# CORRELATION BETWEEN ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF PURE AND TRANSITION METAL DOPED ZINC OXIDE

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# Correlation between electronic structure and magnetic properties of pure and transition metal doped zinc oxide

**by**

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*Dedicated to….*

*.... Parents….*

*who is a constant source of inspiration and encouragement*

# Certificate

*This is to certify that the thesis entitled,* ***"Correlation between electronic structure and magnetic properties of pure and transition metal doped zinc oxide"****, being submitted by* ***Mr. Pushp Sen Satyarthi*** *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 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.*


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Pushp Sen Satyarthi

## Abstract

Owing to semiconducting, magnetic and optical properties, diluted magnetic semiconductor (DMS) and transparent magnetic semiconductor (TMS) materials are the most promising candidates for the spintronics and optoelectronics applications in spin transistors, spin valves, and spin light emitting diodes. These diverse applications depend strongly on the presence of tuning of the ferromagnetic and transparent conducting properties. Transition metal (Fe, Co, Ni) doped and undoped zinc oxide (ZnO) has emerged as potential candidate from both perspectives. These oxide based materials, an intelligent replacement of ferromagnetic metals and semiconductor junctions, demand promising utility in future optoelectronic, spintronic and opto-spintronic devices. However, there are certain fundamental issues which need to be addressed thoroughly before applying these materials in any device. The major issues are: (i) whether the origin of room temperature ferromagnetism (RT-FM) in transition metal (TM) doped ZnO is intrinsic or extrinsic from phase segregation of TM, (ii) how stable the FM properties are at relative higher temperatures in TM doped ZnO based materials, (iii) is it possible to tune the ferromagnetic and transparent conducting properties at the cost of TM, (iv) search of RT-FM in undoped ZnO at normal ambient and (v) detailed correlation of ferromagnetic and transparent conducting properties with electronic and local structure investigation of TM doped and undoped ZnO. The present thesis originates with a motivation to understand these fundamental questions through detailed experimental and theoretical studies. Therefore, main objective of the present thesis is to achieve the tuning of ferromagnetic and transparent conducting properties in ZnO films and single crystals by incorporating the TMs (Ni and Co) and non magnetic inert xenon (Xe) ions. These properties are examined by utilizing the experimental and theoretical analysis of x-ray diffraction (XRD), Raman, x-ray photo electron spectroscopy (XPS), x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) techniques. The origin of these

properties in TM doped and undoped ZnO based DMS and TMS systems support different mechanisms which is discussed briefly in subsequent sections.

The thesis begins with the investigation of RT-FM in Ni ion implanted ZnO/sapphire films by probing the electronic and local structure using the combination of experimental and theoretical analysis of x-ray absorption near edge structure (XANES) and XMCD measurements. It is demonstrated that these measurements have a significant cutting edge over the conventional XRD and magnetometry for understanding the intrinsic origin of FM in $Zn_{1-x}Ni_xO$films.

The stability and reproducibility of RT-FM in TM doped ZnO based DMSs upon high temperature treatment in various environments remains one of the most challenging issues for spintronic applications. The second study of the present thesis aims to examine the robustness of FM in $Zn_{1-x}Ni_xO$ films upon high temperature (650 $^0$C) air annealing. The existence of robust RT-FM in air annealed $Zn_{1-x}Ni_xO$ films is explored from probing the electronic structure and defects through XANES investigations.

The third study of present thesis highlights the tunable spontaneous magnetization triggered in paramagnetic $Zn_{0.95}Co_{0.05}O$ films using inert xenon ion irradiation of different fluences. In order to pinpoint the origin of tunable spontaneous magnetization in $Zn_{0.95}Co_{0.05}O$ films, detailed electronic/local structure and element specific magnetization investigations are employed using the combination of XANES, extended x-ray absorption fine structure (EXAFS), and XMCD measurements.

The fourth study of this thesis unravels the detailed electrical conduction process at variable temperatures for understanding the role of carrier's kinetics in tuning the FM of transparent $Zn_{0.95}Co_{0.05}O$ films. The coexistence of ferromagnetic and transparent conducting properties in as deposited and irradiated $Zn_{0.95}Co_{0.05}O$ films makes these attractive from the perspective various applications in field of opto-spintronics and transparent conductors.

In the view of a great deal of controversies over the role of TM in the origin of FM of DMSs, the last study aims to report the evolution of magnetic properties in undoped ZnO single crystals and polycrystalline films by means of inert xenon ion irradiation with different fluences. These undoped ZnO films with RT-FM can be an alternative to conventional DMSs at the cost of TM.

In a nutshell, this thesis describes the tunability of RT-FM, optical and electrical properties of Ni and Co implanted/doped ZnO films and undoped ZnO films/single crystals. These properties are well correlated with crystal structure, electronic/local structure and defects. The intensive utilization of XPS, XANES, EXAFS and XMCD techniques establishes their critical importance in identifying the phase purity and intrinsic or extrinsic origins of FM in oxide based DMS and TMS systems.

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# NOMENCLATURE

| | |
|---|---|
| Ar | : Argon |
| BMP | : Bound magnetic polaron |
| B. E. | : Binding energy |
| C. B. | : Conduction band |
| CCD | : Charge coupled device |
| DMS | : Diluted magnetic semiconductor |
| DOS | : Density of states |
| EXAFS | : Extended x-ray absorption fine structure |
| FWHM | : Full width at half maximum |
| FAB | : Fast atom beam |
| FM | : Ferromagnetism |
| GAXRD | : Glancing angle x-ray diffraction |
| GMR | : Giant magneto-resistance |
| IC | : Integrated circuit |
| ITO | : Indium tin oxide |
| LEIBF | : Low energy ion beam facility |
| PLD | : Pulsed laser deposition |
| SQUID | : Superconducting quantum interference device |
| TCO | : Transparent conducting oxide |
| TEY | : Total electron yield |
| TFY | : Total fluorescence yield |
| TM | : Transition metal |
| TRIM | : Transport of ions in matter |
| TMS | : Transparent magnetic semiconductor |
| TMR | : Tunneling magneto-resistance |
| UHV | : Ultra high vacuum |
| UV-Vis-NIR | : Ultraviolet-visible-near infrared |
| V. B. | : Valence band |

| | |
|---|---|
| VSM | : Vibrating sample magnetometer |
| XAS | : X-ray absorption spectroscopy |
| XANES | : X-ray absorption near edge structure |
| XLD | : X-ray linear dichroism |
| XMCD | : X-ray magnetic circular dichroism |
| XPS | : X-ray photoelectron spectroscopy |
| XRD | : X-ray diffraction |
| ZFC/FC | : Zero field cooled and field cooled |