Investigation of Structural and Optical Properties of CdTe, ZnTe and HgCdTe Grown using MBE for Photodetector Applications

Subodh Tyagi

DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

Subodh Tyagi

DEPARTMENT OF PHYSICS

Submitted

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DEDICATION

I dedicate this dissertation to my guruji and family, whose blessings, continuous unwavering support, words of enthusiasm, and enduring love have provided me the encouragement and motivation throughout my journey.

CERTIFICATE

This is to certify that the research work presented in the thesis entitled **"Investigation of Structural and Optical Properties of CdTe, ZnTe and HgCdTe Grown using MBE for Photodetector Applications"** being submitted by **Mr. Subodh Tyagi** for the award of the **Doctor of Philosophy (Ph.D)** to the **Department of Physics, Indian Institute of Technology, Delhi,** is a record of authentic and bonafide research work. He has carried out his research work under the guidance and supervision jointly of **Prof. Rajendra Singh, Department of Physics, IIT Delhi, Delhi 110016** and **Dr. Shiv Kumar, Sc-G, Ex-Director, ER & IPR, DRDO HQ, Delhi 110054.** To the best of our knowledge, the research work presented in this thesis has not been submitted in part or full for the award of any other degree, diploma to any other University.

Prof. Rajendra Singh
Department of Physics
IIT Delhi
New Delhi-110016, India

Dr. Shiv Kumar
Scientist-G
Ex- Director, ER-IPR
DRDO, HQ
New Delhi-110054, India

Date: 30th May, 2025

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गुरू ब्रहमा गुरू विष्णु, गुरु देवो महेश्वरा;

गुरु साक्षात परब्रहम, तस्मै श्री गुरुवे नमः

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जाड्यं धियो हरति सिंचति वाचि सत्यं , मानोन्नतिं दिशति पापमपाकरोति |

चेतः प्रसादयति दिक्षु तनोति कीर्तिं , सत्संगतिः कथय किं न करोति पुंसाम् ||

अर्थात्: अच्छे मित्रों का साथ, बुद्धि की जड़ता को हर लेता है ,वाणी में सत्य का संचार करता है, मान और उन्नति को बढ़ाता है और पाप से मुक्त करता है | चित्त को प्रसन्न करता है और हमारी कीर्ति को सभी दिशाओं में फैलाता है | आप ही कहें कि सत्संगतिः मनुष्यों का कौन सा भला नहीं करती |

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ॐ सहना ववतु, सहनौ भुनक्तु

सहवीर्यं करवावहै, तेजस वीणावती तमस्तु

माँ विद्विषावहै, ॐ शांति शांति शाँतिहि

Subodh Tyagi

Date: 30th May 2025

New Delhi, India

ABSTRACT

The II-VI based compound semiconductor materials like ZnTe, CdTe, and HgCdTe have various civilian, medical, astronomical, and strategic defence applications such as radiation detector, Infrared detectors, Solar cells, THz detectors, transistors, lasers, superlattices, LED, etc. The availability of lattice matched substrate is important for good quality crystal growth. However, the size, cost and material properties restrict the substrate choice. In the present work, semi-insulating 3-inch diameter GaAs was used as substrate for epitaxial growth of ZnTe, CdTe and HgCdTe growth. It is challenging to achieve a high crystalline quality of ZnTe and CdTe thin film due to its (7.8% and 14.6% respectively) lattice mismatch with respect to the substrate, GaAs. There are various reports suggesting different methods to grow ZnTe and CdTe thin epitaxial film on GaAs. Low-temperature (LT) nucleation is a novel method for epitaxy on large lattice mismatched GaAs substrates. The critical thickness of CdTe epitaxial layer on GaAs is ~5 nm, leading to stress relaxation either in the form of high density of misfit dislocations at the interface or change in the orientation of the epitaxial layer. The HRXRD and TEM were used to analyse the orientation change in CdTe and ZnTe epitaxial layer.

Annealing of the epitaxial layers annihilates and coalesce the threading dislocations, reduces etch pit defect density (EPD) ~ 4×10^6 cm^{-2} and improves the crystal quality from 100 arcsec to 60 arcsec. To achieve the optimum temperature and source material flux, the thermodynamic aspects have been

considered during growth and annealing of the epitaxial layer. This work aims to achieve a highly crystalline CdTe and ZnTe buffer layer on large area GaAs substrates and further these layers are used for the growth of HgCdTe epitaxial layers in molecular beam epitaxy system.

As grown HgCdTe epitaxial layer is p-type due to Hg vacancies. Ex-situ annealing was carried out under Hg pressure to achieve the desired doping (Hg vacancy) concentration of ~ $0.8\text{-}1\times10^{16}$ cm^{-3} and carrier mobility of 350 – 450 $cm^2/V.sec$. The epitaxial layers were n-type doped using Boron ion implantation. The minority carrier lifetime of p-n junction thus formed was determined using Laser Beam Induced Current (LBIC). HgCdTe epitaxial layers were passivated using thin CdTe layer. The improvement in minority carrier lifetime was observed with the passivation HgCdTe surface.

Epitaxial ZnTe and CdTe layers were used to fabricate the MSM photodetector. Both, ZnTe and CdTe based detectors have demonstrated the broad spectral range in 250-500 nm and 400-850 nm range respectively. Photodetectors fabricated on both the materials have demonstrated the self-powered behaviour with PDCR values ~ 3.7×10^2 and 3.2×10^4 respectively when illuminated with band edge wavelength at zero bias and 25 ℃. The photoelectrical measurements were carried out showing the high spectral responsivity and detectivity. The temporal response of photodetector was studied to analyse the repeatability and stability up to 125 ℃. The device has shown high on/off ratio and excellent switching characteristics of the detectors.

The grown layers were also characterized optically, structurally, topologically, and chemically using FTIR, HRXRD, Raman spectroscopy, AFM, FESEM, SIMS measurements. Electrical characteristics of HgCdTe are evaluated using Hall, LBIC measurements and the detailed photoelectric characteristics were studied at different temperatures ranging from room temperature to 125 ^{0}C.

सार

II-VI आधारित यौगिक अर्धचालक सामग्री जैसे ZnTe, CdTe, और HgCdTe के विभिन्न नागरिक, चिकित्सा, खगोलीय और रणनीतिक रक्षा अनुप्रयोग हैं जैसे कि विकिरण डिटेक्टर, इन्फ्रारेड डिटेक्टर, सौर सेल, THz डिटेक्टर, ट्रांजिस्टर, लेजर, सुपरलैटिस, एलईडी, आदि। अच्छी गुणवत्ता वाले क्रिस्टल विकास के लिए जालीदार सब्सट्रेट की उपलब्धता महत्वपूर्ण है। हालाँकि, आकार, लागत और भौतिक गुण सब्सट्रेट की पसंद को प्रतिबंधित करते हैं। वर्तमान कार्य में, अर्ध-इन्सुलेटिंग 3-इंच व्यास वाले GaAs का उपयोग ZnTe, CdTe और HgCdTe के एपिटैक्सियल विकास के लिए सब्सट्रेट के रूप में किया गया था। सब्सट्रेट, GaAs के संबंध में इसके (क्रमशः 7.8% और 14.3%) जाली बेमेल के कारण ZnTe और CdTe पतली फिल्म की उच्च क्रिस्टलीय गुणवत्ता प्राप्त करना चुनौतीपूर्ण है। GaAs पर ZnTe और CdTe पतली एपिटैक्सियल फिल्म को विकसित करने के लिए विभिन्न तरीकों का सुझाव देने वाली विभिन्न रिपोर्टें हैं। कम तापमान (एलटी) न्यूक्लिएशन बड़े जाली बेमेल GaAs सबस्ट्रेट्स पर एपिटेक्सी के लिए एक उपन्यास विधि है। GaAs पर CdTe एपिटैक्सियल परत की महत्वपूर्ण मोटाई ~ 5 एनएम है, जिससे इंटरफ़ेस पर मिसफिट अव्यवस्था के उच्च घनत्व या एपिटैक्सियल परत के अभिविन्यास में परिवर्तन के रूप में तनाव में छूट मिलती है। एचआरएक्सआरडी और टीईएम का उपयोग CdTe और ZnTe एपिटैक्सियल परत में अभिविन्यास परिवर्तन का विश्लेषण करने के लिए किया गया था।

एपिटैक्सियल परतों की एनीलिंग थ्रेडिंग अव्यवस्था को नष्ट और एकजुट करती है, ईच पिट दोष घनत्व (ईपीडी) को कम करती है और क्रिस्टल की गुणवत्ता में सुधार करती है। इष्टतम तापमान और स्रोत सामग्री प्रवाह को प्राप्त करने के लिए, एपिटैक्सियल परत के विकास और एनीलिंग के दौरान थर्मोडायनामिक पहलुओं पर विचार किया गया है। इस कार्य का लक्ष्य बड़े क्षेत्र वाले GaAs सब्सट्रेट्स पर एक उच्च क्रिस्टलीय CdTe और ZnTe बफर परत प्राप्त करना

है और आगे इन परतों का उपयोग आणविक बीम एपिटेक्सी प्रणाली में HgCdTe एपिटैक्सियल परतों के विकास के लिए किया जाता है।

जैसे-जैसे HgCdTe एपिटैक्सियल परत बढ़ती है, Hg रिक्तियों के कारण P-प्रकार की हो जाती है। ~ 0.8-1×10^{16} सेमी$^{-3}$ की वांछित डोपिंग (एचजी रिक्ति) सांद्रता और 350 - 450 सेमी^{2}/वी.सेकंड की वाहक गतिशीलता प्राप्त करने के लिए एचजी दबाव के तहत एक्स-सीटू एनीलिंग किया गया था। एपिटैक्सियल परतों को बोरोन आयन आरोपण का उपयोग करके एन-प्रकार का डोप किया गया था। इस प्रकार बने पी-एन जंक्शन का अल्पसंख्यक वाहक जीवनकाल लेजर बीम प्रेरित करंट (एलबीआईसी) का उपयोग करके निर्धारित किया गया था। HgCdTe एपिटैक्सियल परतों को पतली CdTe परत का उपयोग करके निष्क्रिय किया गया था। निष्क्रियता HgCdTe सतह के साथ अल्पसंख्यक वाहक जीवनकाल में सुधार देखा गया।

एमएसएम फोटोडिटेक्टर को बनाने के लिए एपिटैक्सियल ZnTe और CdTe परतों का उपयोग किया गया था। ZnTe और CdTe दोनों आधारित डिटेक्टरों ने क्रमशः 250-500 nm और 400-850 nm रेंज में व्यापक वर्णक्रमीय रेंज का प्रदर्शन किया है। दोनों सामग्रियों पर निर्मित फोटोडिटेक्टरों ने शून्य पूर्वाग्रह और 25 डिग्री सेल्सियस पर बैंड एज तरंग दैर्ध्य के साथ प्रकाशित होने पर क्रमशः पीडीसीआर मान ~ 3.7×10^{2} और 3.2×10^{4} के साथ स्व-संचालित व्यवहार का प्रदर्शन किया है। फोटोइलेक्ट्रिकल माप उच्च वर्णक्रमीय प्रतिक्रिया और जासूसी दिखाते हुए किए गए। 125 °C तक पुनरावृत्ति और स्थिरता का विश्लेषण करने के लिए फोटोडिटेक्टर की अस्थायी प्रतिक्रिया का अध्ययन किया गया था। डिवाइस ने उच्च ऑन/ऑफ अनुपात और डिटेक्टरों की उत्कृष्ट स्विचिंग विशेषताओं को दिखाया है।

विकसित परतों को एफटीआईआर, एचआरएक्सआरडी, रमन स्पेक्ट्रोस्कोपी, एएफएम, एफईएसईएम, सिम्स माप का उपयोग करके ऑप्टिकल, संरचनात्मक, टोपोलॉजिकल और रासायनिक रूप से भी चित्रित किया गया था। HgCdTe की विद्युत विशेषताओं का मूल्यांकन

हॉल, LBIC मापों का उपयोग करके किया जाता है और विस्तृत फोटोइलेक्ट्रिक विशेषताओं का अध्ययन कमरे के तापमान से लेकर 125 ^{0}C तक के विभिन्न तापमानों पर किया गया।

TABLE OF CONTENTS

LIST OF FIGURES

ABBREVIATIONS

AFM	Atomic force microscopy
B.A.	Bayard Alpert
BEP	Beam Equivalent Pressure
EDX	Electron diffraction analysis
HRTEM	High-resolution transmission electron microscopy
FESEM	Field emission scanning electron microscope
FM	Frank-van der Merwe
FPA	Focal Plane Array
FTIR	Fourier Transform Infrared spectroscopy
FWHM	Full Width Half Maximum
HgCdTe	Mercury Cadmium Telluride
HRXRD	High Resolution X-ray Diffraction
LBIC	Laser Beam Induced Current
LO	Longitudinal Optic
LPE	Liquid Phase Epitaxy
LWIR	Long wavelength Infrared
MBE	Molecular Beam Epitaxy
MCT	Mercury Cadmium Telluride
MOCVD	Metal Organic Chemical Vapour Deposition
MSM	Metal Semiconductor Metal

MWIR	Mid wavelength Infrared
OM	Optical Microscope
PD	Photo Detector
PDCR	Photo to Dark Current Ratio
PL	Photoluminescence
RHEED	Reflection High Energy Electron Diffraction
RMS	Root Mean Square
SIMS	Secondary Ion Mass Spectroscopy
SK	Stransky Krastanov
SWIR	Short wavelength Infrared
TO	Transverse Optic
ZnTe	Zinc Telluride
UHV	Ultra-High Vacuum
vdW	van der Waals