

**EFFECT OF GAMMA IRRADIATION ON THE
STRUCTURAL, MORPHOLOGICAL, AND
MEMRISTIVE PROPERTIES OF CVD GROWN WS₂
AND ReS₂**

Pallavi Aggarwal



DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

Pallavi Aggarwal

DEPARTMENT OF PHYSICS

Submitted

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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.

CERTIFICATE

This is to certify that the thesis entitled “**Effect of Gamma Irradiation on the Structural, Morphological, and Memristive Properties of CVD Grown WS₂ and ReS₂**” submitted by **Ms. Pallavi Aggarwal**, a Research Scholar in the *Department of Physics*, under *IIT Delhi-NYCU Taiwan Joint Doctoral Program, Indian Institute of Technology Delhi, New Delhi, India*, for the award of the joint degree of **Doctor of Philosophy**, is a record of original and bonafide research work carried out by her under our 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

Moore's Law necessitated miniaturization of devices down to the nano scale, it brought about challenges such as the short channel effect, constrained gate control over channel area, increased power consumption, and heat dissipation. Consequently, selection of a suitable channel material that could provide high level of gate controllability, lower power consumption, while maintaining ultrashort dimensions to sustain the continuation of Moore's Law became important. This led to the emergence of two-dimensional materials (2DMs) inside the semiconductor industry as an alternative to the existing bulk planar technology. Among these materials, the class of 2D transition metal dichalcogenides (TMDCs) came to the forefront. Moreover, while considering the importance of high-density device integration, industrial scale application and cost-effective scalable production, large area synthesis of 2DMs hold immense significance.

One typical example of semiconducting TMDCs is WS_2 . In this work monolayer WS_2 film was synthesized on sapphire substrate at centimeter scale ($1.5 \times 1 \text{ cm}^2$) using NaCl assisted atmospheric pressure chemical vapor deposition (APCVD) technique. The growth mechanism was explained with Volmer-Weber, Stranski-Krastanov and Frank-van der Merwe modes by incorporating the importance of NaCl as a growth promoter, and other parameters like quantity of sulfur, temperature, gas flow rate, and hold time. The optical microscope (OM) images along with the corresponding Raman and

photoluminescence (PL) spectra were employed to examine growth of WS₂ film at different set of synthesis parameters.

Atomic thickness and high surface to volume ratio of 2DMs makes them susceptible to surrounding environment. This makes the understanding of the effect of environmental conditions on physical and electronic properties of 2DMs important. For example, space environment contains different levels of radiation like gamma, proton, etc. This will have effect over the physical and electronic properties of the devices such as satellites or space aircrafts which constitutes 2DMs. Therefore, to ascertain the suitability of 2DMs for space-based applications, where device miniaturization, low power consumption, and reduced weight is highly required, study of the effect of different levels of radiation becomes crucial. Therefore, followed by the synthesis of WS₂, effect of gamma radiation over its surface morphology and surface charge redistribution was studied by comparing the film before and after irradiation (1, 50, 100, 200, and 400 kGy dosage). Surface morphology was monitored through OM and atomic force microscopy (AFM) images. Raman and PL spectra were used to study the irradiation effect on phonon modes and excitonic properties. Results indicated p-type doping and increased trion to exciton transitions. Increase in work function of the film from 4.50 eV for pristine to 4.82 eV for irradiated film (at 200 kGy) was calculated from Kelvin probe force microscopy (KPFM) which indicates shifting of the Fermi level towards the valence band maxima (VBM). Further, VB spectra (VBS) deduced from X-ray photoelectron spectroscopy (XPS) showed a red shift of 0.17 eV after irradiation and deduced p-type doping effect.

WS₂ is a group VI transition metal dichalcogenide which exhibits superior and novel optical and electronic properties only when thinned down to monolayer. However, synthesis of monolayer film is difficult to achieve as it requires very precise control over synthesis parameters, and monolayers also suffer many challenges like environmental degradation, surface damage after characterizations, etc. To circumvent these challenges, we chose ReS₂, which is a group VII TMDC known for its layer independent electronic and optical properties. 1×1 cm² large and few layered ReS₂ film was synthesized on SiO₂/Si substrate through APCVD. Vibrational modes and excitonic peaks observed from the Raman and PL spectra corroborated the formation of ReS₂ film with 1.26 eV bandgap. High resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) pattern inferred polycrystalline nature of the film, while cross-sectional field emission scanning electron microscopy (FESEM) indicated planar growth with ~10 nm thickness. Chemical composition of the film analysed through XPS indicated formation of ReS₂ film with Re:S atomic ratio of 1:1.75, indicating small amount of non-stoichiometric Re_xS_y.

Recent advent in technology requires devices which can mimic human brain and memristors are one of the most studied and suitable device structures in this regard. So, after the basic characterizations, memristors were fabricated over the as-grown ReS₂ film and tested for resistive switching (RS) device application in which the effect of different metal electrodes (Pt/Au and Ag/Au) and different channel width (200, 100, and 50 μm) was studied. Highest memory window equal to 10⁸ was obtained for Ag/Au electrode while Pt/Au showed memory of 10². Furthermore, comparison of devices with Ag/Au

electrode but with different channel widths (50, 100 and 200 μm) gave insightful results on the existence of multiple resistance states, device endurance and retention.

To appreciate the suitability of ReS_2 film for space-based applications, effect of gamma radiation (5, 15, 25, 50 kGy) over its structure, morphology, chemical composition, and memristive behaviour was studied. HRTEM images and SAED pattern inferred phase transition from polycrystalline to amorphous. Besides, XPS deduced an increase in the number of sulfur vacancies (S_V) and formation of Re-O bond with irradiation. Also, valence band offset by 0.34 eV towards lower binding energy indicated shifting of the Fermi level towards the VBM, indicating p-type doping effect. In addition, an increase of work function was determined using KPFM from 3.84 to 5.24 eV, supporting p-type doping effect in irradiated samples. All these characterizations concluded induction of defects in the form of S_V and degradation of film crystallinity along with p-type doping effect. Additionally, the effect of irradiation over memristive property of film was carried out. Decrease in the amplification ratio, $I_{\text{ON}}/I_{\text{OFF}}$, was observed with irradiation which indicate memristor degradation.

सार

मूर का कानून ने उपकरणों को नैनो स्केल तक सुक्ष्मीकरण करने की आवश्यकता पैदा की, जिससे छोटे चैनल प्रभाव, संकुचित गेट नियंत्रण पूरे चैनल पर, बड़ी ऊर्जा खपत और ऊष्मा विसर्पण जैसे चुनौतियों का सामना किया। इस परिणामस्वरूप, एक उपयुक्त चैनल सामग्री का चयन करना जरूरी बन गया जो गेट समायोजन के उच्च स्तर, निम्न विद्वेषण की ऊर्जा खपत को प्रदान कर सकती थी, साथ ही मूर का कानून के निरंतर अनुसरण को बनाए रखने के लिए अत्यल्प आयामों को बरकरार रखने की उत्तरदाता बन सकती थी। इसका परिणामस्वरूप, सेमीकंडक्टर उद्योग में अस्तित्व में आने वाले दो-आयामी (2D) सामग्रियों का उत्थान हुआ, जो मौजूदा थोक तल प्लेनर प्रौद्योगिकी के विकल्प के रूप में आया। इन सामग्रियों में, दो-आयामी संकर्ण धातुएं (TMDCs) का वर्ग प्रमुख बन गया। इसके अलावा, उच्च घनत्व युक्त उपकरण समकरण, औद्योगिक माप का उपयोग और लागत-कुशल विस्तारण महत्वपूर्ण होने का ध्यान रखते हुए, दो-आयामी सामग्रियों के विशाल क्षेत्र संश्लेषण का अत्यधिक महत्व है।

एक उदाहरण सेमीकंडक्टिंग TMDCs का एक वास्तविक उदाहरण WS_2 है। इस कार्य में, सेंटीमीटर स्केल ($1.5 \times 1 \text{ cm}^2$) की एक परत WS_2 फिल्म NaCl सहायित APCVD तकनीक का उपयोग करके संश्लेषित की गई थी। NaCl को एक वृद्धि प्रमोटर के रूप में शामिल करने के महत्व को शामिल करते हुए, वोल्मर-वेबर, स्ट्रांस्की-क्रास्टानोव और फ्रैंक-वैन डेर मर्वे मोड्स के साथ विकास विधि की व्याख्या की गई। ऑप्टिकल माइक्रोस्कोप (OM) छवियों के साथ संबंधित रामन और फोटोल्यूमिनेसेंस (PL) स्पेक्ट्रा का उपयोग विभिन्न संश्लेषण पैमानों पर WS_2 फिल्म के विकास की जाँच करने के लिए किया गया।

2 आयामी सामग्रियों की परमाणु मोटाई और उच्च पृष्ठ से घनात्व अनुपात उन्हें आस-पासी वातावरण के प्रति संवेदनशील बनाता है। इससे 2 आयामी सामग्रियों की भौतिक और इलेक्ट्रॉनिक गुणों पर पर्यावरणीय स्थितियों के प्रभाव को समझना महत्वपूर्ण हो जाता है। उदाहरण के लिए,

अंतरिक्ष वातावरण में गैमा, प्रोटॉन आदि जैसे विभिन्न स्तरों की विकिरण होती है। यह 2 आयामी सामग्रियों से बने उपकरणों जैसे उपग्रह या अंतरिक्ष विमान की भौतिक और इलेक्ट्रॉनिक गुणों पर प्रभाव डालेगी। इसलिए, अंतरिक्ष आधारित अनुप्रयोगों के लिए 2 आयामी सामग्रियों की उपयुक्तता की पुष्टि करने के लिए, जहाँ उपकरण सुक्ष्मीकरण, कम ऊर्जा खपत और कम वजन की आवश्यकता है, विभिन्न स्तरों की विकिरण के प्रभाव का अध्ययन अत्यंत महत्वपूर्ण है।

इसके बाद, WS₂ की संश्लेषण के बाद, उसकी सतह मोर्फोलॉजी और सतह विद्युत आर्द्रता पर गैमा विकिरण के प्रभाव का अध्ययन किया गया था, जिसमें तिररनुक्ति की फिल्म को इरेडेशन से पहले और बाद में तुलना करके (1, 50, 100, 200, और 400 kGy मात्रा)। सतह मोर्फोलॉजी को OM और AFM छवियों के माध्यम से मॉनिटर किया गया। रामन और PL स्पेक्ट्रा का उपयोग फोनन मोड और उत्तेजक गुणों पर प्रभाव का अध्ययन करने के लिए किया गया। परिणाम ने p-प्रकार के डोपिंग और बड़ी त्रियोन से उत्तेजन लाने के परिवर्तनों को सूचित किया। फिल्म के काम-सम्मिश्रण की वृद्धि (पूर्वतः 4.50 eV से इरेडेटेड फिल्म के लिए 200 kGy पर 4.82 eV) ने KPFM के इशारों की ओर फर्मी स्तर का हलका विस्तार कर दिखाया। इसके अलावा, एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी (XPS) से निकाले गए वैलेंस बैंड स्पेक्ट्रा ने इरेडेशन के बाद 0.17 eV के रेड शिफ्ट और निकाले गए p-प्रकार के डोपिंग प्रभाव को दिखाया।

WS₂ एक समूह VI संकरण धातु द्विकालियां है जो केवल मोनोपरत में पतला होने पर ही विशेष और नए प्रकार के आभासी और इलेक्ट्रॉनिक गुण प्रदर्शित करती है। हालांकि, मोनोपरत फिल्म की संश्लेषण अत्यंत यथार्थ नियंत्रण की आवश्यकता है, और मोनोपरत भी अनेक चुनौतियों का सामना करती हैं जैसे पर्यावरणीय पदार्थनशीलता, विश्लेषण के बाद सतह क्षति आदि। इन चुनौतियों को दूर करने के लिए, हमने ReS₂ का चयन किया, जो इसके परत-स्वतंत्र इलेक्ट्रॉनिक और आभासी गुणों के लिए जाना जाता है। 1×1 cm² और कुछ स्तरित ReS₂ फिल्म का SiO₂/Si उपकरण पर APCVD द्वारा संश्लेषित किया गया था। रामन और PL

स्पेक्ट्रा से अवबोधित वाइब्रेशनल मोड और उत्तेजक चोटियों ने ReS_2 फिल्म के उत्थान की पुष्टि की। HRTEM छवियों और SAED पैटर्न से फिल्म की बहुक्रिस्टल प्रकृति की सूचना दी, जबकि क्रॉस-सेक्शनल फील्ड इमिशन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (FESEM) ने लघु गठन के साथ यथासम्भावित यत्राएँ दिखाईं। XPS द्वारा फिल्म के रासायनिक संरचन का विश्लेषण ने 1:1.75 के Re: S परमाणु अनुपात के साथ ReS_2 फिल्म के गठन की सूचना दी, जिससे निःस्थायिक रेक्सी सामग्री की छोटी मात्रा संकेत किया गया।

तकनीक में हाल की प्रगति मानव मस्तिष्क को अनुकरण करने के योग्य उपकरणों की आवश्यकता को उत्पन्न करती है और मेमिस्टर इस संदर्भ में अध्ययन किए गए और सबसे अध्ययन और उपयुक्त उपकरण संरचनाओं में से एक हैं। इसलिए, मौलिक विशेषणों के बाद, मेमिस्टर को उगाने के बाद अस-उगाया गया ReS_2 फिल्म पर और उन्हें प्रतिरोधी स्विचिंग (RS) उपकरण अनुप्रयोग के लिए परीक्षण किया गया, जिसमें विभिन्न धातु इलेक्ट्रोड्स (Pt/Au और Ag/Au) और विभिन्न चैनल चौड़ाई (200, 100 और 50 μm) के प्रभाव का अध्ययन किया गया। सर्वाधिक यादगार खिड़की 10^8 के बराबर मिला, जोकि Ag/Au इलेक्ट्रोड के लिए था, हालांकि Pt/Au ने 10^2 का यादगार दिखाया। इसके अलावा, विभिन्न चैनल चौड़ाई के साथ Ag/Au इलेक्ट्रोड के साथ उपकरणों की तुलना करने पर (50, 100 और 200 μm) विभिन्न प्रतिरोधी स्थितियों, उपकरण सहनशीलता और संभारण के मौद्रिक परिणामों पर अद्भुत नतीजे मिले।

ReS_2 फिल्म की अंतरिक्ष-आधारित अनुप्रयोगों के लिए उपयुक्तता की सराहना के लिए, गैमा विकिरण (5, 15, 25, 50 kGy) के प्रभाव का अध्ययन किया गया था। HRTEM छवियों और SAED पैटर्न से बहुद्वीय निर्वाचन की जानकारी थी कि फिल्म का रासायनिक संरचन से अपशिष्ट से असारमिक चरण में फास परिवर्तन हुआ। इसके अलावा, XPS ने गैमा विकिरण के बाद सल्फर रिक्त स्थानों (S_V) की संख्या और इरेडेशन के बाद p-प्रकार के डोपिंग प्रभाव की घोषणा की। साथ ही, उच्च स्थिति के वृद्धि का पता लगाया गया था, KPFM से 3.84 से

5.24 eV तक, जो इरेडेटेड नमूनों में p-प्रकार के डोपिंग प्रभाव की समर्थन कर रहा था। इन सभी विशेषणों ने डिफेक्ट्स के प्रस्तुति की समापन और पूर्ववर्ती प्रतिरोधी क्षमता की अध्ययन की निष्कर्ष निकाली थी।

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ABBREVIATIONS

vdW	van der Waals
2DMs	Two dimensional materials
3D	Three dimensional
γ	Gamma
TMDCs	Transition metal dichalcogenides
OM	Optical microscope
SPM	Scanning probe microscopy
AFM	Atomic force microscopy
KPFM	Kelvin probe force microscopy
XPS	X-ray photoelectron spectroscopy
B.E.	Binding energy
TEM	Transmission electron microscopy
HRTEM	High-resolution transmission electron microscopy
PL	Photoluminescence
FESEM	Field emission scanning electron microscope
EDX	Electron diffraction analysis
EPMA	Electron probe microanalyzer
APCVD	Atmospheric chemical vapor deposition
CB	Conduction band

VB	Valence band
VBM	Valence band maxima
CBM	Conduction band minima
SP	Surface potential
VCM	Valence change mechanism
VBS	Valence band spectra
S _v	Sulfur vacancy
ECM	Electrochemical metallization
RS	Resistive switching
HRS	High resistance state
LRS	Low resistance state
V _{SET}	SET voltage
V _{RESET}	RESET voltage
I _{cc}	Current compliance
CF	Conducting filament
GR	Generation-Recombination