GROWTH, STRUCTURAL, OPTOELECTRONIC, AND PHOTOELECTROCHEMICAL PROPERTIES OF 2D TRANSITION METAL CHALCOGENIDE-BASED SEMICONDUCTORS AND THEIR HETEROSTRUCTURES

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by

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Dedication

My dear parents and my husband are honoured with my dissertation. They instilled in me the values of tenacity and dedication, and their unwavering love and prayers have kept me going all my life.

CERTIFICATE

This is to certify that the thesis entitled, ***"Growth, structural, optoelectronic, and photoelectrochemical properties of 2D transition metal chalcogenide-based semiconductors and their heterostructures"*** being submitted by ***Ms. Narinder Kaur*** to the Indian Institute of Technology Delhi, New Delhi of significance for the award of ***Doctor of Philosophy*** is a record of the authentic and original research work that she conducted under our supervision. She worked under our supervision and guidance to complete the requirements for submitting this thesis, which in our opinion has reached the requisite standard. The results presented in this thesis have not been submitted, in part or whole, to any other university or institute for the award of any degree/diploma.

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ABSTRACT

The understanding and application of photodetectors and photoelectrochemical water splitting promote the growth and evolution of society. Despite being a century old, standard silicon-based photovoltaic detection technology has reached a limit in its operational wavelength, responsivity, and speed. The manufacturing of silicon-based semiconductors is almost at the limit of Moore's Law. There is a critical need for commercially viable, environmentally friendly, sustainable, and renewable energy sources with photoresponse over a wider UV-Visible wavelength range because of the world's alarmingly rising energy demands and the fast depletion of traditional fossil fuels. Broadband photodetectors are essential for electronic devices, photonic communication, environmental sensing, and other applications. Most 2D TMCs offer various eras for performance across the visible spectrum of wavelength regions. Materials with broad bandgaps perform well in the Ultraviolet region. Although this offers improved charge separation, extended absorbance in the visible range and type-II band alignment heterojunction is an appealing and feasible method to improve their efficiency. To improve the UV-Visible wavelength absorption of 2D materials and fabrication of their heterojunctions with sustained intermediate band gap materials and explore the structural, optical, electronic, morphological, and PEC characteristics of type-II band-aligned heterojunction, a significant portion of this dissertation is concentrated on this method.

The present study showed the photoresponse over the visible range by synthesizing different β-In_2S_3 geometries, including triangles, nanoflakes, and hexagons, on selected substrates, including SiO_2, F-Mica, ZnO, and TiO_2, in a single-zone micro reactor CVD system, followed by RF magnetron sputtering at temperatures ranging from 550-850 ^oC and growth time 5-15 minutes. In Raman spectroscopy investigations, the layer thickness affected the A_g, B_g, and E_g Raman mode intensities. The study concluded that the tetragonal phase of β-In_2S_3 deposited on all the substrates with optimized synthesized conditions that affect the growth in terms of morphology and phase composition. Tetragonal β-In_2S_3 on a SiO_2 and F-Mica substrate displays ohmic current-voltage and temporal characteristics, which indicate a fast photoresponse with a response time of 2 ms. The growth of In_2S_3 onto the ZnO layer enhances the

photoelectrochemical properties of ZnO by enhancing In_2S_3's absorption, as indicated by optical band gap measurements. Measurements of transient photocurrent density at wavelengths of 350 nm and 514 nm, the enhanced current density in the heterojunction was primarily brought about by increased absorption at lower wavelengths and charge-carrier separation at the interface at large wavelength values. Enhanced IPCE efficiency (43%) and excellent electrolyte stability in ZnO/In_2S_3 heterojunction demonstrate the importance of using a 2D layer with tunable properties for PEC applications. However, the same heterojunction was also studied for photodetection over the UV-Visible wavelength region. Compared to ZnO, the study's outcomes show a higher photocurrent density of 0.3 $mAcm^{-2}$ in the UV region and a photoresponse of 0.32×10^{-3} $mAcm^{-2}$. In contrast to In_2S_3 and ZnO layers, establishing type-II band alignment at the interface leads to efficient separation of photoinduced charge carriers, enhancing photodetector response parameters like responsivity, specific detectivity, and external quantum efficiency. The present method of synthesizing heterojunctions with well-known oxide materials and 2D materials with tunable semiconducting properties is an essential strategy.

Further, to achieve the photoresponse over a wider UV-Visible region, a thin layer of intermediate bandgap material WO_3 n-type semiconductor has been introduced in the In_2S_3-ZnO heterojunction, and In_2S_3-WO_3-ZnO multilayers system was formed using a chemical vapor deposition method, followed by an RF sputtering technique. The 2D-1D In_2S_3-WO_3 heterojunction was also studied to enhance the photoelectrochemical water splitting with a photocurrent value of 5.7 $mAcm^{-2}$ at 0.6 V.

सार

फोटोडेटेक्टर्स और फोटोइलेक्ट्रॉनिक वाटर स्प्लिटिंग की समझ और अनुप्रयोग समाज के विकास को बढ़ावा देते हैं। एक सदी पुरानी होने के बावजूद, मानक सिलिकॉन-आधारित फोटोवोल्टिक पहचान तकनीक अपने परिचालन तरंग दैर्ध्य, प्रतिक्रिया और गति में एक सीमा तक पहुंच गई है। सिलिकॉन आधारित अर्धचालकों का निर्माण लगभग मूर के नियम की सीमा पर है। दुनिया की खतरनाक रूप से बढ़ती ऊर्जा मांगों और पारंपरिक जीवाश्म ईंधन की तेजी से कमी के कारण एक व्यापक यूवी-दृश्य तरंगदैर्ध्य रेंज पर फोटोप्रतिक्रिया के साथ व्यावसायिक रूप से व्यवहार्य, पर्यावरण के अनुकूल, टिकाऊ और नवीकरणीय ऊर्जा स्रोतों की एक महत्वपूर्ण आवश्यकता है। इलेक्ट्रॉनिक उपकरणों, फोटोनिक संचार, पर्यावरण संवेदन और अन्य अनुप्रयोगों के लिए ब्रॉडबैंड फोटोडिटेक्टर आवश्यक हैं। अधिकांश 2डी टीएमसी तरंग दैर्ध्य क्षेत्रों के दृश्यमान स्पेक्ट्रम में प्रदर्शन के लिए विभिन्न युगों की पेशकश करते हैं। व्यापक बैंडगैप वाली सामग्री पराबैंगनी क्षेत्र में अच्छा प्रदर्शन करती है। हालांकि यह बेहतर चार्ज पृथक्करण प्रदान करता है, दृश्य सीमा में विस्तारित अवशोषण और टाइप- II बैंड संरेखण विषमता उनकी दक्षता में सुधार करने के लिए एक आकर्षक और व्यवहार्य तरीका है। 2डी सामग्रियों के यूवी-विजिबल वेवलेंथ अवशोषण में सुधार करने और निरंतर मध्यवर्ती बैंड अंतराल सामग्री के साथ उनके हेटेरोजंक्शन के निर्माण और टाइप- II बैंड-संरेखित हेटेरोजंक्शन की संरचनात्मक, ऑप्टिकल, इलेक्ट्रॉनिक, रूपात्मक और पीईसी विशेषताओं का पता लगाने के लिए, इसका एक महत्वपूर्ण हिस्सा शोध प्रबंध इस पद्धति पर केंद्रित है। वर्तमान अध्ययन ने एकल-ज़ोन माइक्रो रिएक्टर सीवीडी में SiO_2, F-Mica, ZnO, और TiO_2 सहित चयनित सबस्ट्रेट्स पर त्रिकोण, नैनोफ्लेक्स और हेक्सागोन्स सहित विभिन्न β-In_2S_3 ज्यामिति को संश्लेषित करके दृश्य सीमा पर फोटोप्रतिक्रिया दिखाई। सिस्टम, इसके बाद 550-850 ^oC के तापमान पर RF मैग्नेट्रॉन स्पटरिंग और ग्रोथ टाइम 5-15 मिनट पर प्रचालन किया। रमन स्पेक्ट्रोस्कोपी जांच में, परत की मोटाई ने A_g, B_g और E_g रमन मोड की तीव्रता को प्रभावित किया। अध्ययन ने निष्कर्ष निकाला कि β-In_2S_3 का चतुष्कोणीय चरण अनुकूलित संश्लेषित स्थितियों के साथ सभी सबस्ट्रेट्स पर जमा होता है जो आकृति विज्ञान और चरण संरचना के संदर्भ में विकास को प्रभावित करता है। SiO_2 और F-मीका सब्सट्रेट पर टेट्रागोनल β-In_2S_3 ओमिक करंट-वोल्टेज और टेम्पोरल विशेषताओं को प्रदर्शित करता है, जो दो एमएस के प्रतिक्रिया समय के साथ एक तेज़ फोटोप्रतिक्रिया का संकेत देता है। ZnO परत पर In_2S_3 की वृद्धि, In_2S_3 के अवशोषण को बढ़ाकर ZnO के फोटोइलेक्ट्रॉनिक गुणों को बढ़ाती है, जैसा कि ऑप्टिकल बैंड गैप माप द्वारा इंगित किया गया है। 350 एनएम और 514 एनएम के तरंग दैर्ध्य पर क्षणिक फोटोकॉर्टिक घनत्व के मापन, विषमता में बढ़ाया वर्तमान घनत्व मुख्य रूप से कम तरंग दैर्ध्य पर बढ़े हुए अवशोषण और बड़े तरंग दैर्ध्य मूल्यों पर

इंटरफ़ेस पर चार्ज-वाहक पृथक्करण द्वारा लाया गया था। बढ़ी हुई IPCE दक्षता (43%) और ZnO/In_2S_3 हेटेरोजंक्शन में उत्कृष्ट इलेक्ट्रोलाइट स्थिरता PEC अनुप्रयोगों के लिए ट्यून करने योग्य गुणों के साथ 2D परत का उपयोग करने के महत्व को प्रदर्शित करती है। हालाँकि, यूवी-विज़िबल वेवलेंथ क्षेत्र पर फोटोडिटेक्शन के लिए समान विषमता का भी अध्ययन किया गया था। ZnO की तुलना में, अध्ययन के परिणाम यूवी क्षेत्र में 0.3 $mAcm^{-2}$ का उच्च प्रकाशिक घनत्व और 0.32×10^{-3} $mAcm^{-2}$ का एक फोटोप्रतिक्रिया दिखाते हैं। In_2S_3 और ZnO परतों के विपरीत, इंटरफ़ेस पर टाइप- II बैंड संरेखण स्थापित करने से फोटोप्रेरित आवेश वाहकों का कुशल पृथक्करण होता है, जिससे जवाबदेही, विशिष्ट पहचान और बाहरी क्वांटम दक्षता जैसे फोटोडेटेक्टर प्रतिक्रिया मापदंडों में वृद्धि होती है। ट्यून करने योग्य अर्धचालक गुणों के साथ प्रसिद्ध ऑक्साइड सामग्री और 2डी सामग्री के साथ हेटेरोजंक्शन को संश्लेषित करने की वर्तमान विधि एक आवश्यक रणनीति है। इसके अलावा, एक व्यापक यूवी-दृश्य क्षेत्र पर फोटोप्रतिक्रिया प्राप्त करने के लिए, इंटरमीडिएट बैंडगैप सामग्री WO_3

n-टाइप सेमीकंडक्टर की एक पतली परत को In_2S_3-ZnO हेटेरोजंक्शन में पेश किया गया है, और एक रासायनिक वाष्प का उपयोग करके In_2S_3-WO_3-ZnO मल्टीलेयर सिस्टम बनाया गया था। निक्षेपण विधि, उसके बाद आरएफ स्पटरिंग तकनीक। 2D-1D In_2S_3-WO_3 विषमता का भी 0.6 V पर 5.7 $mAcm^{-2}$ के फोटोकरंट मान के साथ फोटोइलेक्ट्रॉनिक जल विभाजन को बढ़ाने के लिए अध्ययन किया गया था।

TABLE OF CONTENTS

Contents

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

H_2	Hydrogen gas
O_2	Oxygen gas
Pt	Platinum
H^+	Hydrogen ion
hν	Energy of a photon
e^-	Photogenerated electron
h^+	Photogenerated electron
ΔG_o	Standard Gibb's free energy per mole
NA	Avogadro number
E_{th}	Threshold energy
η	Photoconversion efficiency
J_{ph}	Photocurrent density
I_{ph}	Photocurrent
V_{RHE}	Voltage measured w.r.t reversible hydrogen electrode
P_{in}	Incident light intensity
E_g	Optical band gap
e.g.	Example

etc.	Etcetera
i.e.	That is
w.r.t	With respect to
Ar^+	Argon ion
C	Capacitance
d	Interplanar spacing
θ	Incident angle of X-rays
λ	Wavelength
t	Thickness of film
α	Absorption coefficient
n	Refractive index
k	Extinction coefficient
ε1/ε2	Real/imaginary part of dielectric constant
V_{CPD}	Contact potential difference
Φ_{tip}	Work function of tip
Φ_{sample}	Work function of sample
Z	Atomic number
D	Diameter
E_{kin}	Kinetic energy
E_B	Binding energy

Φ Work function of the spectrophotometer

V_{oc}/V_{mea}/V_{app} Open circuit potential/potential measured/potential applied

R_{ct} Charge transfer resistance

R_s Solution resistance

V_{FB} Flat band potential

N_D Carrier concentration

A Exposed area of electrode

VO Oxygen vacancy

H_i Interstitial hydrogen

K_B Boltzmann constant

T Temperature

E_{CB} & E_{VB} Conduction & valence band edge positions

ΔE_{FB} Fermi level energy offset

E_F Fermi level energy

E_{vac} Vacuum energy level

ABBREVIATIONS

CB Conduction band

VB Valence band

PEC	Photoelectrochemical cell
Ag/AgCl	Silver/silver chloride reference electrode
NR	Nanorod
NT	Nanotube
NW	Nanowire
NP	Nanoparticle
STH	Solar to hydrogen
UV	Ultraviolet
JCPDS	Joint Committee on Powder Diffraction Pattern
ALD	Atomic layer deposition
PVD	Physical vapor deposition
DC	Direct current
RF	Radio frequency
mT	milli Torr
MFC	Mass flow controllers
PID	Proportional integral differential
ITO	Indium doped tin oxide
XRD	X-ray diffraction
CCD	Charge coupled device
2D	Two Dimensional

TMC	Transition metal chalcogenides
CVD	Chemical vapor deposition
AFM	Atomic force microscopy
I-V	Current-voltage
PL	Photoluminescence
KPFM	Kelvin probe force microscopy
Φtip	Tip work function
Φsample	Sample work function
EQE	External quantum efficiency