

**GROUP-IV SEMICONDUCTOR NANOSTRUCTURES
AND THEIR HETEROJUNCTIONS WITH LAYERED
MATERIALS FOR INFRARED DETECTION**

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CENTRE FOR APPLIED RESEARCH IN ELECTRONICS

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Group-IV Semiconductor Nanostructures and their Heterojunctions with Layered Materials for Infrared Detection

by

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*Dedicated to my
Family*

CERTIFICATE

This is to certify that the thesis entitled, “**Group-IV Semiconductor Nanostructures and their Heterojunctions with Layered Materials for Infrared Detection**” being submitted by **Mr. JOHN WELLINGTON J** to the Indian Institute of Technology Delhi for the award of the degree of “**Doctor of Philosophy**”, is a record of bonafide research work carried out by him under our guidance and supervision.

In my opinion, the thesis has reached the standard of fulfilling the requirement of all the regulations regarding to the degree. The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.



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Abstract

Nano-dimensional devices exhibit a variety of unique phenomena that present important opportunities for the development of next-generation electronics with unmatched performance. Infrared (IR) detectors are no exception to it considering its application in military, medical, environmental, industry, and communication fields. Since the invention of IR photodetectors in the 20th century, the focus has been to improve their performance, such as simplifying the fabrication processes, lowering the fabrication cost, and facilitating room temperature operation of devices through advanced nanotechnology fabrication. Group-IV semiconductor nanostructures and layered materials are excellent alternatives to the matured technology based III-V materials like indium antimonide, indium gallium arsenide, and II-VI materials like lead sulphide and mercury cadmium telluride.

In this **dissertation**, firstly, group-IV semiconductor nanowires (NWs) were studied for high sensitive IR detection. To start, germanium (Ge) metal-semiconductor-metal (MSM) devices were made using germanium-on-insulator (GeOI) substrate. Interestingly, a negative photoconductive effect (NPC) in highly arsenic (As) doped NWs is observed. The trapping of photo-carriers leads to high recombination of carriers in the presence of light which lead to NPC. Kelvin probe force microscopy study was done to confirm this effect which showed the depletion of carriers in n-Ge NW in presence of infrared light. The performance of n-type devices was compared with p-type NW detectors, which shows the conventional positive photoconductive behavior with high gain of 10^4 . The observed results can be used to study the application of Ge NWs for various optoelectronic applications involving light tunable memory device applications.

To achieve IR response in Si based devices, germanium quantum dots (Ge QDs) were incorporated in Si NW channel. Ge QDs were grown on silicon-on-insulator (SOI) substrate using molecular beam epitaxy, and NWs were patterned using electron beam lithography. The back gated phototransistor device showed photoresponse up to 1700 nm due to the presence of Ge QDs. The device has shown a very low dark current (~ 20 pA) with a peak detectivity of $\sim 9.33 \times 10^{11}$ Jones at ~ 1500 nm and with remarkably high photoconductive gain of $\sim 10^4$. The superior performance of Ge-QDs/Si nanowire phototransistor in infrared wavelengths is

potentially attractive to integrate electro-optical devices into Si for on-chip optical communications.

To enhance the performance of Group IV semiconductors, heterojunction with layered materials were used. Firstly, black-arsenic/Ge (b-As/Ge) heterostructure was fabricated to investigate the possibility of extending Ge based device response to Mid-Infrared (MIR) range. b-As was selected for MIR light absorption owing to its narrow bandgap of 0.3 eV. The device showed photoresponse from 600 nm to 4000 nm, with high responsivity of 402 A/W at 3000 nm and a high detectivity of 3.78×10^{11} Jones. Also, the device showed low noise equivalent power of $\sim 4.4 \times 10^{-15}$ WHz^{1/2} and high speed of 14.6 μ Sec. This work provides new insight in the use of Ge as a heterojunction with 2-dimensional materials for high-performance devices in short-wave IR (SWIR) applications.

Secondly, silicon-layered material heterojunction was studied for photodetection in IR range to improve the device performance. MoSe₂ was selected among other layered materials owing to its strong optical absorption and higher mobility. Broadband response from 405 nm to 2500 nm is observed in the device because of the existence of oxygen bounded defect states formed in MoSe₂ during the preparation process through hydrothermal process. The fabricated MoSe₂/Si heterojunction broadband photodiode was highly sensitive for a wide spectral range from 405 nm to 2500 nm wavelength with the maximum responsivity of ~ 522 mA/W for 1100 nm of incident light. Furthermore, the photodetector has been fully operational even at zero bias voltage, making it a potential contender for self-powered photodetection.

सार

नैनो-आयामी उपकरण विभिन्न प्रकार की अनूठी घटनाओं को प्रदर्शित करते हैं जो बेजोड़ प्रदर्शन के साथ अगली पीढ़ी के इलेक्ट्रॉनिक्स के विकास के महत्वपूर्ण अवसर प्रस्तुत करते हैं। इन्फ्रारेड (आईआर) डिटेक्टर सैन्य, चिकित्सा, पर्यावरण, उद्योग और संचार क्षेत्र में इसके अनुप्रयोग को देखते हुए इसके अपवाद नहीं हैं। 20वीं सदी में आईआर फोटोडिटेक्टर के आविष्कार के बाद से, उनके प्रदर्शन को बेहतर बनाने पर ध्यान केंद्रित किया गया है, जैसे कि उन्नत नैनो-प्रौद्योगिकी निर्माण के माध्यम से उपकरणों की निर्माण प्रक्रियाएं सरल बनाना, निर्माण लागत को कम करना, और कमरे के तापमान के संचालन को सुविधाजनक बनाना। समूह- IV अर्धचालक नैनोस्ट्रक्चर और स्तरित मटेरियल आधारित परिपक्व प्रौद्योगिकी के उत्कृष्ट विकल्प हैं III-V मटेरियलस जैसे इंडियम एंटीमोनाइड, इंडियम गैलियम आर्सेनाइड, और II-VI मटेरियलस जैसे सीसा सल्फाइड और पारा कैडमियम टेलुराइड।

इस शोध प्रबंध में सर्वप्रथम समूह- IV सेमीकंडक्टर नैनोवायर्स (NWs) का अध्ययन उच्च संवेदनशील आईआर खोज के लिए किया गया है। शुरू करने के लिए, जर्मेनियम (जीई) धातु-अर्धचालक-धातु (एमएसएम) उपकरणों को जर्मेनियम-ऑन-इन्सुलेटर (GeOI) सबस्ट्रेट का उपयोग करके बनाया गया था। दिलचस्प है, एक नकारात्मक अत्यधिक आर्सेनिक (As) डोपेड NWs में photoconductive प्रभाव (NPC) देखा गया है। फोटो-वाहको का प्रकाश की उपस्थिति में फँसना, वाहकों के उच्च पुनर्संयोजन की ओर ले जाते हैं जो एनपीसी की ओर ले जाते हैं। इस प्रभाव की पुष्टि करने के लिए केल्विन जांच बल माइक्रोस्कोपी अध्ययन किया गया जिसमें अवरक्त प्रकाश की उपस्थिति में n-Ge NWs में वाहकों की संख्या में कमी दिखाई दी। n-प्रकार के उपकरणों का प्रदर्शन, पी-टाइप NW डिटेक्टरों की तुलना में, जो पारंपरिक सकारात्मक फोटोकॉन्डक्टिव दिखाता है 10⁴ के उच्च लाभ के साथ व्यवहार देखा गया। देखे गए परिणामों का उपयोग Ge NWs के अनुप्रयोग का विभिन्न ऑप्टोइलेक्ट्रॉनिक अनुप्रयोगों के अध्ययन करने के लिए किया जा सकता है जिसमें लाइट ट्यून करने योग्य मेमोरी डिवाइस अनुप्रयोगों भी शामिल हैं।

Si आधारित उपकरणों में IR प्रतिक्रिया प्राप्त करने के लिए, जर्मेनियम क्वांटम डॉट्स (Ge QDs) को Si NWs चैनल में शामिल किया गया। Ge QDs को सिलिकॉन-ऑन-इन्सुलेटर (SOI) सबस्ट्रेट पर उगाया गया था आणविक बीम एपिटॉक्सी का उपयोग करते हुए, और एनडब्ल्यू (NWs) को इलेक्ट्रॉन बीम लिथोग्राफी का उपयोग करके प्रतिरूपित किया गया था। बैक गेटेड फोटोट्रांसिस्टर डिवाइस ने Ge QDs

की उपस्थिति के कारण 1700 एनएम तक फोटोरिस्पॉन्स दिखाया। डिवाइस ने ~1500 एनएम पर $\sim 9.33 \times 10^{11}$ जोन्स की पीक डिटैक्टिविटी के साथ बहुत कम डार्क करंट (~ 20 पीए) और उल्लेखनीय उच्च फोटोकॉन्डक्टिव लाभ $\sim 10^4$ दिखाया है। इन्फ्रारेड तरंगदैर्घ्य में Ge-QDs/Si फोटोट्रांसिस्टर का बेहतर प्रदर्शन इलेक्ट्रो-ऑप्टिकल उपकरणों को Si ऑन-चिप ऑप्टिकल संचार के लिए एकीकृत करने में संभावित रूप से आकर्षक है।

समूह IV अर्धचालकों के प्रदर्शन को बढ़ाने के लिए, स्तरित के साथ विषमयुग्मन मटेरियलस का प्रयोग किया गया। सबसे पहले, ब्लैक-आर्सेनिक/जीई (b-As/Ge) हेटरोस्ट्रक्चर को जीई (Ge) आधारित डिवाइस की प्रतिक्रिया को मिड-इन्फ्रारेड (एमआईआर) रेंज तक विस्तारित करने की संभावना के लिए जांचा गया। b-As को 0.3 eV के संकीर्ण बैंडगैप के कारण MIR प्रकाश अवशोषण के लिए चुना गया था। उपकरण ने 3000 एनएम पर 402 ए/डब्ल्यू (A/W) की उच्च प्रतिक्रिया और 3.78×10^{11} जोन्स की उच्च डिटैक्टिविटी के साथ, 600 एनएम से 4000 एनएम तक photoresponse दिखाया। साथ ही, डिवाइस ने कम शोर समकक्ष शक्ति $\sim 4.4 \times 10^{-15}$ WHz^{1/2} और 14.6 μ Sec की उच्च गति दिखाई। यह कार्य Ge के 2-आयामी मटेरियलस के साथ एक विषमता के रूप में शॉर्ट-वेव आईआर (एसडब्ल्यूआईआर) अनुप्रयोग में उपकरणों के उच्च-प्रदर्शन में उपयोग के लिए नई अंतर्दृष्टि प्रदान करता है।

दूसरे, सिलिकॉन-लेयर्ड मैटेरियल हेटेरोजंक्शन का अध्ययन IR रेंज फोटोडेटेक्शन में डिवाइस के प्रदर्शन को बेहतर बनाने के लिए किया गया था। MoSe₂ को अन्य स्तरित मटेरियलस के बीच चुना गया था अपने मजबूत ऑप्टिकल अवशोषण और उच्च गतिशीलता के कारण। ऑक्सीजन बाध्य दोष स्टेट जो MoSe₂ में हाइड्रोथर्मल प्रक्रिया के माध्यम से तैयारी प्रक्रिया के दौरान बनता है, के अस्तित्व के कारण डिवाइस में ब्रॉडबैंड प्रतिक्रिया 405 एनएम से 2500 एनएम तक देखा गया। गढ़ा हुआ MoSe₂/Si हेटेरोजंक्शन ब्रॉडबैंड फोटोडायोड ने अत्यधिक संवेदनशीलता के साथ एक विस्तृत वर्णक्रमीय रेंज (405 एनएम से 2500 एनएम) तथा ~ 522 एमए/डब्ल्यू (A/W) की अधिकतम प्रतिक्रिया 1100 एनएम (nm) तरंगदैर्घ्य के इंसीडेंट प्रकाश के साथ दिखाया। इसके अलावा, फोटोडेटेक्टर शून्य पूर्वाग्रह वोल्टेज पर भी पूरी तरह से चालू है, जो इसे स्व-संचालित फोटोडेटेक्शन के लिए एक संभावित दावेदार बनाता है।

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List of Abbreviations and Symbols

Abbreviations

BOX	Buried oxide
CMOS	Complementary Metal Oxide Semiconductor
CVD	Chemical Vapour Deposition
EBL	Electron Beam Lithography
FET	Field Effect Transistor
GeOI	Germanium on Insulator
HSQ	Hydrogen Silsesquioxane
JLT	Junctionless Transistor
FET	Field Effect Transistor
MSM	Metal-Semiconductor-Metal
NW	Nanowire
NEP	Noise Equivalent Power
NIR	Near Infrared
SOI	Silicon on Insulator
SWIR	Short Wavelength Infrared Range
TMDCs	Transition Metal Dichalcogenides
FDTD	Finite-difference time-domain

Symbols

λ	Wavelength
Φ	Barrier Height
σ	Conductivity
P_{in}	Optical Power
J	Current Density
W	Watt
V	Voltage
R	Responsivity
S_I	Noise Spectral Density
D	Detectivity
T	Temperature
$^{\circ}C$	Degree Celsius
eV	Electron Volt
Hz	Hertz
h	Planck Constant
K_B	Boltzmann Constant
τ_r	Rise Time
τ_f	Recovery/Fall Time