

DEFECTS MEDIATED FERROMAGNETISM IN SEMICONDUCTING MATERIALS

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
NEW DELHI-110016, INDIA
OCTOBER 2022**

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Defects mediated ferromagnetism in semiconducting materials

by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

NEW DELHI-110016, INDIA

OCTOBER 2022

Dedicated to....

.... My Parents....

who are a constant source of inspiration and encouragement

Certificate

*This is to certify that the thesis entitled, “Defects mediated ferromagnetism in semiconducting materials”, being submitted by **Mr. Preetam Singh** to the Indian Institute of Technology Delhi, for the award of the degree of ‘**Doctor of Philosophy**’ is a record of bonafide research work carried out by him under our supervision and guidance. He has partially fulfilled the requirements for the submission of the thesis, which to the best of our knowledge has reached the requisite standard.*

The material contained in the thesis has not been submitted in part or in full to any other university or institute for the award of any degree or diploma.

Date: 18/10/2022

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Acknowledgements

This is a memorable moment in my life to finish the writing of doctoral thesis work. I take this opportunity to thank all individuals who have directly or indirectly made the present thesis possible. Foremost, I bow my head with great reverence to ALMIGHTY who is the cause behind everything.

Firstly, I am grateful to my supervisors, Prof. Pankaj Srivastava and Prof. Santanu Ghosh, for suggesting the thesis problem, supervising the work, and being a constant source of support and encouragement throughout the course of this study. I consider myself fortunate to work closely with both experts in the field of electronic/local structure investigations and magnetic interactions which is closely related to my research work. They have invaluable added to the quality of the present thesis with their respective specialized inputs and suggestions. Without their congenial demeanor and intellectual support, this thesis would not have been accomplished so fast.

My research committee members, Prof. Sujeet Chaudhary and Prof. Pintu Das from the Department of Physics and Prof S. Aravindan from Department of Mechanical Engineering IIT Delhi, need to be thanked for their encouragement and valuable suggestions during the semester progress presentations.

I am thankful to Prof. Rajendra Singh and Prof. Sunil Kumar, from the Department of Physics IIT Delhi, for providing MoS₂ films and PL facility, respectively. Dr. Arvind Singh is thanked for doing PL experiment.

I am indebted to Dr. Fouran Singh, for facilitating the Low Energy Ion Beam Implantation experiments at the Inter University Accelerator Center (IUAC) New Delhi. Dr. Sunil Ojha and G.R. Umapathy is specially thanked for kind and continuous support in discussions as well as in the conduct of the Rutherford Backscattering (RBS) experiment.

I would like to extend my heartfelt gratitude and sincere thanks to our collaborators Dr. Shengqiang Zhou and Mr. Kentsch Ulrich (Helmholtz- Zentrum Dresden Rossendorf, Germany) for providing the ion beam implantation facility. I specially thank to Dr. Shenqiang Zhou for providing superconducting quantum interference device (SQUID) facility for magnetic measurements and arranging my stay in Germany. I am thankful to Dr. Frans Munnik for carrying out the RBS experiments for some of the samples.

I am also thankful to our collaborator Dr. S. R. Barman, Mr. Sajal Barman, and Mr. Md. Balal, UGC-DAE Indore for providing X-ray photoelectron (XPS) facility. I am especially thankful to Dr. S. R. Barman for arranging my stay at UGC-DAE Indore during the course of experiments.

I owe gratitude to Dr. Renjith Ramachandran IGCAR, Kalpakkam for doing positron annihilation spectroscopy for some samples. Dr. Vikash Mishra, Department of Physics, IIT Bombay, is thanked for doing density functional theory (DFT) calculations. I am also thankful to Prof. S. Raghavan Centre for Nano Science and Engineering, Indian Institute of Science Bangalore, for doing film deposition of GaN.

I especially thank to my M.Sc. supervisor Prof. Pankaj R. Sagdeo, Department of Physics, IIT Indore, for being the architect of my research interest. I am also thankful to Prof. Rajesh Kumar, Department of Physics, IIT Indore for his help and support all the times whenever needed.

I would like to extend sincere gratitude to my seniors, Dr(s) Sreekanth Maddaka, Parswajit Kalita, and Harsh Gupta for their help and support. These people are specially thanked for providing me the necessary initiation into research, through introducing the preliminary deposition and characterization techniques.

During the course of my PhD, I have been fortunate to have received enormous support and encouragement from my lab mates including Mr. Gulshan Kumar, Mr. Wasim Chaudhary, Miss. Pariksha Malik, and Miss. Sharmistha Dey. Mr. Gulshan Kumar, Miss. Pariksha Malik, and Miss. Sharmistha Dey are especially thanked for being ready for any help during my Ph.D. I shall forever remain indebted to them for their kindness and affection.

Heartfelt gratitude to my close friends Dr. Aditya Singh, Mr. Surendra Kumar Verma, Mr. Gya Prasad, Mr. Rajneesh Joshi, and Mr. Md. Yasir Khan for their constant company and support at all times. These people will always be remembered for lively, humorous and joyous company at most of time during the course of PhD.

Mr. Sunil Jakhar, Mr. Piyush Kumar Gautam, Miss. Pooja Yadav, and Miss. Richa Mudgal are thanked for being the support in tough time during the Ph.D.

The financial support by various funding sources like University Grant Commission (UGC) India, Department of Science and Technology (DST) India, and Indian Institute of Technology Delhi India, is gratefully acknowledged to help by means of scholarship, performing various measurements and attending national and international conferences during the course of PhD.

Finally, I must say “you are the best” to my parents Tara Singh and Asha Devi for being supportive and everything at each stage of my life whatever it is. My parents have given me the inspiration and motivation for pursuing PhD. My other beloved family members also need to be thanked properly, specially, my sisters, brother, uncle, aunty, and cousins, who always used to remind me for a while that there are many more things in life to do other than ZnO, GaN, and MoS₂.

Preetam Singh

Abstract

Owing to their semiconducting, magnetic, and optical properties, dilute magnetic semiconductor (DMS) and transparent magnetic semiconductor (TMS) materials were the most promising candidates up to the last decade for spintronics and optoelectronic applications in spin transistors, spin valves, and spin light emitting diodes. But the most intriguing discovery in the search for DMSs, however, is the RT-FM in non-TM doped wide band gap semiconductors such as HfO_2 , ZnO , TiO_2 , GaN , and SnO_2 , etc. It is to be emphasized that in these wide band gap materials, neither their cations (3d and/or 4f) nor their anions are magnetic. Therefore, the ferromagnetism in pure wide band gap materials is named d^0 ferromagnetism. The observed d^0 FM in many oxides and nitrides shows that TM doping is not essential to induce FM ordering. It can be induced by some inherent or intentionally produced lattice defects. Among many oxides and nitrides, ZnO and GaN have attracted the attention of researchers due to their potential in opto-electronics. Because of the wide band gap of 3.3 eV for ZnO and 3.4 eV for GaN at room temperature, ZnO and GaN can have good optical transmittance (80% and above) in the visible range; good conductivity due to intrinsic defects such as vacancies, anti-site defects, and interstitials; and intrinsic room temperature ferromagnetism with a high Curie temperature. These wide-gap oxides can be exploited for the fabrication of room temperature ferromagnets, which will have a great impact on industrial applications in magneto-optical devices. The two materials, ZnO and GaN , exist in three dimensions (3D) with their intriguing properties.

Besides these 3D materials, nowadays, 2D semiconducting materials have become the centre of attraction among the research community. Among different 2D semiconductors, MoS_2 is one of the most studied semiconducting materials for different electronic applications. Inherent or

intentionally created defects can alter the physical properties of MoS₂ and hence the defect-driven ferromagnetism can also be induced.

These 3D and 2D semiconducting materials, which are intelligent replacements for ferromagnetic metals and semiconductor junctions, show promise in future optoelectronic, spintronic, and opto-spintronic devices. However, there are certain fundamental issues that need to be addressed thoroughly before applying these materials to any device. The major issues are: (i) the observed magnetic moment in pure GaN and ZnO is too low to be used for applications in spintronic based devices; (ii) ZnO makes multicenter bonds with H, due to which carrier concentration can be enhanced and hence carrier mediated exchange interaction is expected and needs to be explored; (iii) there is a need for tunable ferromagnetism (FM) in GaN and the role of the thickness of GaN films in tuning the FM behaviour needs to be explored; and (iv) with some theoretical reports and very few experimental studies on the FM of MoS₂, it is an open field of research and needs to be explored. The present thesis originates with the motivation to understand these fundamental questions through detailed experimental and theoretical studies. Therefore, the main objectives of the thesis are (i) to look into the role of multicenter bond on the FM properties of ZnO; (ii) a comparative study of FM of thick and thin ion implanted GaN films along with tuning of FM ordering by N ion implantation in GaN and their correlation with electronic structure; and (iii) ferromagnetism in low energy ion irradiated mixed phase of MoS₂-MoO_x films and its correlation with electronic structure. The properties are examined by X-ray diffraction (XRD), Raman spectroscopy, Photoluminescence (PL), Rutherford Back Scattering (RBS), X-ray photo electron spectroscopy (XPS), Atomic Force Microscopy (AFM), Secondary Electron Microscopy (SEM), and positron annihilation spectroscopy (PAS).

The thesis begins with the investigation of room temperature ferromagnetism (RT-FM) in H-ambience annealed ZnO films. The tailoring of defect states and enhancement in carrier concentration have been analyzed by PL, PAS, and resistivity measurements. The enhancement in FM ordering has been well co-related with its electronic structure and shows good agreement with density functional theory (DFT) results.

The second study of the present thesis aims to understand the role of the thickness of GaN on FM behaviour of GaN films and the tuning of FM in GaN films with ion implantation. The variation in defect concentration has been observed in thick GaN films after Xe ion irradiation, but the diamagnetic nature of all the films indicates that the threshold defect concentration essential to trigger the FM has not been achieved. On the other hand, RT-FM behaviour has been observed for all the thin films, and a systematic tuning of FM has been achieved with increasing N-ion fluence. The systematic tuning of FM behaviour is due to the incorporation of N-ions at interstitial sites, which shows a good agreement with theoretical DFT results.

The final study of this thesis investigated FM in Xe-ion irradiated mixed phase MoS₂-MoO_x films. A very large magnetic moment has been induced after ion irradiation. The reduction in the oxygen vacancy content for the sample with maximum magnetic moment rules out the possibility of ferromagnetism due to oxygen vacancy. Enhancement in the Mo content in 5+ and 6+ oxidation states due to the occupation of Sulphur vacancy sites by oxygen after ion irradiation, calculated from XPS core level of Mo 3d and S 2p and valence band spectra, has been observed. So, the enhancement in the ferromagnetism in MoS₂ is due to the increase of Mo in the 6+ oxidation state and exchange interaction between the different oxidation states of Mo via the p orbital of the anion and the formation of edged states.

सारांश

अपने अर्धचालक, चुंबकीय और प्रकाशिक गुणों के कारण तनु चुंबकीय अर्धचालक (DMS) और पारदर्शी चुंबकीय अर्धचालक (TMS) पदार्थ स्पिन ट्रांसिस्टर्स, स्पिन वाल्व और स्पिन प्रकाश उत्सर्जक डायोड में स्पिनट्रॉनिक्स और प्रकाशिक स्पिनट्रॉनिक्स के उपयोग के लिए पिछले दशक तक सबसे आशाजनक पदार्थ थे। लेकिन DMS की खोज में हालाँकि सबसे दिलचस्प खोज संक्रमण धातु विहीन वृहत ऊर्जा अंतराल वाले अर्धचालक जैसे कि HfO_2 , ZnO , TiO_2 , GaN , और SnO_2 , इत्यादि में कमरे के ताप पर लौह चुम्बकत्व है। इस बात पर जोर दिया जाना चाहिए कि इन वृहत ऊर्जा अंतराल वाले अर्धचालकों में न तो इनके धनायन (3d और/या 4f) और न ही इनके ऋणायन चुंबकीय है। इसलिए वृहत ऊर्जा अंतराल वाले शुद्ध अर्धचालकों में लौह चुंबकत्व को d^0 लौह चुंबकत्व नाम दिया गया है। कई ऑक्साइड्स और नाइट्राइड्स में देखे गए d^0 लौह चुंबकत्व से पता चलता है कि लौह चुंबकत्व को प्रेरित करने के लिए संक्रमण धातु का मिश्रण आवश्यक नहीं है। यह कुछ अन्तर्निहित अथवा जानबूझकर निर्मित जालक दोषों से प्रेरित हो सकता है। कई ऑक्साइड्स और नाइट्राइड्स में ZnO और GaN ने प्रकाशिक इलेक्ट्रॉनिक्स में अपनी क्षमता के कारण शोधकर्ताओं का ध्यान आकर्षित किया है। कमरे के ताप पर ZnO के लिए ३.३ eV और GaN के लिए ३.४ eV के वृहत ऊर्जा अंतराल के कारण ZnO और GaN में दृश्य परास में अच्छा प्रकाशिक अपवर्तन (८० % और ऊपर); अन्तर्निहित दोष जैसे कि रिक्ति, विरोधी स्थल दोष और इंटरस्टिसियल्स के कारण अच्छी चालकता; और कमरे के ताप पर उच्च क्यूरी ताप के साथ लौह चुंबकत्व। कमरे के ताप पर लौह चुम्बक के निर्माण के लिए इन वृहत ऊर्जा अंतराल वाले ऑक्साइड्स का उपयोग किया जा सकता है। जिसका चुंबकीय प्रकाशिक उपकरणों में औद्योगिक स्तर के उपयोग पर एक बड़ा प्रभाव होगा। ये दो पदार्थ ZnO और GaN अपने विशेष गुणों के साथ त्रिविमीय संरचना में पाए जाते हैं।

इन त्रिविमीय पदार्थों के साथ-साथ, आजकल द्विविमीय अर्धचालक पदार्थ अनुसन्धान समुदायों के बीच आकर्षण का केंद्र बन गए हैं। विभिन्न द्विविमीय अर्धचालकों में MoS_2 विभिन्न इलेक्ट्रॉनिक उपयोगों के लिए सबसे अधिक अध्ययन किये जाने वाले अर्धचालक पदार्थों में एक है। अन्तर्निहित अथवा जानबूझकर निर्मित दोष MoS_2 के भौतिक गुणों को बदल सकते हैं और इसलिए दोष संचालित लौह चुम्बकत्व को भी प्रेरित किया जा सकता है।

ये त्रिविमीय और द्विविमीय अर्धचालक सामग्री जो लौह चुंबकीय धातु और अर्धचालक संधियों का बुद्धिमत्तापूर्ण प्रतिस्थापन हैं, भविष्य के प्रकाशिक इलेक्ट्रॉनिक, स्पिनट्रॉनिक, और प्रकाशिक स्पिनट्रॉनिक उपकरणों में उम्मीद दिखाती हैं। हालाँकि, कुछ मूल-भूत मुद्दे हैं जिन्हें किसी भी उपकरण पर इन सामग्रियों को लागू करने

से पहले अच्छी तरह से सम्बोधित करने की आवश्यकता है। प्रमुख मुद्दे हैं; (i) शुद्ध GaN और ZnO में देखा गया चुंबकीय आघूर्ण स्पिनट्रॉनिक आधारित उपकरणों में अनुप्रयोगों में उपयोग के लिए बहुत कम है; (ii) ZnO, H के साथ बहुकेंद्रीय बंध बनाता है, जिसके कारण वाहक सांद्रता को बढ़ाया जा सकता है और इसलिए वाहक मध्यस्थता विनिमय अन्तः क्रिया की अपेक्षा की जाती है और इसको अन्वेषित किये जाने की आवश्यकता है; (iii) GaN में समंजित करने योग्य लौह चुंबकत्व की आवश्यकता है और GaN में लौह चुंबकीय व्यवहार को समंजित करने में GaN परतों की मोटाई की भूमिका को अन्वेषित किये जाने की आवश्यकता है; और (iv) MoS₂ के लौह चुंबकत्व और बहुत कम प्रयोगात्मक अध्ययनों के साथ, यह अनुसन्धान का एक खुला क्षेत्र है और इसे अन्वेषित किये जाने की आवश्यकता है। वर्तमान थीसिस विस्तृत प्रयोगात्मक और सैद्धांतिक अध्ययनों के माध्यम से इन मौलिक प्रश्नों को समझने की प्रेरणा से उत्पन्न हुई है। इसलिए, थीसिस के प्रमुख उद्देश्य हैं : (i) ZnO के लौह चुंबकीय गुणों पर बहुकेंद्रीय बंध की भूमिका को अन्वेषित करना; (ii) GaN में N आयन प्रत्यारोपण के द्वारा लौह चुंबकत्व के साथ-साथ N आयन प्रत्यारोपित मोटी और पतली GaN परत में लौह चुंबकत्व का तुलनात्मक अध्ययन तथा इनकी इलेक्ट्रॉनिक संरचना के साथ सह सम्बन्ध; और (iii) निम्न ऊर्जा आयन विकरित मिश्रित MoS₂-MoO_x परतों में लौह चुंबकत्व तथा इसका इलेक्ट्रॉनिक संरचना के साथ सह सम्बन्ध। इन गुणों की जाँच एक्स-रे विवर्तन (XRD), रमन स्पेक्ट्रोस्कोपी, फोटोलुमिनेसेन्स (PL), रदरफोर्ड पश्च विकीर्णन (RBS), एक्स-रे प्रकाशिक इलेक्ट्रॉन स्पेक्ट्रोस्कोपी (XPS), परमाणु बल माइक्रोस्कोपी (AFM), स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (SEM), और पॉजिट्रॉन विनाश स्पेक्ट्रोस्कोपी (PAS) द्वारा की गयी। प्राप्त किये गए विभिन्न उद्देश्यों पर बाद के खण्डों में संक्षेप में चर्चा की जाएगी।

थीसिस की शुरुआत H युक्त वातावरण में तप्त ZnO में कमरे के ताप पर लौह चुंबकत्व की खोज से होती है। दोष अवस्थाओं में परिवर्तन और वाहक सांद्रता में वृद्धि का विश्लेषण PL, PAS, और प्रतिरोधकता मापन द्वारा किया गया। लौह चुंबकत्व में वृद्धि इसके इलेक्ट्रॉनिक संरचना के साथ अच्छी तरह से सह सम्बंधित की गयी और यह घनत्व कार्यात्मक सिद्धन्तों (DFT) के साथ अच्छी सहमति दर्शाती है।

वर्तमान थीसिस के दूसरे अध्ययन का उद्देश्य GaN परतों के लौह चुंबकीय व्यवहार पर GaN की मोटाई की भूमिका और आयन प्रत्यारोपण से GaN परतों में लौह चुंबकत्व के समंजन को समझना है। Xe आयन विकिरण के बाद मोटी GaN परतों में दोष सांद्रता में परिवर्तन देखा गया है, लेकिन सभी फिल्मों की प्रतिचुंबकीय प्रकृति दर्शाती है कि लौह चुंबकत्व को सक्रिय करने के लिए आवश्यक देहली दोष सांद्रता प्राप्त नहीं की गयी है। दूसरी ओर सभी पतली फिल्मों के लिए कमरे के ताप पर लौह चुंबकीय व्यवहार देखा गया

और बढ़ते N आयन प्रवाह के साथ लौह चुंबकत्व का एक व्यवस्थित समंजन प्राप्त कर लिया गया है। लौह चुंबकीय व्यवहार का व्यवस्थित समंजन N आयनों के अंतरालीय स्थलों पर समावेशन के कारण है जो सैद्धांतिक DFT परिणामों के साथ अच्छी सहमति दर्शाता है।

वर्तमान थीसिस के अंतिम अध्ययन ने Xe आयन विकिरित $\text{MoS}_2\text{-MoO}_x$ फिर्मों की मिश्रित अवस्था में लौह चुंबकत्व को अन्वेषित किया है। आयन विकिरण के बाद एक बहुत बड़ा चुंबकीय आघूर्ण प्रेरित किया गया है। अधिकतम चुंबकीय आघूर्ण वाले नमूने के लिए ऑक्सीजन रिक्ति की उपस्थिति में कमी (O 1s की XPS कोर अवस्था), O रिक्ति के कारण लौह चुंबकत्व की सम्भावना को खारिज करती है। आयन विकिरण के बाद ऑक्सीजन द्वारा सल्फर रिक्ति स्थलों के अधिग्रहण के कारण मोलिब्डेनम (Mo) की $\nu+$ और $\delta+$ ऑक्सीकरण अवस्था में वृद्धि, जो कि Mo 3d और S 2p के XPS कोर अवस्था और संयोजक बंध स्पेक्ट्रा से प्राप्त हुआ, देखी गयी। इसलिए MoS_2 के लौह चुंबकत्व में वृद्धि Mo की $\delta+$ ऑक्सीकरण अवस्था में वृद्धि एवं एनायन के p कक्षक के द्वारा Mo की विभिन्न ऑक्सीकरण अवस्थाओं के बीच विनिमय अन्तः क्रिया और सीमावर्ती अवस्थाओं के निर्माण के कारण है।

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NOMENCLATURE

Ar	: Argon
B. E.	: Binding energy
C. B.	: Conduction band
CCD	: Charge coupled device
DMS	: Diluted magnetic semiconductor
DOS	: Density of states
FWHM	: Full width at half maximum
FM	: Ferromagnetism
GAXRD	: Glancing angle x-ray diffraction
GMR	: Giant magneto-resistance
IC	: Integrated circuit
LEIBF	: Low energy ion beam facility
PLD	: Pulsed laser deposition
SQUID	: Superconducting quantum interference device
TCO	: Transparent conducting oxide
TM	: Transition metal
TMS	: Transparent magnetic semiconductor
TMR	: Tunneling magneto-resistance
UHV	: Ultra high vacuum
DRS	: Diffuse Reflectance Spectroscopy
V. B.	: Valence band
XPS	: X-ray photoelectron spectroscopy
XRD	: X-ray diffraction
RBS	: Rutherford Backscattering Spectroscopy
PAS	: Positron Annihilation Spectroscopy
PL	: Photoluminescence