas flow rate, power, and sample placement. The deposition rate is primarily controlled through the deposition power and chamber pressure. Deposition pressure is controlled via the process gas flow rates, which directly affects plasma stability. Higher flow rates raise the plasma density and thus the sputtering rate. Low gas flow rates can extinguish or suppress plasma excitation due to an insufficient number of atoms present to sustain ionization. Excessive flow rates can also destabilize the plasma by reducing the MFP of particles in the deposition plume. Ideally, the sample should be placed towards the center of the deposition plume to effectively receive the sputtered material. The stage is rotated continuously to ensure a uniform deposition.

The sputter yield,

Sputter Yield = 
$$\frac{\text{Atoms Removed}}{\text{Incident Ions}}$$
, (4.2.3)

plays a crucial role in determining the deposition rate. It is defined as the ratio of target surface atoms removed to the number of incident ions bombarding the target surface. Various factors influence the sputter yield, including the energy of the incident particles, the target material, the angle of particle incidence, and the crystal structure of the target surface <sup>95</sup>. Overall, magnetron sputtering is an efficient, low temperature PVD process that is widely used in a variety of semiconductor and electronic device manufacturing applications.

## 4.2.4 Rapid Thermal Annealing (RTA)

RTA is a semiconductor manufacturing process where samples are quickly heated to temperatures between 300 °C to 1000 °C in controlled atmosphere, using high-powered lamps. This heating process typically lasts for several seconds to minutes, followed by a swift cooling phase. RTA selectively activates thermal processes within materials, improving metal film properties including surface morphology, optical characteristics, and electrical performance. Specifically, RTA enhances contact quality by promoting grain growth in metal films, thereby reducing contact sheet resistance. Additionally, RTA facilitates metal-metal alloying and metal diffusion into the semiconductor lattice, both of which are essential for the formation of reliable and high-quality electrical contacts. The rapid thermal cycling inherent to RTA minimizes the thermal budget, reducing the potential for damage to the underlying semiconductor while optimizing material properties for device performance.

## 4.3 Planarization and Back-Etching

Planarization was necessary to obtain a planar surface near the NW tips for top contact deposition, as an external <sup>63</sup>Ni source was used to test the device's BV response. Follwing NW characteration, the sample was planarized using Cyclotene 3022-35, a thermosetting spin-on dielectric polymer derived from bisbenzocyclobutene monomers (BCB). BCB was employed to backfill the volume between NWs. Widely used in microelectronics<sup>96</sup>, BCB offers low moisture absorption, a low dielectric constant, high resistivity  $(1 \times 10^{19} \,\Omega \cdot cm)$ 

and a high breakdown voltage  $(5.3 \times 10^6 \text{ V/cm})$ . Its low dielectric constant reduces capacitive coupling and minimizes charge trapping, thereby limiting the buildup of stray charges in the device. Additionally, encapsulating the NWs in BCB enhances structural rigidity, electrically insulates neighboring NWs, and prevents unintended contact between the device's top and bottom electrodes.

The sample was loaded on a spinner (Laurell WS650MZ-23NPP) and BCB was drop-cast onto the stationary sample. After sitting for 5 minutes, the sample was spun at 5000 rpm for 77 s, at a ramp of 300 rpm/s. The sample was then soft-baked on a hotplate at 100 °C for 90 s. Depending on the desired final BCB film thickness, additional BCB layers were deposited by repeating the drop-casting, spinning and soft-baking steps for each additional layer. Following the final soft-bake step, the sample was cured in a nitrogen glove box for 65 min at 250 °C. In total, three layers of BCB were deposited.

Figure 4.6 shows SEM images of top-down and 30° tilted views, respectively, of the cured BCB film encapsulating the Be+Te-doped GaP NW arrays (Section 3.6.3.2) for 360 nm, 600 nm and 1000 nm pitches. The uniformity of the resultant BCB film exhibits significant dependence on array pitch, a relationship primarily governed by the systematic variations in NW morphology across different array pitches. Experimental observations presented in Chapter 3 demonstrate that both NW diameter and length increase with array pitch, a phenomenon attributed to two key mechanisms: reduced competition between adjacent NWs for impinging flux capture and diminished shadowing of incident flux by neighbouring NWs. This scaling behavior manifests in the formation of taller and wider NWs at larger array pitches. The increased inter-NW spacing of larger pitches provides expanded surface area for BCB deposition, facilitating more uniform film infiltration during spin-coating. Moreover, the mechanical stability of the NW array is enhanced at larger pitches, where

the imbalance of tensile and shrinking forces exerted by the film is minimized, resulting in substantially reduced NW bending. This correlation between array pitch and film morphology highlights the crucial role of the structural arrangement of the NWs in achieving optimal film uniformity.



Figure 4.6: SEM images of top-down (a-c) and 30° tilted views (d-f) of the Be+Te-doped NW encapsulated in BCB for 360 nm, 600 nm and 1000 nm pitches, respectively.

Once cured, BCB is chemically inert to most wet etchants and remains largely unaffected by subsequent processing steps. Its demonstrated resistance to SEM electron beam exposure (1 keV to 30 keV) further indicates strong stability under low-energy electron radiation. As such, BCB is well-suited for use in BV devices exposed to sources such as <sup>63</sup>Ni, whose low-energy  $\beta$ s pose minimal risk of polymer degradation. To expose 200 nm to 300 nm of the NW tips for contacting, BCB was selectively removed using RIE in a Technics Series 800 Micro RIE system with a gas mixture of CF<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub>. The back-etch parameters are detailed in Table A10. Prior internal BCB thin film etch rate studies conducted by Ara Ghukasyan (former PhD student) were used to calibrate the estimated BCB etch rate ( $t_{etch} = 26.2 \text{ nm/min}$ ). To minimize surface roughness and reduce damage to exposed

NWs from the physical component of RIE, longer etch times were segmented into shorter intervals (e.g., a 20 min etch was divided into four 5 min steps).

## 4.4 Metal Contact Patterning and Deposition

Photolithography was used to define the top contact positions on the sample surface. Microposit S1818 and S1827 positive resists were employed to pattern the transparent and opaque contacts, respectively. The photoresist was first drop-cast onto the stationary sample, allowing it to sit for 1 min, followed by spinning at 4000 rpm for 30 s. After soft-baking on a hotplate at 110 °C for 2 min, the contact patterns were transferred using a physical chromium shadow mask and manual contact mask aligner (KARL SUSS MJB-3). Following exposure, contact patterns were developed by gentle agitation in MF-319 developer for 50 s. A 90 s rinse in deionized water followed by N<sub>2</sub> drying completed pattern development. Photolithography quality was subsequently evaluated under an optical microscope.

The choice of contact metals is critical to device performance. Materials that form ohmic contacts with both the substrate and NWs are preferred to ensure efficient carrier extraction. Additionally, since the device was exposed to an external <sup>63</sup>Ni source to evaluate its BV response, it was essential that the top contact remain transparent to  $\beta$ -particles in the active area.  $\beta$ -particles interact more strongly (via scattering and energy losses) with high atomic number (Z) materials due to their higher electron density. As a result, gold is significantly more absorptive than indium-tin-oxide (ITO). To address this, an ITO/Au stack was used to form the top contact: 100 nm of ITO was deposited to directly contact the NWs, preserving beta transparency, while 150 nm of Au was added on top to provide a durable probing surface. 400 nm of Al was deposited over the entire rear surface to form the back contact. Two photolithography steps, shown in Fig. 4.7, were used to define the

top contact stack. In the first step, the transparent ITO layer was patterned, followed by the definition of the opaque Au contact pad in the second. Both top and rear contacts were deposited via magnetron sputtering (Torr International CRC-600 DC/RF, see Fig. 4.5). After each deposition, the sample was immersed in an acetone bath to lift off the photoresist mask, leaving the patterned metal layers intact.



Figure 4.7: a) Device top contact patterns. b) Cross-section of the NW pad after lift-off.



Figure 4.8: Processed GaP NW array BV devices, identical to the NW pad layout shown in Fig. 3.10a

Figure 4.8 shows an optical micrograph of the processed NW BV device sample. In certain instances, liftoff can present significant challenges, potentially requiring extended periods ranging from hours to days. When faced with such difficulties, controlled ultrasonic agitation (sonication) may be judiciously employed to facilitate the liftoff process.

In our experimental work, the sample was immersed in acetone for approximately 13 h overnight, with no discernible progress observed in the liftoff process. Subsequently, multiple brief sonication periods of 10 s to 15 s duration were strategically applied to induce delamination of the photoresist mask.

It is crucial to note that sonication, while effective, introduces potential risks of structural damage to the sample, as the mechanical forces generated during this process can inadvertently remove desired layers along with the photoresist. As evidenced in Fig. 4.8, this phenomenon manifested as localized peeling of both the metallic contacts and adjacent regions, exposing the underlying Si substrate beneath the NWs. The structural compromise resulting from sonication-induced damage likely contributed to the suboptimal performance observed in several of the NW contact pads.

## 4.5 Annealing

Thermal annealing was conducted with an RTA unit. The temperature profile consisted of a linear ramp at a rate of 6.66 °C/s until reaching the target temperature of 400 °C. The sample was then maintained at this temperature for 30 s, followed by a controlled cooling phase until the temperature decreased to 50 °C.

Despite its advantages, RTA often induces cracking in fragile ITO films, leading to increased sheet resistance and degraded electrical conductivity. Distinct cracks in the ITO layer are visible in SEM images Fig. 4.9b and c. Similar ITO morphologies were observed at 600 nm and 1000 nm.



Figure 4.9: Top-view SEM images of a 360 nm pitch NW pad with an ITO/Au bilayer top contact. The ITO and Au films exhibit distinct morphologies, with cracks in the ITO layer visible in (b) and (c).

# 4.6 Conclusions

This chapter provided a comprehensive overview of the fabrication processes used to develop the NW devices, beginning with a general discussion of key processing techniques and culminating in a detailed account of the specific procedures implemented. The fabrication workflow was designed to ensure structural integrity and electrical functionality of
the devices, incorporating polymer encapsulation for mechanical stability, selective etching to expose the NW tips, and precise photolithographic patterning for top contact formation. The sequential deposition of metal contacts and final thermal annealing step completed the device processing, establishing the electrical interfaces necessary for subsequent characterization and performance evaluation. The methodologies outlined in this chapter form the foundation for the experimental studies presented in the following sections. A structured approach to NW device fabrication is essential for reproducibility and performance optimization, particularly given the sensitivity of nanoscale architectures to processing conditions.

While the fabrication process was carefully designed, several challenges were encountered. Achieving uniform BCB film thickness across varying NW pitches proved difficult, as differences in NW density affected polymer flow and planarization. Additionally, the photolithography process required optimization to improve contact pattern liftoff, particularly in cases where adhesion between the photoresist and underlying layers led to incomplete metal removal. Another critical issue was minimizing cracking in the ITO top contact layer, which compromised electrical continuity and device performance. Addressing these challenges requires iterative process refinements, highlighting the complexity of integrating NW-based architectures with conventional microfabrication techniques.

# **Chapter 5**

# **Betavoltaic Device Measurements**

#### 5.1 Introduction

Electrical characterization techniques provide validation and essential insights into the fundamental properties and operational performance of electronic devices. For optoelectronic devices, particularly BV generators and solar cells, current-voltage (I-V) characterization serves as a crucial analytical method for quantifying key performance parameters. The I-V characteristic curves are obtained by measuring the device's current response to an applied bias voltage, which is systematically swept across a predetermined range of values. I-V characteristics taken in the dark reveal information about the diode characteristics of the device which can be obtained by fitting the I-V traces to diode models<sup>50</sup>. In the case of BV devices, I-V responses measured under radioisotope exposure provide EHP generation information and energy conversion efficiency data. These parameters include the maximum power point  $P_{mp}$ , the corresponding current  $I_{mp}$  and voltage  $V_{mp}$  at this point, as well as the short-circuit current  $I_{sc}$ , open-circuit voltage  $V_{oc}$ , fill factor FF, and energy conversion efficiency  $\eta$ . Beyond these primary performance metrics, I-V characteristics provide insights into device contact quality (e.g., distinguishing between ohmic and Schottky behavior) and allow for the quantification of material resistivity.

The I-V responses of the p-i-n GaP NW BV device fabricated from the centre 600 nm pitch pad (position  $R_2$ ,  $C_2$ ) in sample E in Chapter 4 were recorded under both dark conditions and exposure to the solid <sup>63</sup>Ni source, using a four-point probe configuration with a Keithley 2400 source meter unit (SMU). The forward biased dark traces are fitted to a lumped parameter equivalent circuit model in Section 5.4 to assess the diode and contact quality. The energy conversion efficiency is derived from the BV response I-V curves and compared to existing devices in literature. Finally, the BV device efficiency is compared to predicted values from the analytical model in Chapter 2.

### 5.2 Four-wire Sensing

Four-wire (or four-point probe) sensing is a precision measurement technique essential for accurate I-V characterization, particularly when measuring low-resistance or high-precision components. This method employs separate pairs of current-carrying and voltage-sensing wires to eliminate measurement errors caused by lead resistance. While conventional two-wire setups include voltage drops from both test leads and the device under testing (DUT) in their measurements, the four-wire configuration isolates these effects. In a typical implementation (illustrated in Fig. 5.1), a test current is applied through the outer probes while the inner probes measure the resultant voltage drop across the sample surface. The sheet resistance is then calculated using this measured voltage and the known applied current.

The effectiveness of this technique stems from the high impedance of the voltmeter's

voltage-sensing circuit, which prevents significant current flow through the voltage measurement path. This configuration effectively eliminates the variable contact resistance at the probe-device interface, which could otherwise introduce random errors between measurements<sup>49</sup>. For I-V characterization of semiconductor devices, the four-wire configuration connects positive current and voltage probes to the device's cathode terminal, while negative current and voltage probes connect to the anode terminal. This arrangement enables simultaneous current measurement and voltage application, ensuring precise characterization of the device's electrical properties.



Figure 5.1: Illustration of the four-point probe method for measuring sheet resistance, where the probes are equally spaced by a distance *s*.

### 5.3 Experimental Methodology

Prior to electrical characterization, the annealed sample was affixed to a 26-gauge (0.455 mm) copper plate using a two-component silver-filled (Ag) epoxy. The copper plate provides a large conductive platform for electrical probe attachment. EPO-TEK H20E, a 100 % solid

Ag-filled epoxy, is specifically formulated for chip bonding in microelectronic and optoelectronic applications<sup>97</sup>. The dispersed Ag particles within the epoxy establish a lowresistance conductive pathway between the sample's rear contact and the copper plate, thereby ensuring a reliable electrical connection with the probes. Additionally, the high thermal conductivity of Ag epoxy (29 W/m–K) facilitates effective heat dissipation, contributing to improved thermal management during operation.

Figures 5.2 and 5.3 depict the solid <sup>63</sup>Ni source and the probing station used for I-V characterization, respectively, which integrates four precision micro-manipulator probes interfaced with a Keithley 2400 source meter unit. The measurement process was automated through custom Python software operated from a laptop computer, enabling precise control over measurement parameters, including voltage sweep range, step size, and current compliance limits, thus ensuring consistent and reproducible electrical character-ization of the DUT. The source activity was estimated to be  $\sim$ 12.15 mCi.



Figure 5.2: A cylindrical <sup>63</sup>Ni source embedded in a repurposed electron capture detector column. The source was fabricated by irradiating a rectangular foil sheet, which was subsequently rolled into a cylinder. Here, h denotes the cylinder height (10.70 ± 0.02 mm), t represents the foil thickness (0.58 ± 0.02 mm), and d is the inner diameter of the resulting structure (6.58 ± 0.02 mm). The cylinder dimensions were measured with digital calipers.





Figure 5.3: Four point probe electrical measurement setup. The bore of <sup>63</sup>Ni source was positioned above the sample at angle (relative to the horizontal) to expose the foil to NW pads below. A Keithley 2400 source meter unit (SMU) was used to simultaneously source the biasing voltage and measure the device current.

### 5.4 Results and Discussion

The current density-voltage (J-V) characteristics presented in Fig. 5.4 were obtained by normalizing the measured device current with respect to the contacted area of the NW pad ( $0.01 \text{ cm}^2$ ). Due to constraints in source positioning—necessary to avoid interference with the micro-manipulator probes—significant results could only be obtained from the central 600 nm pitch NW pad (position  $R_2$ ,  $C_2$ ). Device efficiency was determined as the ratio of output power density  $P_{out}$  to input power density  $P_{in}$ :

$$\eta = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{J_{\text{mp}}V_{\text{mp}}}{\left(\frac{\phi_0\bar{E}}{A}\right)}$$
(5.4.1)

The source activity  $\phi_0$ , mean  $\beta$  particle energy  $\overline{E}$  in Joules, and source area A are the primary parameters governing the input power density. A comprehensive outline of the power input calculation is presented in Appendix XI.

The experimental results presented in Figure 5.4 elucidate the BV effect in GaP NW diodes, wherein  $\beta$  radiation induces carrier generation, enhancing the  $\beta$ -current. The fundamental diode characteristics remain preserved, exhibiting rectifying behavior analogous to conventional PV and photodiode devices. While the J-V profiles under dark and  $\beta$ -irradiated conditions demonstrate substantial overlap, a modest current enhancement is observed at low voltage regimes. In reverse bias, the current density remains small, indicating low leakage current.



Figure 5.4: Electrical characterization of the 600 nm pitch array BV device: a) dark (blue) and active (purple) J-V characteristics on linear scales, b) corresponding J-V characteristics on semilogarithmic scales, c) J-V curve in the power generation region highlighting the short-circuit current density ( $J_{sc}$ , green) and open-circuit voltage, with the shaded region illustrating the suboptimal fill factor, and d) power curve identifying the maximum power point.

The J-V characteristics of the core-shell p-i-n GaP NW diodes are fundamentally governed by both contact architecture and NW morphology. Structural defects in the ITO top contact layer, specifically the formation of microscopic cracks (documented in Fig. 4.9), introduce spatial inhomogeneities in current distribution. These imperfections potentially manifest as increased series resistance and diminished carrier collection efficiency. Although the ITO/Au bilayer contact structure was engineered to optimize charge extraction, discontinuities within the ITO film may induce localized current crowding phenomena, thereby amplifying ohmic resistive losses. Furthermore, while the 400 nm Al back contact typically establishes an ohmic interface with p-type Si substrates, the potential formation of Schottky barriers—arising from either interfacial oxidation or compromised adhesion—may contribute additional contact resistance. As demonstrated by Anchugov et al. in Ref. 98, such Schottky-type contacts characteristically result in degraded fill factors and conversion efficiencies, consistent with the observations presented in Fig. 5.4c and d. The linear behavior observed in the J-V characteristics within the BV-operating regime manifests as a triangular region (shaded region highlighted in Fig. 5.4c), indicative of a low fill factor and suboptimal energy conversion.

Drawing upon the framework established in Chapter 2, we conducted simulations of the J-V characteristics for our GaP NW array BV device with 600 nm pitch spacing. The experimentally determined efficiency parameters in Fig. 5.4 demonstrate significant divergence from the theoretical predictions generated by our model, as detailed in Fig. 5.5. Notably, the measured energy conversion efficiency is approximately 3 times lower than expected. This reduction is primarily attributed to the order of magnitude diminished open-circuit voltage observed in our device. The most significant discrepancies likely arise from two factors: an actual Te doping level that is at least an order of magnitude lower than expected<sup>83</sup>, and cracking in the ITO layer. As discussed and supported by the predictions in Sections 2.3.1.3 and 2.3.1.5, reduced doping levels lead to a wider depletion region, which lowers the built-in electric potential of the junction and consequently results in a smaller open-circuit voltage. In our simulations for the grown NW core diameter, intrinsic and n-shell thicknesses (101 nm, 41 nm, 16 nm, respectively), an actual Te doping on the order of  $1 \times 10^{17}$  cm<sup>-3</sup> is predicted to result in a fullly depleted junction—violating the model assumptions. Unintentional full depletion can also lower the built-in potential and elevate series resistance within the junction, contributing to the observed degraded device performance.

The NW morphology strongly influences the device's electrical characteristics. While the radial p-i-n junction architecture facilitates enhanced carrier separation, thereby minimizing recombination losses and improving rectification properties, the inherent indirect bandgap nature of ZB GaP renders these devices particularly susceptible to surface-state phenomena. Additionally, surface recombination in GaP has been shown to significantly hinder device performance<sup>11</sup>. These surface states function as charge carrier traps and potentially contribute to elevated leakage currents. In scenarios of incomplete surface passivation, enhanced recombination effects become particularly pronounced at low forward bias conditions. Inconsistent dopant incorporation, combined with the absence of a passivating layer, likely led to the formation of surface defects that contribute to an elevated ideality factor. These non-uniformities hinder carrier extraction, degrading overall device performance.

Underestimating source activity and/or the EHP generation rates within the NWs is a strong candidate for explaining the unexpectedly low theoretical  $J_{sc}$  compared to the experimental value, which is directly proportional to the number of generated and collected

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carriers. Structural analysis presented in previous chapters revealed variations in crystal structure along the NW length, which could significantly impact carrier generation and transport. The most significant sources of performance degradation originate from issues related to NW growth and device fabrication challenges. Addressing these limitations in future work will require optimizing top contact deposition to ensure ohmic contact formation and low  $R_s$ , sufficient dopant incorporation within NWs and implementing surface passivation strategies to suppress recombination losses, and enhance charge collection efficiency. Furthermore, the robustness of our model can be improved by incorporating a broader range of NW morphologies, and a more refined treatment of EHP generation within the NWs.



Figure 5.5: Simulated J-V characteristics of the 600 nm pitch GaP NW array BV device. The simulation parameters were D = 215 nm,  $d_p = 101$  nm,  $t_n = 15.5$  nm,  $L = 4.484 \mu$ m,  $N_A = 1 \times 10^{19}$  cm<sup>-3</sup>,  $N_D = 5 \times 10^{18}$  cm<sup>-3</sup> and d : p = 0.3583.

In comparison to previous work, GaP NW BV devices reported by McNamee in Ref. 49 achieved conversion efficiencies ranging from 0.01 % to 0.031 %, providing a useful benchmark for contextualizing these results. The present work demonstrates an order of magnitude enhancement in conversion efficiency, representing a demonstrable advancement in GaP NW-based BV technology.

#### 5.4.1 Equivalent Circuit Diode Model

The net current generated by an ideal biased p-n junction device is governed by the Shockley diode equation in Eq. (5.4.2):

$$I = I_0 \left[ \exp\left\{ \left( \frac{qV}{k_B T} \right) \right\} - 1 \right]$$
(5.4.2)

Here V is the applied voltage,  $I_0$  is the saturation current, q is the elementary charge,  $k_B$  is the Boltzmann constant, and T is the absolute temperature of the diode. In reality, experimental diode I-V characteristics deviate from the ideal diode curve due to the presence of intrinsic and extrinsic parasitic loss mechanisms. Non-ideal diode behaviour is modeled using an ideality factor n, as well as parasitic shunt and series resistances. The ideality factor represents how close the diode behaves to an ideal diode. The series resistance represents the ohmic voltage drop at the contacts and through the semiconductor material<sup>99</sup>. Series resistance mainly acts to reduce the applied voltage available to the junction. The shunt resistances act as sinks for leakage currents. In an ideal diode the series resistance is zero, the shunt resistances are infinite, and the ideality factor is unity. Numerous methods have been developed to extract these diode parameters from experimental forward bias dark I-V characteristics<sup>100</sup>. The majority of these methods extract diode parameters from restricted regions of the forward bias I-V curve. Using different regions of the I-V curve analytically reduces the diode equation to a more manageable form. Within these restricted regions certain parameters (often shunt or series resistance effects) are assumed to be negligible, allowing for other parameters to be readily extracted from the I-V characteristics. These methods are only valid when these distinct regions are present in the I-V characteristics<sup>101</sup>. In the presence of non-negligible series and shunt resistances, most of the methods discussed in Ref. 100 fail.

Ref. 101 provides a single-exponential diode lumped parameter equivalent circuit model to describe the most general case in which both series and shunt resistances are not negligible. The equivalent circuit shown in figure 5.6 assumes a general diode modeled by a single exponential-type ideal junction<sup>101</sup>. The series resistance is given by  $R_s$ , and two parasitic shunt conductances are included for the sake of completeness. To avoid dealing with limiting cases in which the shunt resistances tend to infinity, parasitic shunt conductances,  $G_{p_1}$  and  $G_{p_2}$ , are used in the model.  $G_{p_{1,2}}$  represent shunt conductance at the junction and periphery, respectively.



Figure 5.6: Single-exponential diode equivalent circuit with parasitic loss elements.

The forward bias terminal current *I*, in Fig. 5.6 is given by the transcendental equation:

$$I = I_0 \left\{ \exp\left[\frac{V(1 + R_s G_{p_2}) - IR_s}{nV_{th}}\right] - 1 \right\} + (V - IR_s)G_{p_1} + VG_{p_2}(1 + R_s G_{p_2}) \quad (5.4.3)$$

where *n* is the ideality factor,  $I_0$  is the saturation current,  $V_{th} = k_B T/q$  is the thermal voltage, *q* is the elementary charge,  $k_B$  is the Boltzmann constant, and *T* is the diode temperature. Explicit analytical solutions for the terminal current and voltage in terms of the diode parameters are obtained using the special Lambert *W* function, which is defined

as the solution to Eq.  $(5.4.4)^{101}$ .

$$W(x)exp[W(x)] = x \tag{5.4.4}$$

The explicit analytical solutions for the terminal current and voltage are given by Eqs. (5.4.5) and (5.4.6):

$$I = \frac{nV_{th}}{R_s} W\left\{\frac{I_0 R_s d_1}{nV_{th}} exp\left[\frac{d_1(V+I_0 R_s)}{nV_{th}}\right]\right\} + d_1(V G_{p_1} - I_0) + V G_{p_2}$$
(5.4.5)

$$V = -nV_{th}d_2W\left\{\frac{I_0R_{12}}{nV_{th}d_2}exp\left[\left(I + \frac{I_0}{d_2}\right)\frac{R_{12}}{nV_{th}}\right]\right\} + Id_2\left(R_s + R_{12}\right) + I_0R_{12}$$
(5.4.6)

$$d_2 = \frac{1}{1 + R_s G_{p_2}} \tag{5.4.7}$$

$$R_{12} = \frac{1}{G_{p_1} + G_{p_2} + G_{p_1}G_{p_2}R_s}$$
(5.4.8)

where W represents the principal branch of the Lambert W function, and  $R_{12}$  is expressed in units of resistance. The terminal current consists of real values, therefore, the principal branch of the Lambert W function is used. Based on the J-V characteristics obtained for the NW diode devices fabricated from sample E, the devices were believed to contain considerable parasitic series resistances and shunt conductances. As a result, the model in Ref. 101 was believed to be an appropriate model for the I-V characteristics of sample E devices.

The terminal current model in Eq. (5.4.5) was implemented using the LMFIT Python package<sup>43</sup>, and the diode parameters were obtained using a non-linear least squares curve

fitting routine based on the Levenberg-Marquardt algorithm (LMA) from <sup>43</sup>. The LMA is adequately suited for this problem because it efficiently handles nonlinear least squares models like Eq. (5.4.5), especially when provided with reasonable initial parameter estimates. In contrast, attempts to use methods such as the Trust Region Reflective (TRF) algorithm in this context failed to produce any reasonable fits. This was likely due to the model's strong parameter coupling and sensitivity, which can lead to poor Jacobian approximations and slow convergence.

The LMA determines the model parameters by minimizing the squares of the deviations of the model from the empirical data through an iterative process. An objective function similar to  $S(\mathbf{v})$  in Eq. (5.4.9),

$$S(\mathbf{v}) = \sum_{i}^{N} \left[ y_{i}^{\text{measured}} - y_{i}^{\text{model}}(\mathbf{v}) \right]^{2}$$
(5.4.9)

where  $y_i^{\text{measured}}$  is the set of experimental data,  $y_i^{\text{model}}$  is the resulting data calculated by the model, **v** is the set of parameters to be optimized, was used to determine the model parameter values. An array of initial guess parameter values was passed to the model and the LMA routine was initiated. The resulting fit was assessed by comparing the coefficient of determination ( $R^2$ ) value to a threshold value and iteratively adjusting the initial guess parameters until an acceptable  $R^2$  value was obtained.



Figure 5.7: Equivalent circuit diode model parameter extraction program flowchart.

Theoretical fits to the experimental forward-bias J-V characteristics, depicted in Fig. 5.8, enable quantitative assessment of the agreement between the theoretical model and experimental observations. The BV device from Sample E demonstrated non-ideal diode behavior, characterized primarily by elevated series resistance and a high ideality factor. While diminished shunt resistances typically facilitate deleterious leakage currents—with values below  $1 \,\mathrm{k\Omega} \cdot \mathrm{cm}^2$  known to significantly compromise device performance  $^{102}$ —the observed shunt resistances at both the junction and peripheral regions suggest negligible shunt-induced effects in this particular device. It is noteworthy that elevated saturation current densities frequently correlate with devices exhibiting large shunt resistances. The observed ideality factor of 4.59 indicates substantial deviation from ideal diode behavior, potentially signifying the presence of crystallographic defects within the semiconductor structure. This hypothesis is supported by TEM analysis reported in Ref. 81, which revealed twinned ZB structures throughout GaP NWs fabricated under conditions analogous

to those employed for sample E. Consequently, the presence of similar structural defects within these NWs is anticipated. Furthermore, suboptimal surface passivation, combined with the characteristically high surface recombination velocity of GaP, likely contributed to enhanced surface recombination along the NW sidewalls, degrading diode performance and increasing non-ideal behavior.

n	$R_s$	$R_{p_1}$	$R_{p_2}$	J <sub>0</sub>	$R^2$
	$k\Omega\cdot cm^2$	$\Omega\cdot cm^2$	$\Omega\cdot cm^2$	A/cm <sup>2</sup>	
4.59	1.55	1.35 × 10 <sup>10</sup>	$1.00 \times 10^{10}$	4.35 × 10 <sup>-8</sup>	0.999845

Table 5.1: Sample E 600 nm pitch BV device diode fit parameters.



Figure 5.8: Sample E 600 nm pitch BV device forward bias dark J-V characteristics (grey) and the diode model fit (red) on (a) linear and (b) semilogarithmic scales.

The values presented in Table 5.1 are within acceptable ranges when compared to extracted diode parameter values from various semiconductor diode devices in literature <sup>100,102</sup>.

However, numerous limitations of the LMA algorithm combined with the nature of the experimental J-V data pose limitations to the accuracy with which the diode parameters could be extracted. The primary disadvantage of the LMA algorithm — common to other iterative optimization algorithms — is its inability to guarantee that the resulting parameters that produce the minimized objective function are the parameters corresponding to the global minimum of the objective function. At low voltages, deviations in the model J-V curves from the experimental curves were observed in Fig. 5.8, in which the model J-V curves demonstrated ohmic behaviour as opposed to rectification. At high voltages, however, the model was a near perfect match to the experimental data for all devices. The poor fit observed at low voltages for these devices may have been due to the optimization routine becoming trapped in local minima during optimization. Multiple combinations of parameters exist that yield a local minimum of the objective function, therefore it may be possible that the set of values in Table 5.1 are not unique. In addition, the resulting set of parameters obtained from the LMA fit depend strongly on the initial guess values provided to the algorithm. Wildly different results are produced if the initial parameters are not close to the actual parameter values. This places a constraint upon the user to provide guesses within an acceptable range of the actual parameters, which can be extremely difficult to deduce in the case where many combinations of parameter values exist.

### 5.5 Conclusions

This chapter has detailed the fabrication, characterization, and performance evaluation of GaP NW BV devices, providing insights into the challenges and limitations encountered. The measured J-V characteristics demonstrated significant deviations from the simulated

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predictions, with conversion efficiencies lower than expected. These discrepancies primarily stem from reduced open-circuit voltage, which can be attributed to increased series resistance from ITO cracking, recombination losses due to surface defects, and nonuniformities in  $\beta$  radiation absorption. Using the equivalent circuit model provided in Ref. 101, the diode ideality factor, series and shunt resistances, and saturation current values were successfully extracted from experimentally obtained forward bias J-V characteristics for the NW BV device. The values obtained were within acceptable ranges for each of the diode parameters, however further research is required to determine the accuracy of the values in Table 5.1. Due to the aforementioned limitations of the Levenberg-Marquardt algorithm, the values in Table 5.1 are not necessarily unique. The implementation of a more robust search optimization routine is required to determine if the parameters in Table 5.1 correspond to a global minimum of the objective function. Despite these limitations, the results provide a foundation for further optimization.

# **Chapter 6**

# Conclusions

### 6.1 Thesis Summary

This thesis presented a comprehensive investigation of core-shell GaP NW BV devices, encompassing their growth, theoretical modeling, fabrication, and performance characterization. Our research has advanced the field through developments in controlled NW synthesis, device processing methodologies, and theoretical frameworks, while simultaneously identifying critical challenges and opportunities for future optimization.

A theoretical model was developed to predict the I-V characteristics of NW BV devices, providing a quantitative framework for understanding charge transport in radial p-i-n junctions. By solving Poisson's equation and the minority carrier continuity equations in cylindrical coordinates, analytical expressions were derived to describe carrier transport and recombination. The model highlighted the interplay between NW geometry, doping concentrations, and device efficiency, revealing a trade-off between maximizing absorber volume and source volume. Additionally, it suggested potential performance enhancements through material selection, including GaAs, Si, and alternative BV materials such as SiC, GaN, and diamond. Future validation of this model through experimental measurements will be critical in refining its predictive accuracy, particularly in accounting for stochastic  $\beta$ -particle interactions and charge carrier generation dynamics.

We demonstrated the successful development and optimization of Be+Te-doped coreshell GaP NW growth protocols. Precise tuning of the growth parameters enabled the fabrication of NWs with controlled dimensions, making them suitable for integration into BV devices. A key finding from this work was the discovery of ultrathin GaP NWs exhibiting periodic transitions between zinc-blende (ZB) and wurtzite (WZ) crystal phases, correlating with diameter oscillations. While these structures were not ideal for BV applications, they suggest potential for photonic devices, particularly in single-photon emission and detection.

Device fabrication followed a structured workflow designed to ensure the mechanical stability and electrical functionality of the NW arrays. Key processing steps included polymer encapsulation for structural support, selective etching to expose NW tips, photolithographic patterning for top contact formation, and sequential metal deposition followed by thermal annealing. These steps established the necessary electrical interfaces for subsequent device characterization. Given the sensitivity of nanoscale architectures to processing conditions, reproducibility and optimization of fabrication methodologies remain critical for device performance enhancement.

Experimental characterization of the NW BV devices revealed significant deviations from the predicted J-V characteristics, primarily due to open-circuit voltage losses. These discrepancies were largely attributed to ITO cracking, increased surface recombination, and non-uniformities in  $\beta$  radiation absorption. Several fabrication challenges were identified, including maintaining uniform benzocyclobutene (BCB) film coverage across varying

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NW pitches, photolithographic pattern fidelity during liftoff, and minimizing ITO film cracking. Addressing these limitations will be crucial for improving device efficiency. Overall, this work establishes a foundational understanding of GaP NW BV device development while highlighting key areas for refinement.

### 6.2 Future Work

Future research directions should focus on several key areas for optimization. Regarding NW growth, priorities include mitigating parasitic growth, optimizing conducting comprehensive characterization of dopant distribution, crystal phase transitions, and droplet consumption dynamics. Enhanced understanding of dopant profiles within NWs is crucial for accurate device modeling and likely the most critical path towards higher efficiency NW BV device performance. Doping assessments of the p-i-n GaP NWs—similar to Ref. 83—should be carried out to verify the agreement between the NW doping and thin film calibration samples. Additionally, incorporation of more sophisticated models for  $\beta$  radiation absorption and carrier generation within NW arrays would strengthen the theoretical framework for predicting device behavior.

Device fabrication improvements should concentrate on three primary aspects: optimization of the metal top contact deposition protocols, development of effective surface passivation strategies to suppress recombination phenomena, and refinement of NW encapsulation methodologies to enhance charge collection uniformity are important considerations. Alternative top contact metals such as Ni or Al that may be be more compatible with established the established BV device processing techniques, as well as better suited for BV applications merit investigation. A particularly promising avenue for future investigation is the electrodeposition of top contacts, which could potentially eliminate the need for planarization and back-etching steps. This approach, demonstrated by Monaico et al. in Ref. 103 for various metals on III-V nanoscale semiconductors, offers the potential for conformal Ni coating of NWs. Significantly, this technique could enable direct integration of <sup>63</sup>Ni radioisotope sources, aligning with the three-dimensional source geometry proposed in Chapter 2. Investigation of Through systematic address of these challenges, future iterations of GaP NW BV devices could achieve substantial improvements in efficiency and operational stability, advancing their potential for practical implementation in low-power energy harvesting systems.

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# Appendix

### I. Poisson's Equation

Poisson's equation was solved in cylindrical coordinates to determine the electric field **E** and electric potential  $\Psi$  distributions, within the radial p-i-n junction. The resulting electric potential distribution is subsequently used to determine the core-shell junction structure's radial energy band profiles (as shown in Fig. A1). The edges of the quasi-neutral regions (QNRs) in the p-core and n-shell are denoted by  $r_p$  and  $r_n$ , respectively. The intrinsic shell is defined by the radial positions  $r_1$  and  $r_2$ , with thickness  $t_i = r_2 - r_1$ . R is the NW radius.



Figure A1: Simulated equilibrium energy band diagram for a GaAs p-i-n junction. The band discontinuities at the junction interfaces  $(r_1, r_2)$  arise due to the narrowing of the bandgap in the heavily-doped regions.

In practice, ideal p-i-n junctions are not physically realizable devices. Instead, a background dopant concentration is always present. We assumed that the background doping is n-type. Thus, the p-i-n junction described can be modelled as a p<sup>+</sup>-n<sup>-</sup>-n<sup>+</sup> junction. The complete solution to Poisson's equation is thus characterized by the set of values that determine the extent of the depletion region throughout the junction ( $w = r_n - r_p$ ), and the values of the electric potential in the QNRs of the junction ( $\Psi_{n_0}, \Psi_{p_0}$ ).

The electron energy band profile in Fig. A1 was simulated from the electric field and potential distribution solutions. The energy band profile can serve as an analysis tool for understanding the carrier transport mechanisms underpinning the device current-voltage characteristics.

Bandgap narrowing is one of the commonly observed effects resulting from high dopant impurity concentrations<sup>38</sup>. The resulting misalignment of the bands gives rise to discontinuities ( $\Delta E_{c_{n,p}}$ ,  $\Delta E_{v_{n,p}}$ ) in the conduction and valence band, respectively. The degree of shrinkage  $\Delta E_g$  is split between the conduction and valence band discontinuities according to the relationship,  $\Delta E_g = \gamma \Delta E_c + (1 - \gamma) \Delta E_v$ , where  $\gamma \in [0, 1]$  corresponds to the weighting of bandgap narrowing attributed to the conduction band edge change. Due to limited knowledge of the precise value of  $\gamma$  for materials other than Si<sup>104</sup>, a value of 0.5 was assumed for the other materials examined.

The width of the QNRs are influential in minority carrier collection. Materials with short minority carrier diffusion lengths can often benefit from thin QNRs to minimize the distance diffusing minority carriers must travel to reach the depletion region. This can serve to increase the collection efficiency of the minority charge carrier species by increasing the likelihood of the carriers reaching the junction and being swept across the junction by the internal electric field. Note that we have chosen the range of device parameters (n-shell thickness, p-core diameter, doping) such that complete depletion of the p-core or n-shell never occurs, otherwise the open-circuit voltage would be reduced.

The current-voltage characteristics presented in the subsequent sections were constructed by computing the solutions for  $r_p$  and  $r_n$  for each value of the applied bias voltage, yielding  $(r_p(V), r_n(V))$  for a given junction configuration.

Poisson's equation is expressed in the forms given by Eqs. (A1) and (A2),

$$\nabla \cdot \mathbf{E} = \frac{1}{r} \frac{\mathrm{d}}{\mathrm{d}r} \left( rE(r) \right) = \frac{\mathrm{d}E}{\mathrm{d}r} + \frac{E}{r} = \frac{\rho}{\varepsilon}$$
(A1)

$$\nabla^2 \Psi = \frac{\mathrm{d}^2 \Psi}{\mathrm{d}r^2} + \frac{1}{r} \frac{\mathrm{d}\Psi}{\mathrm{d}r} = -\frac{\rho}{\varepsilon} \tag{A2}$$

where,  $\varepsilon = \varepsilon_0 \varepsilon_r$  is the electric permittivity and  $\rho$  is the charge density distribution.

Equation (A1) is obtained from Gauss's law in Eq. (A3), which relates the net bulk electric charge density distribution  $\rho$  to the resulting electric field distribution throughout the junction

$$\nabla \cdot \mathbf{D} = \rho \tag{A3}$$

$$\mathbf{E} = \varepsilon \mathbf{D} \tag{A4}$$

The resulting electric potential distribution is related to the charge density distribution via Eq. (A5).

$$\mathbf{E} = -\nabla \Psi \tag{A5}$$

$$\nabla^2 \Psi = \frac{d^2 \Psi}{dr^2} + \frac{1}{r} \frac{d\Psi}{dr} = \frac{dE}{dr} - \frac{E}{r} = -\frac{q}{\varepsilon} \left( p - n + N_D^+ - N_A^- \right) \tag{A6}$$

The charge density distribution is given by

$$\rho = q(p - n + N_D^+ - N_A^-) = \begin{cases} 0, & 0 < r < r_p \\ -q(N_A - N_B), & r_p < r < r_1 \\ qN_B, & r_1 < r < r_2 \\ q(N_D + N_B), & r_2 < r < r_n \\ 0, & r_n < r < R \end{cases}$$
(A7)

where  $N_A^-$  is the concentration of ionized acceptor dopants,  $N_D^+$  is the concentration of ionized donor dopants,  $N_A$  is the concentration of shallow acceptor atoms,  $N_D$  is the concentration of shallow donor atoms, and  $N_B$  is the background dopant concentration. Shallow dopants were assumed to be completely ionized  $(N_A^- \approx N_A, N_D^+ \approx N_D)$ .

The edges of the quasi-neutral regions (QNRs) in the p-core and n-shell are denoted by  $r_p$  and  $r_n$ , respectively. The intrinsic shell is defined by the radial positions  $r_1$  and  $r_2$ , with thickness  $(r_2 - r_1)$ . R is the radius.

Equations (A8) and (A9) are used to reflect existence of nominal background dopant concentrations<sup>1</sup>.

$$N_{A'} = N_A - N_B \tag{A8}$$

$$N_{D'} = N_D + N_B \tag{A9}$$

<sup>&</sup>lt;sup>1</sup>In  $\lim_{N_B\to 0}$ , the charge density distribution (Eq. (A7)) approaches the form corresponding to an ideal p-i-n junction.

### a. Electric Field Boundary Conditions

The electric field is assumed to be zero within the p and n-shell QNRs, respectively. The electric field must also be continuous throughout the junction since it is assumed no surface or interface state charge densities are present in the region of interest<sup>105</sup>. The electric field boundary conditions are given by

$$\begin{cases} E^{-}(r_{p}) = E^{+}(r_{p}), & \text{B.C. 1} \\ \\ E^{-}(r_{1}) = E^{+}(r_{1}), & \text{B.C. 2} \\ \\ E^{-}(r_{2}) = E^{+}(r_{2}), & \text{B.C. 3} \\ \\ E^{-}(r_{n}) = E^{+}(r_{n}), & \text{B.C. 4} \end{cases}$$
(A10)

### b. Electric Potential Boundary Conditions

The electric potential is assumed to be constant within the p and n-shell QNRs, respectively, and must be continuous throughout the junction (otherwise  $E = \infty$  at discontinuities<sup>105</sup>). The electric potential boundary conditions are given by,

$$\begin{cases} \Psi^{-}(r_{p}) = \Psi^{+}(r_{p}), & \text{B.C. 5} \\ \\ \Psi^{-}(r_{1}) = \Psi^{+}(r_{1}), & \text{B.C. 6} \\ \\ \Psi^{-}(r_{2}) = \Psi^{+}(r_{2}), & \text{B.C. 7} \\ \\ \Psi^{-}(r_{n}) = \Psi^{+}(r_{n}), & \text{B.C. 8} \end{cases}$$
(A11)

#### c. Solving Poisson's Equation

The electric field distribution is obtained by integrating Eq. (A1),

$$\nabla \cdot \mathbf{E} = \frac{1}{r} \frac{d}{dr} \left( rE(r) \right) = \frac{\rho(r)}{\varepsilon}$$
$$\frac{d}{dr} \left( rE(r) \right) = r \frac{\rho(r)}{\varepsilon}$$
$$\int d\left( rE(r) \right) = \int dr \left\{ r \frac{\rho(r)}{\varepsilon} \right\}$$
$$r \cdot E(r) = \int dr \left\{ r \frac{\rho(r)}{\varepsilon} \right\} + C$$

The general solutions of E(r) and  $\Psi(r)$  are given by,

$$E(r) = \begin{cases} 0, & 0 < r < r_{p} \\ -\frac{qN_{A'}}{2\varepsilon}r + \frac{1}{r}C_{1a}, & r_{p} < r < r_{1} \\ \frac{qN_{B}}{2\varepsilon}r + \frac{1}{r}C_{iB}, & r_{1} < r < r_{2} \\ \frac{qN_{D'}}{2\varepsilon}r + \frac{1}{r}C_{2a}, & r_{2} < r < r_{n} \\ 0, & r_{n} < r < R \end{cases}$$
(A12)

$$\Psi(r) = -\int dr \cdot E(r) = \begin{cases} \Psi_{p_0}, & 0 < r < r_p \\ \frac{q_{N_{A'}}}{2\varepsilon} \left[\frac{1}{2}r^2 - r_p^2 \ln(r)\right] + C_{1_b}, & r_p < r < r_1 \\ -\frac{q_{N_{B'}}}{2\varepsilon} \frac{1}{2}r^2 - C_{iB} \ln(r) + C_3, & r_1 < r < r_2 \\ -\frac{q_{N_{D'}}}{2\varepsilon} \left[\frac{1}{2}r^2 - r_n^2 \ln(r)\right] + C_{2_b}, & r_2 < r < r_n \\ \Psi_{n_0}, & r_n < r < R \end{cases}$$
(A13)

Applying the aforementioned boundary conditions to Eqs. (A12) and (A13) yields the following integration constants, given by Eqs. (A14) to (A19), which define the particular solutions given by Eqs. (A26) and (A27).

$$C_{1_a} = \frac{qN_{A'}}{2\varepsilon}r_p^2 \tag{A14}$$

$$C_{1_{b}} = \Psi_{p_{0}} - \frac{qN_{A'}}{2\varepsilon} r_{p}^{2} \left[ \frac{1}{2} - \ln(r_{p}) \right]$$
(A15)

$$C_{2_a} = -\frac{qN_{D'}}{2\varepsilon}r_n^2 \tag{A16}$$

$$C_{2b} = \frac{qN_{D'}}{2\varepsilon} r_n^2 \left[ \frac{1}{2} - \ln(r_n) \right]$$
(A17)

$$C_{3} = C_{3_{a}}$$

$$= \frac{qN_{A'}}{2\varepsilon} \left[ r_{1}^{2} \left[ \frac{1}{2} - \ln(r_{1}) \right] - r_{p}^{2} \left[ \frac{1}{2} - \ln(r_{p}) \right] \right] + \frac{qN_{B}}{2\varepsilon} r_{1}^{2} \left[ \frac{1}{2} - \ln(r_{1}) \right] + \Psi_{p_{0}}$$
(A18)

$$C_{3} = C_{3_{b}}$$

$$= \frac{qN_{B}}{2\varepsilon}r_{1}^{2}\left[\frac{1}{2} - \ln(r_{2})\right] + \frac{qN_{D'}}{2\varepsilon}\left[r_{n}^{2}\left[\frac{1}{2} - \ln(r_{n})\right] - r_{2}^{2}\left[\frac{1}{2} - \ln(r_{2})\right]\right] + \Psi_{n_{0}}$$
(A19)

The integration constants within the intrinsic region  $C_{3_{a,b}}$  are obtained by applying either of the boundary conditions at the right-, or left-hand sides of the intrinsic region (i.e.,  $r_1$  or  $r_2$  respectively), yielding the constants in Eqs. (A20) and (A21), respectively. Both of these constants must evaluate to the same value in order for the electric field and electric potential distributions to be valid solutions.

$$C_{iB_{1}} = -\frac{qN_{A'}}{2\varepsilon} \left(r_{1}^{2} - r_{p}^{2}\right) - \frac{qN_{B}}{2\varepsilon}r_{1}^{2}$$
(A20)

$$C_{iB_2} = \frac{qN_{D'}}{2\varepsilon} \left(r_2^2 - r_n^2\right) - \frac{qN_B}{2\varepsilon}r_2^2$$
(A21)

The radial positions of the depletion region edges in the p-core and n-shell, ( $r_p$  and  $r_n$ , respectively), are determined by matching the sets of solutions for the integration constants ( $C_{iB}$ ,  $C_3$ ) within the portion of the depletion region that spans the intrinsic shell of

the junction.

Matching the solutions of  $C_3$  and rearranging, we obtain a transcendental equation in terms of unknown values  $r_p$  and  $r_n$ ,

$$C_{3_{a}} = C_{3_{b'}}$$

$$\frac{qN_{A'}}{2\varepsilon} \left[ r_{1}^{2} \left[ \frac{1}{2} - \ln(r_{1}) \right] - r_{p}^{2} \left[ \frac{1}{2} - \ln(r_{p}) \right] \right]$$

$$+ \frac{qN_{B}}{2\varepsilon} r_{1}^{2} \left[ \frac{1}{2} - \ln(r_{1}) \right] - \frac{qN_{B}}{2\varepsilon} r_{1}^{2} \left[ \frac{1}{2} - \ln(r_{2}) \right]$$

$$+ \frac{qN_{D'}}{2\varepsilon} \left[ r_{n}^{2} \left[ \frac{1}{2} - \ln(r_{n}) \right] - r_{2}^{2} \left[ \frac{1}{2} - \ln(r_{2}) \right] \right] = \Psi_{n_{0}} - \Psi_{p_{0}}$$

$$\equiv V_{bi}$$
(A22)

$$V_{bi} = \Psi_{n_0} - \Psi_{p_0} \tag{A23}$$

where  $V_{bi}$  is the equilibrium built-in electric potential of the junction. The built-in potential is proportional to the energy barrier that diffusing majority carriers in the p-doped core and n-doped shell must overcome to traverse the junction.

The electrostatic potential in the p and n-shell QNRs,  $(\Psi_{n_0}, \Psi_{p_0})$ , respectively, is determined from Fermi-Dirac statistics as per the procedure in Refs. 106, 107 (or Boltzmann statistics where reasonable).

In the presence of a constant applied external electric field, the junction's built-in electric potential is the superposition of the equilibrium built-in potential and the externally applied potential  $V_a$ .

$$V_{bi} - V_a = (\Psi_{n_0} - \Psi_{p_0}) - V_a$$
(A24)

Matching solutions of  $C_{iB}$  in Eqs. (A20) and (A21), we obtain an expression for  $r_n$  in terms of  $r_p$ , given by Eq. (A25). Substituting Eq. (A25) into Eq. (A22) reduces Eq. (A22) to a transcendental equation with a single unknown,  $r_p$ . The resulting equation can now be solved for the value of  $r_p$ . The solution is substituted back into Eq. (A25) to determine the extent of the junction's space-charge region.

$$\rightarrow C_{iB_1} = C_{iB_2} - \frac{qN_{A'}}{2\varepsilon} \left(r_1^2 - r_p^2\right) - \frac{qN_B}{2\varepsilon} r_1^2 = \frac{qN_{D'}}{2\varepsilon} \left(r_2^2 - r_n^2\right) - \frac{qN_B}{2\varepsilon} r_2^2 r_n = \sqrt{r_2^2 + \frac{N_{A'}}{N_{D'}} \left(r_1^2 - r_p^2\right) - \frac{N_B}{N_{D'}} \left(r_2^2 - r_1^2\right)}$$
(A25)

The complete solution to Poisson's equation is thus characterized by the set of values that determine the extent of the depletion region throughout the junction ( $w = r_n - r_p$ ), and the values of the electric potential in the QNRs of the junction ( $\Psi_{n_0}, \Psi_{p_0}$ ).

The particular solutions are thus,

$$E(r) = \begin{cases} 0, & 0 < r < r_{p} \\ -\frac{qN_{A'}}{2\varepsilon} \frac{1}{r} \left(r^{2} - r_{p}^{2}\right), & r_{p} < r < r_{1} \\ \frac{qN_{B}}{2\varepsilon} \frac{1}{r} \left(r_{1}^{2} - r^{2}\right) - \frac{qN_{A'}}{2\varepsilon} \left(r_{1}^{2} - r_{p}^{2}\right) \frac{1}{r} \\ = \frac{qN_{B}}{2\varepsilon} \frac{1}{r} \left(r^{2} - r_{2}^{2}\right) + \frac{qN_{D'}}{2\varepsilon} \left(r_{2}^{2} - r_{n}^{2}\right) \frac{1}{r}, & r_{1} < r < r_{2} \\ \frac{qN_{D'}}{2\varepsilon} \frac{1}{r} \left(r^{2} - r_{n}^{2}\right), & r_{2} < r < r_{n} \\ 0, & r_{n} < r < R \end{cases}$$
(A26)

$$\Psi(r) = \begin{cases} \Psi_{p_{0}}, & 0 < r < r_{p} \\ \frac{qN_{A'}}{2\varepsilon} \left[ \frac{1}{2} \left( r^{2} - r_{p}^{2} \right) - r_{p}^{2} \ln \left( \frac{r}{r_{p}} \right) \right] + \Psi_{p_{0}}, & r_{p} < r < r_{1} \\ \frac{qN_{A'}}{2\varepsilon} \left( r_{1}^{2} - r_{2}^{2} \right) \left[ \frac{1}{2} + \ln \left( \frac{r}{r_{p}} \right) \right] + \\ \frac{qN_{B}}{2\varepsilon} \left[ \frac{1}{2} \left( r_{1}^{2} - r^{2} \right) + r_{1}^{2} \ln \left( \frac{r}{r_{1}} \right) \right] + \Psi_{p_{0}} = \\ \frac{qN_{B'}}{2\varepsilon} \left[ \frac{1}{2} \left( r_{2}^{2} - r^{2} \right) + r_{2} \ln \left( \frac{r}{r_{2}} \right) \right] + \\ \frac{qN_{B}}{2\varepsilon} \left[ r_{1}^{2} \ln \left( \frac{r}{r_{n}} \right) - r_{2}^{2} \ln \left( \frac{r}{r_{2}} \right) + \frac{1}{2} \left( r_{n}^{2} - r_{2}^{2} \right) \right] + \Psi_{n_{0}}, \quad r_{1} < r < r_{2} \\ \frac{qN_{p'}}{2\varepsilon} \left[ \frac{1}{2} \left( r_{n}^{2} - r^{2} \right) + r_{n}^{2} \ln \left( \frac{r}{r_{n}} \right) \right] + \Psi_{n_{0}}, \quad r_{2} < r < r_{n} \\ \Psi_{n_{0}}, \quad r_{n} < r < R \end{cases}$$

The electric field and electric potential and distribution solutions for a core-shell p-i-n GaAs NW are shown in Fig. A2.



Figure A2: a) Electric field and b) electric potential distribution solutions for a GaAs p-i-n junction with  $N_A = 5 \times 10^{18}$ ,  $N_D = 1 \times 10^{19}$ ,  $d_p = 130$  nm,  $t_n = 20$  nm,  $t_i = 15$  nm, D = 200 nm.  $V_{bi}$  is the built-in potential of the junction.

### **II.** Continuity Equations

The minority carrier continuity equations are given by

$$\frac{\partial n}{\partial t} = \frac{1}{q} \left( \nabla \cdot \mathbf{J_n} \right) + G_n - R_n \tag{A28}$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q} \left( \nabla \cdot \mathbf{J}_{\mathbf{p}} \right) + G_p - R_p \tag{A29}$$

where q is the elementary charge, n and p are the minority electron and hole carrier concentrations,  $G_{n,p}$  are the minority carrier generation rates, and  $R_{n,p}$  are the minority carrier recombination rates. **J**<sub>n,p</sub> are the corresponding minority carrier current densities given by

$$\mathbf{J}_{\mathbf{n}} = q\mu_n n \mathbf{E} + q D_n \nabla n \tag{A30}$$

$$\mathbf{J}_{\mathbf{p}} = q\mu_p p \mathbf{E} - qD_p \nabla p \tag{A31}$$

where **E** is the electric field distribution,  $D_{n,p}$  are the minority carrier diffusion constants and  $\mu_{n,p}$  are the minority carrier mobilities. In the QNRs, the electric field is assumed to be zero ( $\mathbf{E} = 0, \forall r \in [0, r_p]$  and  $[r_n, R]$ ). Thus, the first term in the current density drops out, and only the diffusive term remains.

Under steady-state conditions, the LHS of Eqs. (A28) and (A29) vanish, and the general forms of the excess minority carrier continuity equations within the QNRs are

$$\nabla^2 \Delta n - \beta_n^2 \Delta n = g_n \tag{A32}$$

$$\nabla^2 \Delta p - \beta_p^2 \Delta p = g_p \tag{A33}$$

where

$$g_{n,p} = -\frac{G_{n,p}}{D_{n,p}}$$
$$\frac{R_{n,p}}{D_{n,p}} = \beta_{n,p}^2 \Delta n, p$$
$$\beta_{n,p} = \frac{1}{L_{n,p}}$$
$$L_{n,p} = \sqrt{D_{n,p}\tau_{n,p}}$$

where  $\Delta n = n - n_0$  and  $\Delta p = p - p_0$  are the excess minority electron and hole concentrations,  $L_{n,p}$  are their respective diffusion lengths, and  $\tau_{n,p}$  are their respective minority carrier lifetimes.  $n_0$  and  $p_0$  are the equilibrium minority electron and hole concentrations, respectively. The minority carrier lifetimes, mobilities and diffusion lengths within

the QNRs were computed as a function of the dopant concentrations  $(N_A, N_D)$ . The minority carrier diffusion constants were determined from the minority carrier mobilities via the Einstein relation. Material parameter values are listed in Tables A1 to A7 in the following sections.

By exploiting the azimuthal symmetry of the cylindrical geometry, and assuming carrier transport occurs purely along the radial direction, we can ignore variations along the azimuthal  $\theta$  and axial z coordinates on the LHS of Eqs. (A32) and (A33). The resulting steady-state free electron and hole carrier concentration continuity equations take the form of modified Bessel equations of 0<sup>th</sup> order given by:

$$\frac{\mathrm{d}^2 \Delta n}{\mathrm{d}r^2} + \frac{1}{r} \frac{\mathrm{d}\Delta n}{\mathrm{d}r} - \frac{\Delta n}{L_n^2} = -\frac{G_n}{D_n} = g_n \tag{A34}$$

$$\frac{\mathrm{d}^2 \Delta p}{\mathrm{d}r^2} + \frac{1}{r} \frac{\mathrm{d}\Delta p}{\mathrm{d}r} - \frac{\Delta p}{L_p^2} = -\frac{G_p}{D_p} = g_p \tag{A35}$$

#### a. Green's Function Formalism

Green's method is used to determine the solutions to the modified Bessel equations for the general forcing function, g(z). The Green's function is the system's impulse response to an inhomogeneous linear differential operator on the domain specified by the boundary conditions. The ODE solution is the convolution of the Green's function and the forcing term. Thus, once the Green's function is known, the solutions for any forcing term can be obtained.

$$y = G * g \tag{A36}$$

The original problem is first reformulated to yield a new sub-problem in terms of the

Green's function,  $G(r, \xi)$ . The sub-problem is constructed by applying the differential operator to the Green's function while setting the forcing term equal to an impulse  $\delta(r - \xi)$  positioned at a point  $\xi$  on the interval [a, b]:

$$\mathcal{L}\left\{y\right\} = \nabla^2 G(r,\xi) - \beta G(r,\xi) = \delta(r-\xi) \tag{A37}$$

The ODE solutions are constructed from the superposition of the impulse response and a set of boundary terms. The set of boundary terms are given by  $S(r, \xi)$ , as expressed in Eq. (A38).

$$y = \int_{a}^{b} d\xi G(r,\xi) g(z) - \left[ S(r,\xi) \right]_{\xi=a}^{\xi=b}$$
(A38)

The domain is divided in two sub-intervals,  $a \le r < \xi$  and  $\xi < r \le b$ , about the point  $\xi$ , corresponding to regions of the domain in which r is less than, or greater than  $\xi$ , respectively. The Green's function solutions are expressed according to Eq. (A40), for which the solutions are obtained by solving Eq. (A39) in each sub-interval of the domain.

$$\nabla^2 G(r,\xi) - \beta G(r,\xi) = 0 \tag{A39}$$

$$G(r,\xi) = \begin{cases} u_{<}(r) & a \le r < \xi \\ u_{>}(r) & \xi < r \le b \end{cases}$$
(A40)

The Green's function must satisfy the boundary conditions of our original differential equation<sup>2</sup>, and must be continuous at the point  $\xi$ . Its derivative must also be discontinuous

<sup>&</sup>lt;sup>2</sup>i.e. on  $\Delta n$  and  $\Delta p$ .

at  $\xi$ , as expressed in Eqs. (A41) and (A42)<sup>108</sup>, respectively,

$$u_{<}(r)\Big|_{r=\xi} = u_{>}(r)\Big|_{r=\xi}$$
 (A41)

$$\left. \frac{\mathrm{d}G}{\mathrm{d}r} \right|_{r=\xi} = \lim_{\varepsilon \to 0} \left. \frac{\mathrm{d}G}{\mathrm{d}r} \right|_{r=\xi-\varepsilon}^{r=\xi+\varepsilon} = \frac{1}{p(\xi)} = -W[u_{<}, u_{>}] \tag{A42}$$

where  $W[u_{\leq}, u_{\geq}]$  is the Wronskian, and p is an arbitrary function of  $\xi$ .

Additionally, symmetry of the Green's function in r and  $\xi$  requires the Green's function satisfy Eq. (A43).

$$G(r,\xi) = G(\xi,r) \tag{A43}$$

The excess minority carrier concentration continuity equations are a special class of second order linear differential equation referred to as *Sturm-Liouville* equations. As a consequence, solutions to these types of differential equations can be constructed from the superposition of a set of orthonormal basis functions. For the modified Bessel equation, the orthonormal basis functions are modified Bessel functions<sup>109,108</sup>. Thus, within the p and n-QNRs, solutions to Eq. (A39) take the form,

$$G(r,\xi) = \begin{cases} A(\xi)I_{0}(\beta r) + B(\xi)K_{0}(\beta r) & a \le r < \xi \\ \\ C(\xi)I_{0}(\beta r) + D(\xi)K_{0}(\beta r) & \xi < r \le b \end{cases}$$
(A44)

where A, B, C, and D are constants with respect to r, and  $I_i$  and  $K_i$  are i<sup>th</sup> order modified Bessel functions of the first and second kinds, respectively. The coefficients are obtained by applying the corresponding boundary conditions in Eqs. (A45) and (A48) for  $\Delta n$  and  $\Delta p$ , respectively.

$$\begin{cases} \lim_{r \to 0} |\Delta n(r)| < \infty \\ \Delta n(r) \Big|_{r=r_p} = n_0 \left( e^{\frac{qV}{k_B T}} - 1 \right) \\ \Delta p(r) \Big|_{r=r_n} = p_0 \left( e^{\frac{qV}{k_B T}} - 1 \right) \\ \left\{ \Delta p(r) \Big|_{r=r_n} = p_0 \left( e^{\frac{qV}{k_B T}} - 1 \right) \\ S_p \Delta p(r) \Big|_{r=R} = -D_p \frac{\partial \Delta p}{\partial r} \Big|_{r=R} \\ \left\{ \lim_{r \to 0} |\Delta n(r, z)| < \infty \\ \Delta n(r, z) \Big|_{r=r_p} = 0 \\ \left\{ \Delta p(r, z) \Big|_{r=r_n} = 0 \\ S_p \Delta p(r, z) \Big|_{r=R} = -D_p \frac{\partial \Delta p}{\partial r} \Big|_{r=R} \\ (A48) \\ \end{cases} \end{cases}$$

In the absence of exogenous carrier generation mechanisms the beta EHP generation rates in Eqs. (A34) and (A35) vanish. The resulting excess minority electron carrier concentration distribution is given by Eq. (A49).

$$\Delta n(r) = \left[\frac{n_0 \left(\exp\left(\frac{qV}{kT}\right) - 1\right)}{I_0 \left(\beta_n r_p\right)}\right] I_0 \left(\beta_n r\right) \tag{A49}$$

The excess dark minority hole carrier concentration distribution is given by Eq. (A50).

$$\Delta p(r) = p_0 \left[ \exp\left(\frac{qV}{kT}\right) - 1 \right] \times \left[ \gamma^{-1} I_0 \left(\beta_p r\right) + \zeta^{-1} K_0 \left(\beta_p r\right) \right]$$

$$\gamma = 1 + \frac{\left[\beta_{p}I_{1}\left(\beta_{p}R\right) - \frac{S_{p}}{D_{p}}I_{0}\left(\beta_{p}R\right)\right]}{\left[\beta_{p}K_{1}\left(\beta_{p}R\right) + \frac{S_{p}}{D_{p}}K_{0}\left(\beta_{p}R\right)\right]} \left[\frac{K_{0}(\beta_{p}(R - x_{1}))}{I_{0}(\beta_{p}(R - x_{1}))}\right]$$
(A50)

$$\zeta = K_0 \left( \beta_p \left( R - x_1 \right) \right) + \frac{\left[ \beta_p K_1 \left( \beta_p R \right) + \frac{S_p}{D_p} K_0 \left( \beta_p R \right) \right]}{\left[ \beta_p I_1 \left( \beta_p R \right) - \frac{S_p}{D_p} I_0 \left( \beta_p R \right) \right]} I_0 \left( \beta_p \left( R - x_1 \right) \right)$$

The dark excess minority electron and hole diffusion current densities in the QNRs are given by Eqs. (A51) and (A52), respectively.

$$J_{\text{dark}}^{\Delta n} = \frac{1}{\pi R^2} \int_{\theta=0}^{\theta=2\pi} \int_{z=0}^{z=L} r d\theta dz \left\{ q D_n \frac{\partial \Delta n}{\partial r} \Big|_{r=r_p} \right\}$$

$$= \frac{2q D_n L r_p}{L_n R^2} n_0 \left[ \exp\left(\frac{q V}{k_B T}\right) - 1 \right] \frac{I_1 \left(\beta_n r_p\right)}{I_0 \left(\beta_n r_p\right)}$$
(A51)

$$J_{\text{dark}}^{\Delta p} = \frac{1}{\pi R^2} \int_{\theta=0}^{\theta=2\pi} \int_{z=0}^{z=L} r d\theta dz \left\{ -q D_p \frac{\partial \Delta p}{\partial r} \Big|_{r=R-x_1} \right\}$$

$$= -\frac{2q D_p L r_n}{L_p R^2} p_0 \left[ \exp\left(\frac{q v}{kT}\right) - 1 \right]$$

$$\times \left[ \chi^{-1} I_1(\beta_p r_n) - v^{-1} K_1(\beta_p r_n) \right]$$

$$\chi = I_0(\beta_p r_n) + \frac{\left[ \beta_p I_1(\beta_p R) + \frac{S_p}{D_p} I_0(\beta_p R) \right]}{\left[ \beta_p K_1(\beta_p R) - \frac{S_p}{D_p} K_0(\beta_p R) \right]} K_0(\beta_p r_n)$$

$$\nu = K_0(\beta_p r_n) + \frac{\left[ \beta_p R_1(\beta_p R) - \frac{S_p}{D_p} K_0(\beta_p R) \right]}{\left[ \beta_p I_1(\beta_p R) + \frac{S_p}{D_p} I_0(\beta_p R) \right]} I_0(\beta_p r_n)$$
(A52)

Under short-circuit conditions the Green's function in the p-QNR for the excess minority electrons takes the form given by Eq. (A53),

$$G(r,\xi) = \begin{cases} \left[ I_0\left(\beta_n\xi\right) \left(\frac{\kappa_0(\beta_n r_p)}{I_0(\beta_n r_p)}\right) - K_0\left(\beta_n\xi\right) \right] I_0(\beta_n r), & 0 \le r < \xi \\\\ I_0\left(\beta_n\xi\right) \left(\frac{\kappa_0(\beta_n r_p)}{I_0(\beta_n r_p)}\right) \times \\\\ \left[ I_0\left(\beta_n r\right) - \left(\frac{\kappa_0(\beta_n r_p)}{I_0(\beta_n r_p)}\right) K_0(\beta_n r) \right], & \xi \le r < r_p \end{cases}$$
(A53)

where  $r_p$  is the p-QNR width, and R is the NW radius.

Applying the same procedure in the n-QNR for the excess minority holes, we obtain

the corresponding Green's function in Eq. (A54),

$$G(r,\xi) = \begin{cases} \gamma \left[ I_0(\beta_p r) - \frac{I_0(\beta_p r_n)}{K_0(\beta_p r_n)} K_0(\beta_p r) \right], & r_n \le r < \xi \\ \\ \chi \left[ I_0\left(\beta_p r\right) - \left[ \frac{\frac{S_p}{D_p} I_0(\beta_p R) + \beta_p I_1(\beta_p R)}{\frac{S_p}{D_p} K_0(\beta_p R) - \beta_p K_1(\beta_p R)} \right] K_0\left(\beta_p r\right) \right], & \xi < r \le R \end{cases}$$

$$\chi = \frac{I_0\left(\beta_p\xi\right) - \frac{I_0(\beta_p r_n)}{K_0(\beta_p r_n)}K_0\left(\beta_p\xi\right)}{\left[\frac{\frac{S_p}{D_p}I_0(\beta_p R) + \beta_p I_1(\beta_p R)}{\frac{S_p}{D_p}K_0(\beta_p R) - \beta_p K_1(\beta_p R)}\right] - \frac{I_0(\beta_p r_n)}{K_0(\beta_p r_n)}}$$
(A54)

$$\gamma = \frac{I_0\left(\beta_p\xi\right) - \left[\frac{\frac{S_p}{D_p}I_0(\beta_p R) + \beta_p I_1(\beta_p R)}{\frac{S_p}{D_p}K_0(\beta_p R) - \beta_p K_1(\beta_p R)}\right]K_0\left(\beta_p\xi\right)}{\left[\frac{\frac{S_p}{D_p}I_0(\beta_p R) + \beta_p I_1(\beta_p R)}{\frac{S_p}{D_p}K_0(\beta_p R) - \beta_p K_1(\beta_p R)}\right] - \frac{I_0(\beta_p r_n)}{K_0(\beta_p r_n)}}$$

where  $r_n$  is radial position of the edge of the n-QNR. Applying Eq. (A38) to Eqs. (A53) and (A54), yields the excess minority electron and hole concentration distributions Eqs. (A55)

and (A56), respectively.

$$rI_{0}(\beta_{n}r)[I_{1}(\beta_{n}r) + \gamma K_{1}(\beta_{n}r)] +$$

$$r_{p}I_{0}(\beta_{n}r)[I_{1}(\beta_{n}r_{p}) + \gamma K_{1}(\beta_{n}r_{p})]]$$

$$\gamma = \frac{I_{0}(\beta_{n}r_{p})}{K_{0}(\beta_{n}r_{p})}$$
(A56)

The excess minority carrier short-circuit current densities within the QNRs are obtained

using the same procedure in Eq. (A51) and Eq. (A52).

$$J_{sc}^{\Delta n} = \frac{1}{\pi R^2} \int_{\theta=0}^{\theta=2\pi} \int_{z=0}^{z=L} r d\theta dz \left\{ q D_n \frac{\partial \Delta n}{\partial r} \Big|_{r=r_p} \right\}$$
$$= \frac{2q r_p^2}{R^2} \left[ \gamma I_1(\beta_n r_p) + K_1(\beta_n r_p) \right]$$
$$\times \frac{G_0 L}{v} \times \left\{ \left[ -\left(\alpha(-L)\right)^v \right]^{-\frac{1}{v}} \times \Gamma\left(\frac{1}{v}, -(-L\alpha)^v\right) \right\}$$
$$\gamma = \frac{K_0\left(\beta_n r_p\right)}{I_0\left(\beta_n r_p\right)}$$
(A57)

$$J_{sc}^{\Delta p} = \frac{1}{\pi R^2} \int_{\theta=0}^{\theta=2\pi} \int_{z=0}^{z=L} r d\theta dz \left\{ -q D_p \frac{\partial \Delta p}{\partial r} \Big|_{r=R-x_1} \right\}$$

$$= \frac{2q r_n \Gamma_0}{R^2} \times \left\{ \frac{(\nu-\zeta) I_1 \left(\beta_p r_n\right) + (\nu \gamma - \chi \zeta) K_1 \left(\beta_p r_n\right)}{(\chi-\gamma)} \right\} \times \left[1 - e^{-\alpha_n L}\right]$$

$$\chi = \frac{\left[\frac{S_p}{D_p} I_0 \left(\beta_p R\right) + \beta_p I_1 \left(\beta_p R\right)\right]}{\left[\frac{S_p}{D_p} K_0 \left(\beta_p R\right) - \beta_p K_1 \left(\beta_p R\right)\right]}$$

$$\gamma = \frac{I_0 \left(\beta_p r_n\right)}{K_0 \left(\beta_p r_n\right)}$$

$$\zeta = r_n \left[I_1 \left(\beta_p r_n\right) + \gamma K_1 \left(\beta_p r_n\right)\right]$$

$$\nu = R \left[I_1 \left(\beta_p R\right) + \chi K_1 \left(\beta_p R\right)\right]$$
(A58)

where  $\Gamma$  is the incomplete gamma function. The stretched exponential EHP generation rate for the 2D source configuration was used to obtain the forms of Eqs. (A51) and (A52).

The generation currents within the depletion region take the form given by Eq. (A59). They are characterized by the linear EHP generation rate G(x),

$$J_{\rm sc}^{\rm dep} = \frac{q}{\pi R^2} \iiint dVG = \frac{2q}{R^2} \iint r dr dzG \tag{A59}$$

$$G(x) = \begin{cases} G_0 \exp\left(-\left(\alpha x\right)^{\nu}\right), & \text{2D source above NWs} \\ G(R), & \text{3D source in between NWs} \end{cases}$$
(A60)

where x was taken as the axial coordinate for the 2D source geometry and the radial coordinate for the 3D source geometry, respectively. In these equations,  $\alpha$  represents the semiconductor's absorption coefficient. The constant EHP generation rate for the 3D source configuration was obtained by evaluating the stretched exponential expression for the 2D source geometry's EHP generation rate at a penetration depth equivalent to the NW radius *R*.

### III. Bandgap Narrowing

At elevated levels of impurity concentration, the overall symmetry of the crystal lattice becomes disrupted by the presence of impurity atoms. As these impurity atoms integrate into the host lattice, they introduce an underlying sub-symmetry, consequently disturbing the overall lattice symmetry. This disruption can lead to the formation of impurity bands of states, distinct from the conduction and valence bands, where charge carriers can participate in conduction. At high dopant concentrations, the dopant impurity states within the bandgap become delocalized. Sufficient delocalization of these impurity states results in the overlapping of their wavefunctions, forming what we refer to as 'impurity bands'. The presence of these impurity bands distorts the parabolic nature of the energy bands due to fluctuations in the density of states (DOS) resulting from the random distribution of high dopant impurity concentrations. Consequently, the DOS distribution becomes directly contingent on the impurity concentration, thereby impacting the crystal's band structure. Hence, the energy bandgap within the crystal undergoes alterations.

Bandgap narrowing — denoted  $\Delta E_g$  — in III-V materials was modeled using the semiempirical formula Eq. (A61), presented by Jain et al.<sup>110</sup>,

$$\Delta E_g = AN^{\frac{1}{3}} + BN^{\frac{1}{4}} + CN^{\frac{1}{2}}$$
(A61)

where N is the net dopant concentration, and A, B, C are fitting parameters.

Semiconductor	$A \times 10^{-9}$	$B \times 10^{-7}$	$C \times 10^{-12}$
	$eV cm^{-3}$	$eV cm^{-3}$	eV cm <sup>-3</sup>
n-GaAs	16.5	2.39	91.4
p-GaAs	9.83	3.90	3.90
n-GaP	10.7	3.45	9.97
p-GaP	12.7	5.85	3.90

Table A1: Bandgap narrowing formula parameters for III-V materials<sup>110</sup>.

The bandgap narrowing of Si was computed using Slotboom's empirical formula<sup>104</sup>,

$$\Delta E_g = E' \times \left\{ \ln\left(\frac{N}{N_0}\right) + \left[\ln^2\left(\frac{N}{N_0}\right) + C\right]^{\frac{1}{2}} \right\}$$
(A62)

where E',  $N_0$  and C are fitting constants, and N is the net impurity dopant concentration. Values of the fitting constants are listed in Table A2.

$N_0$	E'	С
cm⁻³	meV	-
$1 \times 10^{17}$	9.0	0.5

Table A2: Slotboom bandgap narrowing parameters<sup>104</sup>.

The increase of the intrinsic carrier concentration is a concomitant effect of bandgap narrowing in semiconductors<sup>38</sup>. The intrinsic carrier concentration,  $n_i$ , is incremented by the square root of a Boltzmann factor of the magnitude of the bandgap shrinkage.

$$n_{i_{\text{eff}}}^2(N,T) = n_{i_0}^2(T) \exp\left[\frac{q\Delta E_g(N)}{k_B T}\right]$$
(A63)

$$n_i^2(T) = N_c(T)N_v(T)\exp\left[\frac{-qE_g}{k_BT}\right]$$
(A64)

The conduction and valence band effective density of states,  $N_c$  and  $N_v$ , respectively, were computed according to the formulae provided in the *NSM Archive* for GaP, GaAs and Si<sup>111</sup>.

## **IV.** Carrier Mobility

Dopant-dependent low-field carrier mobility values were computed using the models presented by Arora<sup>39</sup> and Sotoodeh<sup>40</sup>, for Si and the III-V materials, respectively. Fitting parameters for Eqs. (A65) and (A66) are listed in Tables A3 and A4, respectively.

$$\mu_{\rm Si}(N,T) = \mu_{\rm min} + \frac{\mu_0}{1 + \left(\frac{N}{N_{\rm ref}}\right)^{\alpha}} \tag{A65}$$

Semiconductor	Minority Carrier	$\mu_{min}$	$\mu_0$	$N_{\rm ref}  imes 10^{17}$	α
		$cm^{-2}V^{-1}s^{-1}$	$cm^{-2}V^{-1}s^{-1}$	cm <sup>-3</sup>	
Si	Electrons	88.3	1241.8	1.295	0.891
	Holes	54.3	406.9	2.35	0.88

Table A3: Si mobility fitting parameters<sup>39</sup>.

$$\mu_{\text{III-V}}(N,T) = \mu_{\text{min}} + \frac{\mu_{\text{max}} \left(\frac{300K}{T}\right)^{\theta_1} - \mu_{\text{min}}}{1 + \left(\frac{N}{N_{\text{ref}} \left(\frac{T}{300K}\right)^{\theta_2}}\right)^{\lambda}}$$
(A66)

The minority carrier mobilities were related to the minority carrier diffusion constants via the Einstein relation,

$$D_{n,p} = \frac{kT}{q} \mu_{n,p} \tag{A67}$$

Semiconductor	Minority Carrier	$\mu_{ m max}$ cm <sup>-2</sup> V <sup>-1</sup> s <sup>-1</sup>	$\mu_{ m min}$ cm <sup>-2</sup> V <sup>-1</sup> s <sup>-1</sup>	$N_{ m ref}  imes 10^{17}$ $ m cm^{-3}$	λ	$\theta_1$	$\theta_2$
GaAs	Electrons	9400	500	0.6	0.394	2.1	3.0
	Holes	491.5	20	1.48	0.38	2.2	3.0
GaP	Electrons	152.5	10	44	0.80	1.6	0.71
	Holes	147	10	10	0.85	1.98	0

Table A4: GaP and GaAs mobility fitting parameters<sup>40</sup>.

### V. Minority Carrier Diffusion Length and Carrier Lifetimes

The dopant-dependent minority carrier lifetimes in the QNRs were computed using the fitting function Eq. (A68) in Refs. 39, 41 for Si and GaAs, respectively.

$$\tau(N) = \frac{\tau_0}{1 + \left(\frac{N}{N_{\text{ref}}}\right)} \tag{A68}$$

The minority carrier diffusion lengths in the GaP QNRs were computed using Eq. (A69) from Ref. 37.

$$L(N) = \frac{L_0}{1 + \left(\frac{N}{N_{\text{ref}}}\right)^d}$$
(A69)

Table A5: Si and GaAs minority carrier lifetime fitting parameters<sup>39,41</sup>.

Semiconductor	Minority Carrier	$\tau_0 \qquad N_{\rm ref} \times 10^{17}$	
		μs	cm <sup>-3</sup>
GaAs	Electrons	1	0.1
	Holes	0.02	20
Si	Electrons	17	0.017
	Holes	395	0.071

Semiconductor	Minority Carrier	L <sub>0</sub>	$N_{\rm ref}  imes 10^{17}$	d
		μm	cm⁻³	
GaP	Electrons	0.0503	0.0345	0.08734
	Holes	0.001	6.78	2.239

Table A6: GaP minority carrier diffusion length fitting parameters<sup>37</sup>.

### VI. Carrier Recombination

#### a. Shockley-Read-Hall Recombination

Shockley-Read-Hall (SRH) recombination is a non-radiative recombination process mediated by deep level traps residing within the bandgap. This phenomenon was first investigated by Shockley, Read and Hall in 1952<sup>112</sup> and has since been shown to be one of the primary non-radiative recombination processes occurring within semiconductor materials. SRH recombination reduces the material's radiative efficiency by promoting nonradiative carrier recombination and consequently the minority carrier lifetimes, via the localized (charged) deep centers. These highly localized deep centers can compensate shallow dopant states, and thus reduce the carrier concentration as a consequence. Deep centers also act to effectively reduce the carrier mobility as a consequence of scattering<sup>38</sup>. In a p-n junction, the reduction of the carrier mobility due to the high concentration of impurity atoms increases the minority carrier's likelihood of interaction with the localized charged states. This decreases the likelihood of minority carriers diffusing within the vicinity of the space-charge region where they can be swept across the junction by the built-in electric field. Sah et al.<sup>113</sup> demonstrated the recombination rate reaches a maximum value when the Fermi level crosses the midpoint of the forbidden energy gap. The recombination current density was determined by:

$$U_{\text{SRH}} = \frac{\sigma_n \sigma_p v_{th} N_T (pn - n_i^2)}{\sigma_n \left[ n + n_i exp(\frac{E_T - E_i}{k_B T}) \right] + \sigma_p \left[ p + n_i exp(\frac{E_i - E_T}{k_B T}) \right]}$$
(A70)

where  $\sigma_{n,p}$  are the minority electron and hole capture cross-sections, respectively,  $N_T$  is the trap state,  $n_i$  is the intrinsic carrier concentration,  $E_T$  is the trap state energy,  $E_i$  is the intrinsic Fermi level,  $v_{th}$  is the thermal velocity, given by Eq. (A71). Due to variability in effective mass values, the electron rest mass  $m_0$  was used in place of the effective mass as conventional convenience<sup>114,115</sup>.

$$v_{th} = \left(\frac{3k_BT}{q}\frac{1}{m_0}\right)^{\frac{1}{2}}$$
 (A71)

The maximum recombination rate due to Shockley-Read-Hall recombination in the space-charge region is given by Eq. (A72)<sup>116–118</sup>:

$$U_{\text{SRH}}^{\text{max}} = \frac{n_i \sinh\left(\frac{qV}{2k_BT}\right)}{\sqrt{\tau_{n_0,p_0}} \left[\exp\left(\frac{-qV}{2k_BT}\right) + 1\right]}$$
(A72)

The volume of maximum recombination is determined by a characteristic collection length,  $L_c$ , about the point of maximum recombination in the depletion region  $r^*(V)$ . These points  $(r_1^*(V), r_2^*(V))$  define the volume about the point within the depletion region for which the recombination rate is maximized:

$$L_c = \frac{\pi}{3} \frac{k_B T}{q} \times \frac{w(V)}{(V_{bi} - V)} \tag{A73}$$

$$r^{*}(V) = r_{p}(V) + \frac{\Psi_{p_{0}}}{V_{bi}}w(V)$$
(A74)

$$\begin{cases} r_1^*(V) = r^*(V) - L_c \\ r_2^*(V) = r^*(V) + L_c \end{cases}$$
(A75)

where w(V) is the depletion region width.

The electron and hole minority carrier lifetimes, in the space-charge region ( $\tau_{n_0}$ ,  $\tau_{p_0}$ ), are determined by the density of trap states within the space-charge region,  $N_T$ , and the corresponding carrier capture cross-sections  $\sigma_{n,p}$  via the relationship:

$$\tau_{n_0,p_0} = \frac{1}{\sigma_{n,p} v_{th} N_T} \tag{A76}$$

The values of  $\sigma_{n,p}$  for Si, GaP, and GaAs were taken from Refs. 111, 119.

#### b. Auger Recombination

Auger recombination is a non-radiative recombination process involving three carriers. In such instances, the excess energy released from the annihilation of an EHP is transferred to another carrier within the same band in lieu of the emission of a photon, giving rise to the intra-band excitation of the recipient carrier. The excited carrier will subsequently go on to return to thermal equilibrium with the lattice via the emission of phonons within the lattice. Due to the necessity of three participating carriers, the likelihood of Auger recombination events is notably low unless substantial carrier densities are present in the crystal. Numerous factors including temperature, dopant impurity concentrations, and device geometry, can influence the conditions required to induce Auger recombination processes.

However, materials capable of supporting high carrier densities are more susceptible to Auger processes due to the increased likelihood of multi-carrier interactions. The effects of Auger recombination on carrier transport, and ultimately device performance, are often second-order effects for typical devices, and are hence rarely the limiting mechanisms in device performance.

The maximum Auger recombination rate in the space-charge region was determined by applying a similar procedure to the procedure used for the determination of the Shockley-Read-Hall recombination rate<sup>116</sup>.

$$U_{\text{Aug}} = C_p p^2 n + C_n n^2 p \tag{A77}$$

$$U_{\text{Aug}}^{\text{max}} = 4n_i^3 \sqrt{C_p C_n} \exp\left(\frac{qV}{k_B T}\right) \sinh\left(\frac{qV}{2k_B T}\right)$$
(A78)

where  $C_{n,p}$  are the minority electron and hole Auger coefficients, respectively.

#### c. Radiative Recombination

Radiative recombination events are characterized by the emission of a photon when an electron occupying an excited state within the conduction band relaxes back to valence band and annihilates a hole. This process is highly dependent on the alignment of the conduction band minimum and valence band maximum in reciprocal (i.e. crystal-momentum) space, which determines the direct or indirect nature of the energy bandgap. Indirect bandgap materials often have low rates of radiative recombination. Of the materials investigated, GaP and Si are both indirect bandgap materials, whereas GaAs is a direct gap material.
The radiative recombination rate within the space-charge region is given by <sup>116</sup>

$$U_{\rm rad} = B n_i^2 \left[ \exp\left(\frac{qV}{k_B T}\right) - 1 \right] \tag{A79}$$

where B is the radiative recombination coefficient.

#### d. Recombination Parameters

The recombination coefficients for each material are summarized in Table A7.

Table A7: Auger, radiative, Shockley-Read-Hall and surface recombination parameters for GaP, GaAs and Si.

Semiconductor	$C_n \times 10^{-30}$	$C_p  imes 10^{-30}$	$B \times 10^{-13}$	$N_T$	$\sigma_n  imes 10^{-15}$	$\sigma_p  imes 10^{-15}$	$S_p$
	cm <sup>6</sup> s <sup>-1</sup>	cm <sup>6</sup> s <sup>-1</sup>	cm <sup>3</sup> s <sup>-1</sup>	cm <sup>-3</sup>	cm <sup>2</sup>	cm <sup>2</sup>	cm s
GaP	1	1	1	2 × 10 <sup>16</sup>	2	2	10 <sup>4</sup>
GaAs	0.15	2	10 <sup>3</sup>	$8 \times 10^{13}$	1	1	10 <sup>3</sup>
Si	0.28	0.099	0.11	$8 \times 10^{13}$	1	1	10

## VII. Radioisotope Source Parameters

The emitted power of a radioactive source depends primarily on the source mass and the geometry of the source <sup>36</sup>, whose effects are realized via self-absorption and the directional dependence of the source, respectively. Planar-source devices in which the semiconductor contacts only a single side of the beta emitter, often suffer from high directionality losses due to the isotropic radioactive emission pattern of the beta source. The decaying radioisotope source radiates equally in all directions. In this way, at most, up to 50 % of

the beta electrons emitted from a slab source can be captured by the semiconductor, immediately limiting the upper-bound source efficiency to 50% for single-sided betavoltaic devices employing a slab source. The directional efficiency of a (one-sided) slab source can be modelled by a geometric form factor as expressed in Ref. 21, 36. Self-absorption refers to the phenomenon where radiation emitted by a decaying radioisotope is partially re-absorbed within the radioisotope material itself. This effect becomes more significant as the thickness and mass of the radioisotope material increase, leading to a higher likelihood of interactions between the emitted radiation and the surrounding source material. By reducing the source activity, self-absorption therefore reduces the amount of power that can be collected from a source. In conjunction, self-absorption and directional losses have been shown to be responsible for over 80% of source efficiency losses<sup>36</sup>.

Another prominent loss mechanism within radioisotope sources is backscattering, in which emitted beta particles are redirected back towards the emission source from within the target medium. Backscattering results from collisions between the beta particles and the surrounding medium. It is more pronounced at low incident beta electron energies, as well as within higher-density host materials, due to the increased probability of scattering. Reducing the source film thickness as well as selecting lower-density source materials can help to mitigate backscatter losses.

Various techniques have been investigated to address source efficiency losses in planar betavoltaic devices. Modifying the device structure, and optimizing the source output characteristics have proved to be the most common approaches used. Layered device structures consisting of alternating films of source material and semiconductor layers is a commonly used approach to overcome the directional losses of planar sources and achieve greater source input power densities<sup>36,30,120,121</sup>. Belghachi et al. addressed these issues

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using metal beta particle reflectors films<sup>36</sup> to simultaneously reduce back-side emission of beta particles and enhance front-side emission of beta particles of planar sources used in single-sided betavoltaic devices.

Radioisotope material properties are listed in Table A8. The EHP generation rate was determined by integrating the product of the stopping power and radioisotope energy probability distribution over the energy. EHP generation rate profiles for GaP are shown in Fig. A3.

Table A8: <sup>63</sup>Ni radioisotope properties<sup>11</sup>.

Radioisotope	Specific Activity	Density	Ē
	$\mathrm{Ci}\mathrm{g}^{-1}$	g cm <sup>-3</sup>	keV
<sup>63</sup> Ni	56.03	8.908	17.45



Figure A3: EHP generation rate distribution in GaP as function of penetration depth x. The fit (green dashed curve) was generated according to a stretched exponential distribution  $-G(x) = G_0 \exp^{(-(\alpha x)^v)}$  — with parameters:  $\alpha = 638 \text{ cm}^{-1}$ ,  $G_0 = 9 \times 10^{15} \text{ cm}^{-3} \text{ s}^{-1}$ , v = 2.3.

# VIII. Simulation Program Flowchart



Figure A4: Simulation program control flow chart.

# IX. GaAs and Si Betavoltaic Device Simulation Results

 $J_{\rm sc}$ ,  $V_{\rm oc}$ , FF,  $\eta$  surface plots for the best GaAs and Si devices are shown in Figs. A5 to A8.



Figure A5: Simulated GaAs betavoltaic devices for a 3D source configuration with properties a)  $J_{sc}$  b)  $V_{oc}$ , c) FF, d) efficiency.  $N_A = 10^{19} \text{ cm}^{-3}$ ,  $N_D = 5 \times 10^{18} \text{ cm}^{-3}$ , D = 200 nm, L = 10 µm, d : p = 0.4.



Figure A6: Simulated GaAs betavoltaic devices for a 2D source configuration with properties a)  $J_{sc}$  b)  $V_{oc}$ , c) FF, d) efficiency.  $N_A = 10^{19} \text{ cm}^{-3}$ ,  $N_D = 5 \times 10^{18} \text{ cm}^{-3}$ , D = 900 nm, L = 1 µm, d : p = 0.9.



Figure A7: Simulated Si betavoltaic devices for a 3D source configuration with properties a)  $J_{sc}$  b)  $V_{oc}$ , c) FF, d) efficiency.  $N_A = 10^{19} \text{ cm}^{-3}$ ,  $N_D = 5 \times 10^{18} \text{ cm}^{-3}$ , D = 200 nm,  $L = 10 \,\mu\text{m}$ , d : p = 0.4.



Figure A8: Simulated Si betavoltaic devices for a 2D source configuration with properties a)  $J_{sc}$  b)  $V_{oc}$ , c) FF, d) efficiency.  $N_A = 10^{19} \text{ cm}^{-3}$ ,  $N_D = 5 \times 10^{18} \text{ cm}^{-3}$ , D = 900 nm,  $L = 1 \mu \text{m}$ , d : p = 0.9.



Figure A9: Efficiency as a function of the NW p-core diameter and n-shell thickness for simulated 2D source geometry GaP betavoltaic devices. The NW length was varied from a) 1 µm b) 5 µm c) 10 µm, while the NW diameter, dopant concentrations, and diameter-pitch ratio were fixed at D = 900 nm,  $N_A = 10^{19}$  cm<sup>-3</sup>,  $N_D = 5 \times 10^{18}$  cm<sup>-3</sup>, and d : p = 0.9, respectively.

# X. Sample Preparation and Device Fabrication Procedure Supplementary Information

#### a. BHF Etch Rate Calibration

The SiO<sub>x</sub> etch rate was determined from a series of BHF etches. 51.24 nm of SiO<sub>x</sub> was deposited on a  $\langle 111 \rangle$  Si substrate. The wafer was cleaved into 6 pieces. Five wafer pieces were etched for 5 s, 10 s, 15 s and 25 s, respectively. The remaining unetched wafer piece served as a reference calibration sample. The resultant oxide film thicknesses were measured by ellipsometry, and are summarized in Table A9. An average etch rate of 0.722 nm/s was calculated from the data points in Fig. A10.

Table A9: Ellipsometry measurements of film thickness and etch depth vs etch time. Etch depths were calculated from the reference sample oxide thickness of  $(51.240 \pm 0.004)$  nm.

Etch Time	Oxide Thickness	Etch Depth
(s)	(nm)	(nm)
0	51.240 ± 0.004	0
5	44.910 ± 0.005	6.33
10	42.510 ± 0.007	8.73
15	40.570 ± 0.006	10.67
20	34.940 ± 0.009	16.3
25	32.830 ± 0.009	18.41



Figure A10: Etch depth vs etch time. An etch rate of 0.708 nm/s was calculated from the linear fit.

## b. **RIE Etch Parameters**

Table A10:	BCB	RIE	back-etch	recipe
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Parameter	Value
RF Power (W)	50
Chamber Pressure (mTorr)	~ 460
CF <sub>4</sub> (sccm)	35.8
O <sub>2</sub> (sccm)	5.4
N <sub>2</sub> (sccm)	1.8
Water-cooling	Yes
Etch Rate (nm/min)	26.2

# c. Magnetron Sputter Deposition Parameters

Table A11: ITO sputter deposition parameters.

Parameter	Value
Ar flow rate (sccm)	5
Base pressure (Torr)	$9.42 \times 10^{-6}$
Deposition pressure (mTorr)	1.8–1.9
Deposition rate (Å/s)	1.3
Forward RF power (W)	55
Reflected RF power (W)	0
Tooling factor	160
Water-cooling	Yes
Sample rotation setting	5

Parameter	Value
Ar flow rate (sccm)	5
Base pressure (Torr)	$2.12 \times 10^{-4}$
Deposition pressure (mTorr)	3.8–3.9
Deposition rate (Å/s)	0.5
DC voltage (V)	385
DC current (mA)	95
Tooling factor	183
Water-cooling	Yes
Sample rotation setting	5

#### Table A12: Au sputter deposition parameters.

#### Table A13: Al sputter deposition parameters.

Parameter	Value
Ar flow rate (sccm)	5
Base pressure (Torr)	2.33 × 10 <sup>-6</sup>
Deposition pressure (mTorr)	2.3–3.3
Deposition rate (Å/s)	1.4
Forward RF power (W)	55
Reflected RF power (W)	0
Tooling factor	160
Water-cooling	Yes
Sample rotation setting	7

Material	Density (g/cm <sup>3</sup> )	Z-ratio	Sputter Type
Al	2.7	1.08	RF
Au	19.3	0.38	DC
ITO	7.1	1.00	RF

Table A14: Sputtering target material properties.

## XI. Input Power Density Calculations

When unrolled, the cylindrical foil can be approximated as a planar source, as detailed in Chapter 2. For a uniform isotropic emission of  $\beta$  particles from the foil surface, a maximum of approximately 50% of the emitted flux theoretically contributes to energy conversion, though practical considerations significantly reduce this fraction.

In the cylindrical configuration, the emission geometry becomes more complex. Beta particles emitted in upward and downward trajectories may escape through the cylinder's openings, while others undergo absorption or scattering events at the inner cylinder wall. To establish an upper bound for the input power density, we developed a first-order approximation based on the cylindrical geometry of the <sup>63</sup>Ni source. This approximation considers the fraction of  $\beta$  particles escaping through the bottom opening of the cylinder. Since the emission is assumed to be isotropic, the distribution of emission points is effectively uniform along the cylinder's height. The average emission height of all these points is at the geometric midpoint of the cylinder. The fraction of escaping  $\beta$ s should be proportional to the fraction of the total available space through which they can travel without hitting an obstruction. Given  $\beta$  particles travel in all directions from the source, their ability to escape should thus be proportional to the solid angle subtended by the opening at

a point z directly above the center of circular opening.

Using the solid angle approximation in spherical coordinates, for  $(z = \frac{h}{2})$ ,  $f_{esc}$  is found to be:

$$f_{esc} = \frac{\int_{0}^{2\pi} \int_{0}^{\theta} \sin \theta' d\theta' d\phi}{2\pi}$$
  
=  $\frac{2\pi \left[ -\cos \theta' \right]_{0}^{\theta}}{2\pi}$   
=  $1 - \cos \theta$   
=  $1 - \frac{z}{\sqrt{z^{2} + \left(\frac{d}{2}\right)^{2}}}$  (A80)  
=  $1 - \frac{\frac{h}{2}}{\sqrt{\left(\frac{h}{2}\right)^{2} + \left(\frac{d}{2}\right)^{2}}}$   
=  $1 - \frac{5.35 \text{ mm}}{\sqrt{(5.35 \text{ mm})^{2} + (3.29 \text{ mm})^{2}}}$   
=  $14.82 \%$ 

corresponding to:

$$P_{\rm in} = \frac{f_{\rm esc}\phi_0\bar{E}}{A}$$
  
=  $\frac{0.1482 \times \phi_0\bar{E}}{\pi dh}$   
=  $\frac{0.1482 \times 12.15 \times 10^{-3} \,\text{Ci} \times 3.7 \times 10^{10} \,\text{Bq/Ci} \times 17.45 \times 10^3 \times 1.602 \times 10^{-19} \,\text{J/beta}}{\pi \times 0.658 \,\text{cm} \times 1.070 \,\text{cm}}$   
=  $84.13 \,\text{nW/cm}^2$ 

The use of the solid angle method to estimate  $f_{\rm esc}$  is justified by established principles in radiation transport<sup>122</sup>. In Ref. 122, Jaffey states that for an isotropic source, the

solid angle subtended by an aperture directly determines the fraction of emitted radiation that escapes through it. This principle underpins our approach, where the fraction of  $\beta$ particles escaping through the bottom opening of the cylinder is estimated using the solid angle subtended by the aperture. While the solid angle is not expressible in closed form for an arbitrarily positioned source<sup>122</sup>, it simplifies when the source is on the axis of the circular aperture. For off-axis sources, the solid angle expands into an infinite series, requiring numerical methods for evaluation. Given the complexity of such calculations, we adopted the simplest applicable case by assuming an effective emission height ( $0 \le z \le h$ ) along the central axis, approximated as  $z = \frac{h}{2}$ . This ensures that the problem remains analytically tractable while capturing the spatial distribution of emission. Since  $\beta$  particles originate from the inner surface of the rolled foil, averaging over this distribution leads to a central axis approximation, making the use of a single effective source height reasonable. Thus, the solid angle approach provides a physically meaningful and reasonably-justified approximation for determining  $f_{esc}$ .