SCALABLE MBE GROWTH AND CHARACTERIZATION OF 2D-$MoSe_2$ AND ITS HETEROSTRUCTURES FOR ADVANCED PHOTODETECTION APPLICATIONS

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by

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Dedication

I dedicate this dissertation to my family, whose unwavering support, blessings, words of encouragement, and enduring love have been my foundation throughout my journey. I also want to sincerely thank my teachers, whose counsel, insight, and encouragement have moulded my career and stoked my curiosity.

CERTIFICATE

This is to certify that the thesis entitled **"Scalable MBE Growth and Characterization of 2D-$MoSe_2$ and Its Heterostructures for Advanced Photodetection Applications"** submitted by **Mr. Santanu Kandar**, a Research Scholar in the *Department of Physics, Indian Institute of Technology Delhi, New Delhi, India,* for the award of degree of **Doctor of Philosophy,** is a record of original and bonafide research work carried out by him under my supervision and guidance. The results contained in it have not been submitted in part or full to any other university or institute for the award of any degree/diploma.

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"The expert at anything was once a beginner" -Helen Hayes

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ABSTRACT

The growing demand for miniaturized, high-performance optoelectronic and electronic devices has driven research into two-dimensional (2D) materials, known for their unique properties that differ from their bulk counterparts. These materials offer tunable band structures, high carrier mobility, and strong light-matter interactions, making them promising candidates for next-generation applications. Transition metal dichalcogenides (TMDCs), a prominent class of 2D materials, are particularly interesting due to their semiconducting nature and direct bandgaps in monolayer form. Within the TMDC family, molybdenum diselenide ($MoSe_2$) has garnered significant attention due to its exceptional optical and electronic properties, including layer-dependent bandgaps and strong photoluminescence, positioning it as a key material for advanced device applications.

To fully exploit the potential of $MoSe_2$ in device applications, high-quality growth on technologically relevant substrates is essential. Achieving uniformity, crystallinity, and stoichiometry remains a critical challenge. This study addresses these requirements by systematically exploring the growth of ultrathin $MoSe_2$ films on Si (111) and c-plane sapphire substrates using molecular beam epitaxy (MBE). For the Si (111), the growth temperatures ranging from 450-550 °C were investigated, with 500 °C identified as the optimum for achieving crystalline, uniform films. Characterization using reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), and Raman spectroscopy confirmed the structural and compositional

quality of the films. X-ray diffraction (XRD) revealed c-axis-oriented growth and photoluminescence spectroscopy identified a bandgap of 1.57 eV for few-layer $MoSe_2$ on Si (111). Annealing experiments in a low selenium environment further improved sample quality by enhancing grain size from 70 nm to 135 nm and providing a stronger luminescence than the un-annealed sample. On the c-plane sapphire, $MoSe_2$ films demonstrated excellent uniformity and composition, providing a robust platform for detailed investigations.

The thickness of 2D materials significantly influences their optical and electrical properties, demanding systematic studies for device optimization. This work examines the layer-dependent properties of $MoSe_2$ films grown on c-plane sapphire, ranging from 1 to 7 layers. Spectroscopic ellipsometry (SE), a non-destructive optical technique, revealed substantial variations in optical constants across the spectral range of 0.73 to 5.04 eV. The bandgap decreased from 1.62 eV for monolayers to 1.19 eV for seven layers, highlighting quantum confinement effects. Band diagram analysis indicated a reduction in the energy gap between the conduction band edge and the Fermi level from 0.50 eV to 0.40 eV with increasing thickness, reflecting enhanced n-type behavior. Electrical measurements corroborated these findings, showing a current increase from 10^{-9} to 10^{-5} amperes at 3 V when film thickness changes from 1 to 7 layers. These results underline the tunability of $MoSe_2$'s properties through precise thickness control, offering valuable insights for tailoring its behavior for specific applications.

To expand the functionality of $MoSe_2$, its integration into heterostructures is vital, enabling enhanced and tunable properties for advanced devices. This

study explores $MoSe_2/WSe_2$ and $MoSe_2/GaTe$ heterostructures, focusing on large-area growth and band alignment. The $MoSe_2/WSe_2$ heterostructures grown on c-plane sapphire show uniform growth with nearly stoichiometric layers. The heterostructure layers also demonstrate a crystalline nature evidenced by RHEED streaks. For $MoSe_2/GaTe$ heterostructure grown on SiO_2/Si substrate, a type-III band alignment enabled efficiency for optoelectronic devices. These results demonstrate the potential of $MoSe_2$-based heterostructures for achieving tailored optoelectronic properties.

The growing need for efficient, high-performance photodetectors has driven interest in 2D material-based heterostructures. This study presents a $MoSe_2/GaTe$ heterostructure photodetector that exhibits exceptional performance across visible and NIR wavelengths. Under 780 nm illumination, the device achieved rapid response times of 44 ms (rise) and 67 ms (decay), while at 1000 nm, response times were 242 ms (rise) and 340 ms (decay). Enhanced ultraviolet (UV) responsivity of 0.6 A/W was observed at 200 nm, though with slower switching speeds of 3.7 s (rise) and 1.94 s (decay) at 300 nm. Dynamic response spikes under 780 nm illumination were attributed to pyroelectric and photoelectric effects in GaTe. These results underscore the potential of $MoSe_2/GaTe$ heterostructures for advanced photodetection applications, combining high responsivity, tunable spectral response, and fast operation.

This comprehensive study connects the growth, optimization, and application of $MoSe_2$ films and heterostructures, illustrating their tunable properties and versatile functionalities. By systematically addressing the requirements for high-quality growth, layer-dependent property modulation, and integration

into heterostructures, this work establishes a strong foundation for $MoSe_2$-based electronic and optoelectronic devices, particularly in photodetection applications.

सार

दो-आयामी (2D) पदार्थ की बढ़ती मांग, उच्च प्रदर्शन वाले छोटे आकार के ऑप्टोइलेक्ट्रॉनिक और इलेक्ट्रॉनिक उपकरणों के विकास को प्रोत्साहित कर रही है। इन सामग्रियों के अद्वितीय गुण, जो उनकी थोक संरचना से भिन्न होते हैं, उन्हें अगली पीढ़ी के अनुप्रयोगों के लिए आशाजनक उम्मीदवार बनाते हैं। इनमें बैंड संरचना को ट्यून करने की क्षमता, उच्च वाहक गतिशीलता और प्रकाश के साथ मजबूत अंतःक्रिया शामिल हैं। संक्रमण धातु डाइचेल्कोजेनाइड्स (TMDCs), 2D पदार्थ की एक प्रमुख श्रेणी है, जो उनकी अर्धचालक प्रकृति और प्रत्यक्ष बैंडगैप ट्रांजिशन के कारण विशेष रुचि उत्पन्न करती है। TMDC परिवार में, मोलिब्डेनम डाईसेलेनाइड ($MoSe_2$) अपनी असाधारण ऑप्टिकल और इलेक्ट्रॉनिक गुणों के कारण महत्वपूर्ण ध्यान आकर्षित करता है, जैसे कि परत-निर्भर बैंडगैप और मजबूत फोटोलुमिनेसेंस, जो इसे उन्नत उपकरण अनुप्रयोगों के लिए एक प्रमुख पदार्थ के रूप में स्थापित करते हैं।

$MoSe_2$ की संभावनाओं का पूरी तरह से दोहन करने के लिए, प्रौद्योगिकी के लिए प्रासंगिक सब्सट्रेट्स पर उच्च गुणवत्ता वाली परतों का विकास आवश्यक है। एकसमानता, क्रिस्टलीयता और स्टॉयकियोमेट्री प्राप्त करना अभी भी एक महत्वपूर्ण चुनौती है। इस अध्ययन में Si (111) और c-प्लेन सैफायर सब्सट्रेट सब्सट्रेट पर मोलिक्यूलर बीम एपिटैक्सी (MBE) का उपयोग करके अल्ट्राथिन $MoSe_2$ परतों के विकास की व्यवस्थित जांच की गई। Si (111) पर 450-550 °C के बीच तापमान पर विकास का अध्ययन किया गया, जिसमें 500 °C को क्रिस्टलीय और समान परतें प्राप्त करने के लिए आदर्श तापमान के रूप में पहचाना गया। रिफ्लेक्शन हाई-एनर्जी इलेक्ट्रॉन डिफ्रैक्शन (RHEED), एटॉमिक फोर्स माइक्रोस्कोपी (AFM), और रमन स्पेक्ट्रोस्कोपी का उपयोग करके परतों की संरचनात्मक और संघटनात्मक गुणवत्ता की पुष्टि की गई। एक्स-रे डिफ्रैक्शन (XRD) ने c-अक्ष के साथ उन्मुख विकास दिखाया, और फोटोलुमिनेसेंस स्पेक्ट्रोस्कोपी ने Si (111) पर few-layer $MoSe_2$ के लिए 1.57 eV का बैंडगैप पहचाना। कम सेलेनियम पर्यावरण में एनिलिंग प्रयोगों ने sample की गुणवत्ता को और बढ़ाया, जिससे grain का आकार 70 nm से 135 nm तक बढ़ा और बिना एनिलिंग वाले sample की तुलना में बेहतर प्रकाश उत्सर्जन देखा गया। c-प्लेन नीलम पर $MoSe_2$ परतों ने उत्कृष्ट समानता और संरचना प्रदर्शित की, जो विस्तृत अध्ययन के लिए एक ठोस आधार प्रदान करती है।

2D पदार्थ की मोटाई उनके ऑप्टिकल और इलेक्ट्रिकल गुणों को महत्वपूर्ण रूप से प्रभावित करती है, जो उपकरणों के अनुकूलन के लिए व्यवस्थित अध्ययन की मांग करती है। इस अध्ययन में c-प्लेन

सैफायर पर 1 से 7 परतों तक की मोटाई वाली $MoSe_2$ परतों के परत-निर्भर गुणों की जांच की गई। स्पेक्ट्रोस्कोपिक एलिप्सोमेट्री (SE) नामक गैर-विनाशकारी ऑप्टिकल तकनीक ने 0.73 से 5.04 eV के वर्णक्रमीय क्षेत्र में ऑप्टिकल स्थिरांकों में महत्वपूर्ण बदलाव दिखाए। बैंडगैप मोनोलियर के लिए 1.62 eV से घटकर सात परतों के लिए 1.19 eV हो गया, जो क्वांटम प्रतिबंध प्रभावों को उजागर करता है। बैंड आरेख विश्लेषण ने मोटाई बढ़ने के साथ कंडक्शन बैंड से फर्मी स्तर के ऊर्जा अंतर में 0.50 eV से 0.40 eV की कमी को दिखाया, जो बढ़ी हुई n-टाइप प्रवृत्ति को दर्शाता है। विद्युत मापन ने इन निष्कर्षों की पुष्टि की, जिसमें 1 परत से 7 परतों तक फिल्म की मोटाई बदलने पर 3 V पर धारा में 10^{-9} से 10^{-5} एंपियर तक की वृद्धि देखी गई। ये परिणाम $MoSe_2$ के गुणों को सटीक मोटाई नियंत्रण के माध्यम से ट्यून करने की क्षमता को रेखांकित करते हैं, जो विशिष्ट अनुप्रयोगों के लिए इसके व्यवहार को तैयार करने के लिए मूल्यवान अंतर्दृष्टि प्रदान करते हैं।

$MoSe_2$ की कार्यक्षमता का विस्तार करने के लिए, इसे हेटेरोस्ट्रक्चर्स में एकीकृत करना महत्वपूर्ण है, जिससे उन्नत उपकरणों के लिए बेहतर और अनुकूलन योग्य गुण सक्षम होते हैं। इस अध्ययन में $MoSe_2/WSe_2$ और $MoSe_2$/GaTe हेटेरोस्ट्रक्चर्स का अन्वेषण किया गया, जो बड़े क्षेत्रीय विकास और बैंड संरेखण पर केंद्रित है। c-प्लेन नीलम पर विकसित $MoSe_2/WSe_2$ हेटेरोस्ट्रक्चर्स ने लगभग स्टॉयकियोमेट्रिक परतों के साथ समान विकास दिखाया। परतों की क्रिस्टलीय प्रकृति को RHEED धारियों द्वारा प्रमाणित किया गया। SiO_2/Si सब्सट्रेट पर विकसित $MoSe_2$/GaTe हेटेरोस्ट्रक्चर ने ऑप्टोइलेक्ट्रॉनिक उपकरणों के लिए दक्षता सक्षम करने के लिए एक पूरक प्रकार-III बैंड संरेखण प्रदर्शित किया। ये परिणाम उन्नत ऑप्टोइलेक्ट्रॉनिक गुणों को प्राप्त करने के लिए $MoSe_2$-आधारित हेटेरोस्ट्रक्चर्स की क्षमता को प्रदर्शित करते हैं।

प्रभावी, उच्च प्रदर्शन वाले फोटोडिटेक्टरों की बढ़ती आवश्यकता ने 2D पदार्थ-आधारित हेटेरोस्ट्रक्चर्स में रुचि बढ़ाई है। इस अध्ययन में $MoSe_2$/GaTe हेटेरोस्ट्रक्चर फोटोडिटेक्टर प्रस्तुत किया गया है, जो दृश्यमान और निकट-अवरक्त (NIR) तरंग दैर्ध्य में उत्कृष्ट प्रदर्शन दिखाता है। 780 nm प्रकाश डालन पर, डिवाइस ने 44 ms (उदय) और 67 ms (अवरोह) के तेज प्रतिक्रिया समय प्राप्त किए, जबकि 1000 nm पर प्रतिक्रिया समय 242 ms (उदय) और 340 ms (अवरोह) था। 200 nm पर पराबैंगनी (UV) प्रतिक्रिया क्षमता में 0.6 A/W का वृद्धि देखा गया, हालांकि 300 nm पर 3.7 s (उदय) और 1.94 s (अवरोह) के धीमे स्विचिंग गति के साथ। 780 nm प्रकाश डालन के तहत गतिशील प्रतिक्रिया स्पाइक्स को GaTe की गैर-केन्द्रसमी प्रकृति में पाइरोइलेक्ट्रिक और फोटोइलेक्ट्रिक प्रभावों के संयोजन के लिए जिम्मेदार ठहराया गया, जो प्रकाश अवशोषण के दौरान ताप प्रभाव का कारण बनता है। ये परिणाम उन्नत फोटोडिटेक्शन अनुप्रयोगों के लिए $MoSe_2$/GaTe

हेटेरोस्ट्रक्चर की क्षमता को रेखांकित करते हैं, जो उच्च प्रतिक्रिया क्षमता, ट्यून करने योग्य वर्णक्रमीय प्रतिक्रिया और तेज संचालन को संयोजित करता है।

यह व्यापक अध्ययन $MoSe_2$ परतों और हेटेरोस्ट्रक्चर्स के विकास, अनुकूलन और अनुप्रयोग को जोड़ता है, इसके ट्यून करने योग्य गुणों और बहुमुखी कार्यात्मकताओं को दर्शाता है। उच्च गुणवत्ता वाले विकास, परत-निर्भर गुणों के संशोधन और हेटेरोस्ट्रक्चर्स में एकीकरण की आवश्यकताओं को व्यवस्थित रूप से संबोधित करते हुए, यह कार्य $MoSe_2$-आधारित इलेक्ट्रॉनिक और ऑप्टोइलेक्ट्रॉनिक उपकरणों, विशेष रूप से फोटोडिटेक्शन अनुप्रयोगों के लिए एक मजबूत आधार स्थापित करता है।

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ABBREVIATIONS

vdW	van der Waals
MBE	Molecular beam epitaxy
2DMs	Two dimensional materials
3D	Three dimensional
TMDCs	Transition metal dichalcogenides
OM	Optical microscope
AFM	Atomic force microscopy
KPFM	Kelvin probe force microscopy
XPS	X-ray photoelectron spectroscopy
B.E.	Binding energy
HRTEM	High-resolution transmission electron microscopy
PL	Photoluminescence
NIR	Near Infrared
SEM	Scanning electron microscope
FESEM	Field emission scanning electron microscope
EDAX	Electron diffraction analysis
CVD	Chemical vapour deposition
MOCVD	Metalloorganic chemical vapour deposition
CB	Conduction band
VB	Valence band

VBM	Valence band maxima
CBM	Conduction band minima
SP	Surface potential
VBS	Valence band spectra
UHV	Ultra-high vacuum