III-V COMPOUND SEMICONDUCTOR NANOSTRUCTURES BASED NANOHETEROSTRUCTURES

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SEPTEMBER 2020

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by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy
to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

SEPTEMBER 2020

This thesis is dedicated

to

my Baba ji

Late Pt. Sitaram Sharma

who blessed me with patience and

perseverance.

CERTIFICATE

This is to certify that the thesis entitled, "**III-V Compound Semiconductor Nanostructures based Nanoheterostructures**", being submitted by **Jaya Lohani** for the award of the degree of **Doctor of Philosophy** in Chemistry to the Indian Institute of Technology Delhi, is a record of bonafide research work carried out by her under our guidance and supervision. In our opinion, the thesis has reached the standard of fulfilling the requirements of all the regulations related to the degree. The results contained in this thesis have not been submitted in part or full, to any other University or Institute for the award of any degree or diploma.

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ACKNOWLEDGEMENTS

The thesis is based on the research work performed from the year 2014 to 2020 at MOCVD Division, Solid State Physics Laboratory, DRDO, Delhi and Department of Chemistry, Indian Institute of Technology Delhi, India. With immense gratitude I express my thanks to all the people who encouraged, guided, and supported me throughout the course of this work.

First of all, I am thankful to my supervisor Prof. Sameer Sapra who accepted me as his student and infused me with lot of positivity and research attitude. Every time I met him, I learnt new things to upgrade my technical skills and personal attributes. He stood beside me as bulwark and showed me the ways to carry this work forward. He developed my analytical skills to scientifically comprehend the experimental results. The measurements, fittings, and analysis of photoemission, absorption, & transient emission characteristics of nanostructures have been solely learnt from him. His expertise has been of immense help not only to accomplish this work but also to complete my professional assignments.

At the same time, I express my sincere thank and heartfelt gratitude to my co-supervisor, Dr. Renu Tyagi who provided me with ample resources and guided me at every step. She educated me on material growth aspects like surface diffusion, nucleation, coalescence, etc. and particularly developed in me a sound understanding of threading dislocations and their consequences on material characteristics. In one of the several discussions with her, I got the inspiration to fabricate nanowires by utilizing the otherwise undesired threading dislocations in MOVPE grown GaN material. Her keen interest in the progress of my work, kept me motivated all the time.

I would also like to thank my student research committee (SRC) members for their helpful suggestions related to this work. I take privilege to express my sincere gratitude to Director, IIT Delhi and Director, SSPL for their kind support, encouragement, and providing me opportunities to conduct this work and present it at different forums.

I am also indebted to my Divisional Officer at SSPL, Smt. MVG Padmavati, as without her support in office, I could not have found time to conclude this work. She always protected me and provided timely help and solutions to my problems. She stood with me as a deep friend throughout this journey.

I am extremely grateful to Dr. D. S. Rawal for his unconditional help in etching the samples used for the fabrication of the nanowires. His vibrant personality and unparalleled technical zeal always infused me with energy and made me believe that all goals can be achieved with scientific vigor and temperament.

A special thank is also punched for my colleagues and friends Dr. Sonalee Chopra, Dr. Janesh Kaushik, Sh. Akhilesh Pandey, Sh. Sunil Sharma, Dr. Arkjyoti, Dr. Sushma Yadav, Dr. Mona Mittal, Mohd. Samim, and Shivani Varshney who helped me in various ways at different stages of my pursuit.

I would also like to thank Central Research Facility (CRF) of IIT Delhi for timely characterization of the samples of nanostructures prepared by me using advanced techniques like AFM, SEM, & TEM etc. and to facilitate my research work smoothly. I sincerely acknowledge the cooperation of administrative staff of Department of Chemistry, Library, and PG Section of IIT Delhi in regards to all official activities related to my work.

At a personal note, I am indebted to my little daughter who allowed me to steal the time that she deserved for my academics. I express my appreciation from the bottom of my heart for my husband who shouldered greater responsibilities at home and took good care of the family. I deeply express my gratitude for my mother and father who kept faith in me and provided unconditional love, care, and support to my daughter and me at critical times. I am thankful to Tvishaa, Astu, Sejal, Yukt, Prajal, Abhishree, and Abhay who unburdened my apprehensions at times with their innocence and sweet smiles. I am also thankful to my brother, sister, and in-laws as without their support and well wishes this could not have been achieved.

Last but not the least, I acknowledge the blessings of my late grandparents who always avert all my adversities, and would have rejoiced this moment the most, had they been with me alive in this physical world.

Jaya Lohani

ABSTRACT

The nanostructures of III-V compound semiconductors have been widely studied for the development of next generation of photonic and electronic devices. Immense research efforts are ongoing to develop economical methods to obtain device quality uniform semiconductor nanostructures in high yield and having good structural, optical, & electrical characteristics. The present thesis is mainly focused on working out convenient and easily scalable methods for preparation of good optical quality uniform epitaxial nanostructures of GaAs, and GaN, in high yield to fabricate nanoheterostructures (NHSs) for energy/charge transfer applications. Both, bottom-up and top-down approaches have been adopted to prepare high quality, uniform nanostructures. The bottom-up approach involved the epitaxial growth of GaAs nanostructures using self-assembled Ga droplets as catalyst by Metalorganic Vapor Phase Epitaxy (MOVPE). In top-down approach, epitaxial GaN nanostructures have been prepared by plasma etching of GaN epilayers and AlGaN/GaN heterostructures grown by MOVPE.

First two chapters (Chapter 1 and 2) present an account of extensive literature survey of recent research work in the field of growth and fabrication of III-V compound semiconductor nanostructures for device application along with brief description of various methods and techniques employed for the growth, fabrication, and characterization in this work. In Chapter 3, an understanding of evolution of self-assembled structure of Ga under different growth conditions of MOVPE has been developed, as the droplets have to be used as catalyst for the growth of GaAs nanostructures. In addition, fabrication and characterization of the novel Ga-Ga_2O_3 core-shell NHSs obtained by *ex situ* oxidation of the droplets have been presented as major spin-off of the study. In Chapter 4, growth of good optical quality and highly

uniform, vertical, epitaxial, hexagonal GaAs nanostructures with six symmetric sidewall facets by MOVPE has been presented. In addition, efficient resonance energy transfer from CdSe quantum dots (QDs) to GaAs nanostructures has been demonstrated that has led to enhanced quenching of the fluorescence of QDs due to non-radiative relaxation on the surface of six {110} side facets of the nanostructures through shallow traps.

Convenient top-down fabrication schemes of GaN nanostructures and nanowires based on mask and maskless etchings have been presented in Chapters 5 and 6, respectively. The first scheme involved three easy process steps, namely, thin film coating, rapid thermal annealing (RTA), and plasma etching. The first two steps resulted in fabrication of mask comprising the self-assembled nanoparticles by RTA of thin film of Ni deposited on GaN epilayer. A good mask composed of sub-50 nm agglomerated nanoparticles in high density has been fabricated that led to the formation of reasonably uniform conical GaN nanostructures in the third step by inductively coupled plasma reactive ion etching (ICP-RIE). The second scheme has been based on a highly convenient single step novel fabrication of GaN nanowires by maskless plasma etching without using the ICP and a mask to cut down the overall process cost and the complexity. Vertically aligned GaN nanowires and nanowires comprising AlGaN/GaN axial NHSs with sub-50 nm diameter have been fabricated in high density for charge transfer application using the maskless scheme by etching GaN epilayers with high density of threading dislocations (TDs). Effective passivation of the NHSs by suitable polymer has led to significant enhancement in the emission characteristics with negligible effect on the charge transfer.

सार

फोटो और इलेक्ट्रॉनिक उपकरणों की अगली पीढ़ी के विकास के लिए III-V यौगिक अर्धचालक का नैनोस्ट्रक्चर व्यापक रूप से अध्ययन किया गया है । अत्यधिक उपज में और अच्छी संरचनात्मक, ऑप्टिकल और विद्युत विशेषताओं वाले उपकरण की गुणवत्ता समान अर्धचालक नैनोस्ट्रक्चर प्राप्त करने के लिए किफायती तरीकों को विकसित करने के लिए अपार अनुसंधान प्रयास जारी हैं । वर्तमान थीसिस मुख्य रूप से ऊर्जा/चार्ज ट्रांसफर अनुप्रयोगों के लिए नैनोहोट्रोस्ट्रक्चर (NHS) की छलरचना के लिए GaAs और GaN के अच्छे ऑप्टिकल गुणवत्ता वर्दी एपिटैक्सियल नैनोस्टेस्ट्रक्चर की उच्च उपज में तैयारी के लिए सुविधाजनक और आसानी से स्केलेबल तरीकों पर ध्यान करने पर केंद्रित है । उच्च गुणवत्ता, समान नैनोकणों को तैयार करने के लिए दोनों, नीचे-ऊपर और ऊपर-नीचे दृष्टिकोण को अपनाया गया है। नीचे-ऊपर अप्रोच में मेटलकार्बनिक वेपर फेज एपिटेक्सि (MOVPE) द्वारा उत्प्रेरक के रूप में स्व-इकट्ठे Ga बूंदों का उपयोग करके GaAs नैनोस्ट्रक्चर की उपज शामिल थी । टॉप-डाउन दृष्टिकोण में, MOVPE द्वारा उगाए गए GaN एपिलेयर्स और AlGaN/GaN हेट्रोस्ट्रक्चर के प्लाज्मा निक्षारण द्वारा एपिटैक्सियल GaN नैनोसंरचना तैयार किया गया है ।

पहले दो अध्याय (अध्याय 1 और 2), विकास डिवाइस अनुप्रयोग के लिए III-V यौगिक अर्धचालक नैनोस्ट्रक्चर के उपज और निर्माण के क्षेत्र में हाल के शोध कार्यों के व्यापक साहित्य सर्वेक्षण के साथ उपज, छलरचना, तथा निरूपण के लिए कार्यरत विभिन्न तरीकों और तकनीकों का संक्षिप्त विवरण प्रस्तुत करते हैं । अध्याय 3 में, MOVPE की विभिन्न विकास स्थितियों के तहत Ga के स्व-इकट्ठे ढांचे के उपज की समझ विकसित की गई है, क्योंकि बूंदों को GaAs नैनोस्ट्रक्चर के विकास के लिए उत्प्रेरक के रूप में उपयोग किया जाना है । इसके अलावा, बूंदों के बाहरी ऑक्सीकरण द्वारा प्राप्त किए गए नव Ga-Ga2O3 कोर-शेल NHS के निर्माण और निरूपण को प्रमुख स्पिन-ऑफ के रूप में प्रस्तुत किया गया है । अध्याय 4 में, अच्छी ऑप्टिकल गुणवत्ता, अत्यधिक समरूप, अक्षीय, एपिटैक्सियल, छह सममित साइडवॉल पहलुओं के साथ हेक्सागोनल GaAs नैनोस्ट्रक्चर की उपज प्रस्तुत की गई है । इसके अलावा, CdSe क्वांटम डॉट्स (QDs) से GaAs नैनोस्ट्रक्चर तक कुशल अनुनाद ऊर्जा हस्तांतरण का

प्रदर्शन किया गया है, जिसने QDs के प्रतिदीप्ति की शमन वृद्धि को नैनोस्ट्रक्चर के छह {110} साइड पहलुओं पर उथले पाश के माध्यम से गैर-विकिरण विश्रांति के कारण जन्म दिया है ।

मास्क और मास्क रहित निक्षारण के आधार पर GaN नैनोस्ट्रक्चर और नैनोवायरस की सुविधाजनक टॉप-डाउन फैब्रिकेशन योजनाएँ क्रमशः अध्याय 5 और 6 में प्रस्तुत की गई हैं। पहली योजना में तीन आसान प्रक्रिया चरण शामिल थे, अर्थात्, पतली फिल्म कोटिंग, रैपिड थर्मल एनीलिंग (आरटीए), और प्लाज्मा निक्षारण । पहले दो चरणों में GaN एपिलेयर पर जमा Nickel की पतली फिल्म की तेज थर्मल annealing (RTA) द्वारा मुखौटा का निर्माण किया गया जिसमें स्व-इकट्ठे नैनोकण शामिल थे। उच्च घनत्व में उप -50 nm agglomerated नैनोकणों से बना एक अच्छा मुखौटा, तीसरे चरण में उचित रूप से युग्मित प्लाज्मा प्रतिक्रियाशील आयन निक्षारण (ICP-RIE) द्वारा यथोचित रूप से समान शंक्वाकार GaN नैनोस्ट्रक्चर के निरूपण का कारण बना । दूसरी योजना ICP का उपयोग किए बिना मास्क रहित प्लाज्मा निक्षारण द्वारा GaN nanowires के एक अत्यधिक सुविधाजनक एकल चरण नव निर्माण पर आधारित है जो समग्र प्रक्रिया लागत और जटिलता में कटौती करने के लिए है । चार्ज ट्रांसफर एप्लिकेशन के लिए उच्च घनत्व में लंबवत संरेखित उप-50 nm व्यास के GaN नैनोवायरों और AlGaN/GaN अक्षीय NHS युक्त GaN नैनोवायरों की छलरचना मास्क रहित योजना का उपयोग करते हुए उच्च थ्रेडिंग डिस्लोक्शंस (TDs) वाले GaN एपिलेयर के निक्षारण के द्वारा की गई है । उपयुक्त बहुलक द्वारा NHS के प्रभावी पारित होने से चार्ज हस्तांतरण पर नगण्य प्रभाव के साथ उत्सर्जन विशेषताओं में महत्वपूर्ण वृद्धि हुई है ।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	Percent
ν	Frequency
λ	Wavelength
θ	Theta
τ	Lifetime
Å	Angstrom
μ	Micro
°C	Degree centigrade
1D	One-dimensional
AFM	Atomic force microscopy
AlGaN	Aluminium Gallium Nitride
As	Arsenic
AsH_3	Arsine
CdSe	Cadmium Selenide
Eg	Bandgap
e.g.	For example
eV	Electron volt
FESEM	Field emission scanning electron microscopy
Ga	Gallium
GaAs	Gallium Arsenide
GaN	Gallium Nitride
HDD	High dislocation density
HRXRD	High resolution X-ray diffraction
ICP-RIE	Inductively coupled plasma-reactive ion etching

LDD	Low dislocation density
LO	Longitudinal optical
MBE	Molecular beam epitaxy
min	minute
MO	Metalorganic
MOVPE	Metalorganic vapor phase epitaxy
NHSs	Nanoheterostructures
Ni	Nickel
nm	nanometer
ns	nano seconds
P3HT	Poly-3-hexylthiophene
PL	Photoluminescence
QDs	Quantum dots
RIE	Reactive ion etching
RTA	Rapid thermal annealing
TDs	Threading dislocations
TEM	Transmission electron microscopy
TMAl	Trimethylaluminium, $Al(CH_3)_3$
TMGa	Trimethylgallium, $Ga(CH_3)_3$
TO	Transverse optical
TRPL	Time resolved photoluminescence
VLS	Vapor-liquid-solid
VPE	Vapor phase epitaxy
XPS	X-ray photoemission spectroscopy