MBE GROWTH OF 2D $MoTe_2$ AND HETEROSTRUCTURES WITH INVESTIGATIONS ON PHASE ENGINEERING AND CHARGE TRANSFER EFFECTS

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DEPARTMENT OF PHYSICS

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by

KAMLESH

DEPARTMENT OF PHYSICS

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To my parents, Shri Jaikishan and Smt. Kamla,

and my sister Sunanda

Certificate

This is to certify that the thesis entitled **"MBE Growth of 2D $MoTe_2$ and Heterostructures With Investigations on Phase Engineering and Charge Transfer Effects"** submitted by **Mr. Kamlesh**, a research scholar in the *Department of Physics*, Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy,** is a record of original and bonafide research work carried out by him. He has worked under my guidance and supervision, and has fulfilled the requirements, which, to my knowledge, have reached the requisite standard for the submission of the thesis. The results contained in it 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

The fundamental limitations of bulk silicon at the nanoscale, such as quantum tunneling, short-channel effects, and reduced gate controllability, pose critical challenges to further scaling of semiconductor-based devices. These limitations have motivated the exploration of alternative materials that can extend beyond Moore's law. In this context, two-dimensional (2D) layered materials have emerged as promising candidates owing to their atomic-scale thickness, tunable electronic properties, and potential for seamless heterointegration. Among them, molybdenum ditelluride ($MoTe_2$) is uniquely suited for integration and device engineering because its semiconducting 2H and semimetallic 1T′ phases are separated by only a small ground state energy (~40–60 meV per atom), enabling controllable phase switching as well as access to rich physics beyond the semiconducting aspect. The dual-phase stability, coupled with its narrow bandgap in the near-infrared (NIR) range, makes $MoTe_2$ a compelling material for next-generation electronics and optoelectronics, as well as for exploring rich material aspects.

In this thesis, molecular beam epitaxy (MBE) has been employed to achieve large-area, phase-pure growth of $MoTe_2$ thin films on technologically relevant substrates, including silicon and sapphire. Initially, a tellurium-rich pre-wetting growth recipe is combined with careful optimization of growth temperature to achieve the direct integration of crystalline 2H-$MoTe_2$ on silicon, overcoming the interface challenges posed by dangling bonds. This achievement represents a crucial step toward the integration of 2D semiconductors with established silicon platforms.

Leveraging this foundation, the growth conditions have been established to selectively stabilize semiconducting 2H-$MoTe_2$ as well as the semimetallic 1T′ phase. By systematically tuning the effective concentration ratio of Mo and Te during MBE growth, the study clarifies the existing discrepancies in the literature regarding phase stability. Both the semiconducting 2H and semimetallic 1T′ phases, as well as their coexistence, have been achieved

uniformly over centimeter-scale areas in a controllable manner. The findings have shown that the phase engineering in $MoTe_2$ can be achieved independently of a single growth parameter, such as growth temperature or flux, which is crucial for seamless integration of the hetero phase-based 2D-2D vertical heterostructures and superlattices for tailoring the material properties.

With precise phase control achieved, the thesis advances towards fabricating van der Waals heterostructures, where $MoTe_2$ is combined with other layered chalcogenides such as $MoSe_2$ and GaSe. First, scalable layer-by-layer growth of $MoSe_2/MoTe_2$ heterostructures is demonstrated, focusing on probing interfacial electronic interaction effects. Using XPS, UPS and Kelvin probe force microscopy, unconventional interfacial charge transfer effects have been observed in the heterostructure band alignment. The tunable probing depth of angle-dependent XPS has been utilized to understand this anomaly, which shows that site-to-site interactions between Se and Te alter the intrinsic chemical bonding near the interface. The Te vacancies pin the $MoTe_2$ Fermi level, while modified bonding in $MoSe_2$ raises its valence-band maximum abnormally. Overall, the experimentally observed heterostructure band alignment shows a reduced barrier for the holes, which can be advantageous for bidirectional carrier transport.

Insights from these vacancy-induced carrier doping have further motivated us to carry out intrinsic charge carrier-type control in 2H-$MoTe_2$ without extrinsic dopants. The chalcogen-to-metal flux has been tuned precisely to achieve n-type behavior in $MoTe_2$ via Te-vacancies and p-type behavior via Te-rich incorporation. Further, UHV annealing has been demonstrated as an approach to drive p-to-n type transition in $MoTe_2$. The Fermi-level shifts in the valence band spectra validate this stoichiometry-driven doping, enabling reliable, wafer-scale ambipolar tuning.

Finally, the potential of the 2D-2D heterostructures has been explored through optoelectronic device demonstrations. The MBE-grown, few-layer GaSe/$MoTe_2$ heterostructure has revealed a type-II band alignment with a relatively higher conduction-band offset. The heterostructure-based device shows a low dark current and asymmetric I–V behavior. The device has achieved a stable and repeatable photoresponse across UV to NIR wavelengths with fast response times on the sub-millisecond scale. Furthermore, the high-frequency optical response of the device is studied, which shows switching of the device up to 3 kHz with an optical response bandwidth of ~2 kHz at 660 nm, highlighting its potential for high-speed optoelectronic applications.

Collectively, this work has established a comprehensive platform for $MoTe_2$-based device engineering, from scalable synthesis and phase control to interfacial effects in heterostructures, intrinsic ambipolar control and functional heterostructure devices, which significantly contributes to the future integration of 2D materials into practical semiconductor technologies.

सार

नैनोस्तर पर बल्क सिलिकॉन की मूलभूत सीमाएँ, जैसे क्वांटम टनलिंग, शॉर्ट-चैनल प्रभाव तथा गेट नियंत्रण क्षमता में कमी, अर्धचालक आधारित उपकरणों की विस्तार-क्षमता के लिए गंभीर चुनौतियाँ प्रस्तुत करती हैं। इन सीमाओं ने वैकल्पिक पदार्थों की खोज के लिए प्रेरित किया गया है, जो मूर के नियम से आगे बढ़ने की क्षमता रखते हों। इस संदर्भ में द्वि-आयामी (2D) परतदार पदार्थ अपने परमाण्विक-स्तर की मोटाई, नियंत्रित किए जा सकने वाले इलेक्ट्रॉनिक गुणों तथा निर्बाध विषम एकीकरण की क्षमता के कारण अत्यंत आशाजनक प्रत्याशी के रूप में उभरे हैं। इनमें, मोलिब्डेनम डाइटेल्युराइड ($MoTe_2$) समाकलन और डिवाइस अभियांत्रिकी के लिए विशिष्ट रूप से उपयुक्त है, क्योंकि इसकी अर्धचालक 2H और अर्धधात्विक 1T′ अवस्थाएँ केवल ~40–60 meV प्रति परमाणु की आधार अवस्था ऊर्जा से पृथक होते हैं। यह सूक्ष्म ऊर्जा-अंतर $MoTe_2$ को नियंत्रित अवस्था-परिवर्तन तथा अर्धचालक गुणों से परे भी समृद्ध भौतिकी तक पहुंच को सक्षम करता है। इसकी द्वि-अवस्था स्थिरता तथा निकट-अवरक्त (NIR) क्षेत्र में संकीर्ण बैंडगैप इसे अगली पीढ़ी के इलेक्ट्रॉनिक्स व ऑप्टोइलेक्ट्रॉनिक्स के साथ-साथ समृद्ध पदार्थीय पहलुओं की खोज के लिए एक अत्यंत आकर्षक पदार्थ बनाते हैं।

इस शोध-प्रबंध में मॉलिक्यूलर बीम एपिटैक्सी (MBE) तकनीक का उपयोग करके तकनीकी दृष्टि से महत्त्वपूर्ण सब्सट्रेट्स — जैसे सिलिकॉन (Si) और सैफायर ($Al2O_3$) — पर $MoTe_2$ की विस्तृत क्षेत्रफल और शुद्ध अवस्था वाली पतली परतों की वृद्धि हासिल की गई है। प्रारंभ में, सिलिकॉन पर क्रिस्टलीय 2H-$MoTe_2$ के प्रत्यक्ष एकीकरण को प्राप्त करने के लिए परत निर्माण तापमान के सावधानीपूर्वक अनुकूलन के साथ एक टेल्यूरियम-समृद्ध पूर्व-प्रसंस्करण प्रक्रिया को जोड़ा जाता है, जिससे सतह के असंतृप्त बंधनों द्वारा उत्पन्न इंटरफेस चुनौतियों पर काबू पाया जा सका है। यह उपलब्धि स्थापित सिलिकॉन प्लेटफार्मों के साथ 2D अर्धचालकों के समाकलन की दिशा में एक महत्वपूर्ण कदम का प्रतिनिधित्व करती है।

इस आधार का लाभ उठाते हुए, परत निर्माण-स्थितियों को इस प्रकार स्थापित किया गया कि अर्धचालक 2H-$MoTe_2$ तथा धात्विक 1T′-$MoTe_2$ अवस्था को चयनात्मक रूप से स्थिर किया जा सके। MBE द्वारा निर्माण के दौरान मोलिब्डेनम (Mo) और टेल्यूरियम (Te) के प्रभावी सांद्रण अनुपात को व्यवस्थित ढंग से नियंत्रित करके, साहित्य में उपलब्ध अवस्था-स्थिरता संबंधी असंगतियों को स्पष्ट

किया गया। दोनों अवस्थाएँ (2H और 1T') तथा उनका सह-अस्तित्व, सेंटीमीटर स्तर पर नियंत्रित रूप से प्राप्त किया गया। यह निष्कर्ष दर्शाता है कि $MoTe_2$ में अवस्था-अभियांत्रिकी को किसी भी निर्माण पैरामीटर, जैसे तापमान या फ्लक्स से स्वतंत्र रूप से प्राप्त किया जा सकता है, जो 2D–2D ऊर्ध्वाधर हेटरोस्ट्रक्चर तथा सुपरलेट्टिस के निर्बाध एकीकरण हेतु महत्त्वपूर्ण है।

सटीक अवस्था-नियंत्रण प्राप्त होने के पश्चात् शोध कार्य वैन डेर वाल्स हेटरोस्ट्रक्चर (विषमसंरचना) निर्माण की ओर अग्रसर हुआ, जहाँ $MoTe_2$ को अन्य परतदार चाल्कोजेनाइड्स (जैसे $MoSe_2$ और GaSe) के साथ संयोजित किया गया। सर्वप्रथम, $MoSe_2/MoTe_2$ हेटरोस्ट्रक्चरों का विस्तारक्षम परत-दर-परत निर्माण प्रदर्शित किया गया, जिसका उद्देश्य इंटरफेस (अंतरफलक) पर इलेक्ट्रॉनिक अंतःक्रिया प्रभावों की जांच करना था। XPS तथा केल्विन प्रोब फोर्स माइक्रोस्कोपी का उपयोग करके हेटरोस्ट्रक्चर बैंड-संरेखण में असामान्य इंटरफेस चार्ज-ट्रांसफ़र (आवेश अंतरण) प्रभाव देखे गए। कोण-निर्भर XPS की परिवर्तनीय जांच-गहराई का उपयोग इस असामान्यता को समझने हेतु किया गया, जिसने दर्शाया कि Se और Te के पारस्परिक प्रभाव इंटरफेस के पास आंतरिक रासायनिक बंधन को परिवर्तित करते हैं। टेल्युरियम रिक्तियाँ $MoTe_2$ के फर्मी-स्तर का स्थिरीकरण करती हैं, जबकि $MoSe_2$ में संशोधित बंधन उसके वैलेंस-बैंड अधिकतम को ऊपर उठाते हैं। समग्र रूप से प्रयोगात्मक रूप से देखा गया कि प्राप्त हेटरोस्ट्रक्चर बैंड-संरेखण होल के लिए बाधा को घटाता है, जो द्विदिश वाहक-परिवहन हेतु लाभकारी हो सकता है।

इन होल-प्रेरित वाहक-डोपिंग अंतर्दृष्टियों ने आगे 2H-$MoTe_2$ में बाहरी मिश्रक के बिना अंतर्निहित विद्युतीय प्रकृति-नियंत्रण की दिशा में प्रेरित किया। चाल्कोजेन-धातु फ्लक्स को सटीक रूप से नियंत्रित करके Te-रिक्तियों द्वारा n-प्रकार चरित्र तथा Te-समृद्ध संरचना द्वारा p-प्रकार चरित्र प्राप्त किया गया। इसके अतिरिक्त, UHV एनीलिंग को $MoTe_2$ में p-से-n प्रकार संक्रमण को प्रेरित करने की रणनीति के रूप में प्रदर्शित किया गया। वैलेंस-बैंड स्पेक्ट्रा में फर्मी-स्तर का स्थानांतरण इस स्टोइकियोमेट्री-प्रेरित डोपिंग की पुष्टि करता है, जिससे विश्वसनीय, वेफर-स्तरीय द्विध्रुवीय नियंत्रण संभव होती है।

अंततः, ऑप्टोइलेक्ट्रॉनिक उपकरण प्रदर्शनों के माध्यम से 2D–2D विषम संरचनाओं की क्षमता का पता लगाया गया है। MBE-विकसित, कुछ-परतों वाले $GaSe/MoTe_2$ हेटरोस्ट्रक्चर ने अपेक्षाकृत उच्च कंडक्शन-बैंड ऑफ़सेट के साथ टाइप-II बैंड-संरेखण प्रदर्शित किया। हेटरोस्ट्रक्चर-आधारित उपकरण ने कम डार्क करंट (अप्रकाश प्रवाह) और असममित I–V(धारा-वोल्टेज) व्यवहार दिखाया। इस उपकरण ने उप-मिलीसेकंड पैमाने पर तीव्र प्रतिक्रिया समय के साथ पराबैंगनी (UV) से समीप-

अवरक्त (NIR) तरंग दैर्ध्य में एक स्थिर और पुनरुत्पादक फोटोरेस्पॉन्स हासिल किया है। इसके अलावा, डिवाइस की उच्च आवृत्ति ऑप्टिकल प्रतिक्रिया का अध्ययन किया गया, जिसने 3 kHz तक स्विचिंग तथा ~2 kHz (किलोहर्ट्ज़) की ऑप्टिकल प्रतिक्रिया-बैंडविड्थ प्रदर्शित की है, जो उच्च-गति वाले ऑप्टोइलेक्ट्रॉनिक अनुप्रयोगों के लिए इसकी क्षमता को रेखांकित करता है।

समग्र रूप से, यह कार्य $MoTe_2$-आधारित उपकरण-अभियांत्रिकी हेतु एक व्यापक मंच स्थापित करता है — स्केलेबल (विस्तृत) निर्माण और अवस्था-नियंत्रण से लेकर, हेटरोस्ट्रक्चरों में इंटरफेस प्रभावों, द्विध्रुवीय नियंत्रण तथा कार्यात्मक हेटरोस्ट्रक्चर उपकरणों तक — जो व्यावहारिक अर्धचालक प्रौद्योगिकियों में 2D पदार्थों के एकीकरण को महत्त्वपूर्ण रूप से अग्रसर करता है।

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List of Abbreviations

2D	Two-dimensional
5N	99.999 %
6N	99.9999%
AC	Armchair
AD-XPS	Angle-dependent X-ray photoelectron spectroscopy
AFM	Atomic force microscopy
ALD	Atomic layer deposition
ARPES	Angle-resolved photoelectron spectroscopy
BEOL	Back-end-of-line
BEP	Beam equivalent pressure
CBO	Conduction band offset
CPD	Contact potential difference
CVD	Chemical vapor deposition
DFT	Density Functional Theory
DI	Deionised
DOS	Density of states
EAL	Effective attenuation length
ECR	Effective concentration ratio
FET	Field effect transistor
FWHM	Full-width half-maxima
Gr. Temp.	Growth temperature
HOPG	Highly oriented pyrolytic graphite
ILCT	Inter-layer charge transfer
IMFP	Inelastic mean free path
IPA	Isopropyl alcohol
KPFM	Kelvin probe force microscopy
MBE	Molecular beam epitaxy
MGB	Mirror grain boundary
NIR	Near infrared
PBN	Pyrolytic boron nitride

PLD	Pulsed laser deposition
RGA	Residual gas analyzer
rGO	Reduced graphene oxide
RHEED	Reflection high-energy electron diffraction
RMS	Root mean square
RSF	Relative sensitivity factor
SE	Spectroscopic ellipsometry
SOC	Spin-orbit coupling
STM	Scanning tunnelling microscopy
TMDC	Transition metal dichalcogenide
UHV	Ultra-high vacuum
UV	Ultraviolet
VB	Valence band
VBM	Valence band maxima
VBO	Valence band offset
vdW	van der Waals
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZZ	Zigzag