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Studies on diluted oxide magnetic semiconductors for spin electronic applications

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Studies on diluted oxide magnetic semiconductors for spin electronic applications

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DECLARATION

I, Germanas Peleckis, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting and Electronic Materials, in the Faculty of Engineering, University of Wollongong, is wholly original work unless otherwise referenced or acknowledged. This thesis has not been submitted for qualifications at any other academic institution.

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ABSTRACT

Conventional semiconductor electronics is based on the charge of the electron. For a long time the spin of the electron has been ignored in the field of conventional electronics. Spintronics, also called spin electronics, magnetoelectronics or magnetotronics, is a newly emerging field in solid state physics and information technology. One of the major challenges for semiconductor spintronic devices is to develop suitable novel spin-polarized magnetic semiconducting materials that will effectively allow spin-polarized carriers to be injected, transported, and manipulated. Therefore, searching for new materials has become crucial from the viewpoints of both fundamental research and practical applications.

Diluted magnetic semiconductors (DMS) are one of the most promising candidates for spintronic application. The research on the DMS materials which has been carried out worldwide in the past decade has been reviewed in this thesis. A DMS material can be realized when a conventional host semiconductor, such as GaAs, ZnO, etc., is doped with magnetic impurities, usually transition metal (TM) ions. For practical application, DMS material should favorably be ferromagnetic (FM) at room temperature. Early studies on DMS materials showed that FM can be induced in Mn doped III-V semiconductors. However, these materials are not suitable for practical applications as their Curie temperatures are quite low. On the other hand, some theoretical works predicted room temperature ferromagnetism in TM doped oxide semiconductors. This fact has boosted research in the field of DMS materials. The number of reports on observations of room temperature FM in Co, Mn, Ni, and Cr doped ZnO and TiO_2 semiconducting oxides is constantly growing.

The aim of this thesis was to study the doping effects of transition metal ions on the structure, transport, and diluted magnetic properties of various host oxide semiconductors. The oxide semiconductors investigated in this work are: ZnO, CuO, Ga_2O_3, and In_2O_3. A search for room temperature ferromagnetic semiconductors was the key point of this research. In addition, we have tried to understand and explain the

possible origins of the magnetic properties of the samples produced, because at the present time there is no firm theoretical model that could explain magnetism in DMS materials.

The majority of the samples studied in this research were prepared by a conventional solid state synthesis technique. We have carried out X-ray diffraction and electrical-magnetic transport measurements to determine the crystal structure, electrical and magnetic properties of our samples. In order to investigate the valence state of transition metal ions in the prepared materials, X-ray absorption near edge spectroscopy analysis was used.

The major results from this PhD study are:

(1) Polycrystalline Co-doped ZnO oxide samples were prepared with Co doping levels varying between 1 and 10%. All samples were found to be paramagnetic without any trace of ferromagnetism at room temperature and were insulators. Introduction of In ions into the system decreased the electrical resistivity of the samples. The spin state assessment revealed that strong spin-orbital coupling is present in In containing samples. Valence state assessment showed that in ZnO Co is present in the 2+ valence state.

(2) Mn doped CuO bulk samples showed a ferromagnetic transition at 80 K. All the samples prepared were insulating. In and Zn were used as charge donors. It was found that the In solubility limit in CuO lattice is very limited, less than 1%. The magnetic properties that were measured showed a large decrease in the magnetic susceptibility of (Mn,Zn) and (Mn,In) co-doped CuO samples. This could be attributed to the formation of large amounts of antiferromagnetic impurities and phase segregation in the samples. Valence state assessment showed that Mn is present in the 2+ valence state, eliminating the possibility of a double exchange interaction mechanism in this system.

(3) Various transition metal ions, such as Mn, Fe, Cr, and Ni, were doped into In_2O_3 and indium-tin oxide (ITO). In contrast to the reported data, our Fe doped In_2O_3 samples were paramagnetic. Paramagnetism was also observed in Cr doped In_2O_3. Mn doped

In_2O_3 samples were insulators with a Curie temperature of 46 K, while Mn doped ITO samples were typical semiconductors with the same Curie temperature. Furthermore, these samples showed a large positive MR effect below the ferromagnetic transition temperature, reaching 20% at a temperature of 5 K. Ni doped In_2O_3 and ITO samples were also found to be ferromagnetic at room temperature. Electrical transport properties, though, were different in nature. Ni doped In_2O_3 was found to be a typical semiconductor, while the electrical conductivity of Ni doped ITO was found to be characteristic of metallic materials.

(4) (Fe,Mn) co-doped In_2O_3 and ITO samples were ferromagnetic at room temperature, being both conducting and insulating depending on the host semiconductor. The change in lattice parameter *a* was very dependent on the ratio of Mn to Fe in the system, with decrease in lattice parameter *a* as Fe content increased. The maximum saturation magnetization was found for an $In_{1.80}Mn_{0.12}Fe_{0.08}O_3$ sample, which reached 0.35 μ_B/(Mn,Fe) ions at a temperature of 300 K. (Mn,Fe) co-doped In_2O_3 samples were insulating at room temperature, while (Fe,Cr) co-doped In_2O_3 samples were both conducting and ferromagnetic at room temperature. In addition, (Fe,Cr) co-doped samples showed a large positive MR effect, *i.e.* 5% at 5 K. On the contrary, despite being good conductors, (Mn,Fe) co-doped ITO samples did not exhibit similar MR features.

(5) (*RE*,Fe) co-doped In_2O_3 polycrystalline samples were semiconducting and showed giant positive magnetoresistance at 5 K. The obtained magnetoresistance in (Eu,Fe) co-doped In_2O_3 reached 80 % at 5 K. This value is the largest reported MR value for any diluted magnetic semiconductor. In addition (*RE*,Fe) co-doped samples showed clear ferromagnetic hysteresis behavior at 300 K. TEM studies of these samples revealed that particles are well formed and are about 100 nm in size.

Based on the results, among the transition metal doped oxide semiconductors studied, In_2O_3 and ITO are the most promising candidates for diluted semiconductor materials with possible practical applications in spintronic devices.

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List of Symbols and Abbreviations

A	Cross section area	Fig	Figure
Å	Angstrom	FM	Ferromagnetism
AC	Alternating Current	g	Gram
B, $\vec{B}$	Magnetic induction	g_e	Spectroscopic splitting factor
$B_J(y)$	Brillouin function	g_J	Landé spectroscopic factor
BMP	Bound magnetic polaron	GM	Granulated Metal
C	Curie constant; Celsius	GMR	Giant Magnetoresistance
cm	Centimetre	h	Hour
DC	Direct Current	$\vec{H}$, H	Magnetic field
DMS	Diluted Magnetic Semiconductor	HS	High Spin
DS	Degenerate Semiconductor	i	Initial state of carrier hopping
e	Electron	I	Current
e.g.	Exempli gratia, in Latin meaning "for example	*i.e.*	Id est, in Latin meaning "that is"
EDS	Energy Dispersive Spectroscopy	ICDD	International Centre for Diffraction Data
E_F	Fermi energy	IS	Intermediate Spin
E_g	Energy gap at room temperature	ITO	Indium Tin Oxide
emu	Electro-magnetic unit	j	Final state of carrier hopping
Eq	Equation	$\vec{J}$	The total angular momentum
et al.	Et al ii, in Latin meaning "and others"	K	Kelvin
eV	Electronvolt	k, k_B	Boltzmann constant
exp	Exponential	l	The orbital angular momentum quantum number
FC	Field Cooled	$\vec{l}_i$	The orbital angular momentum

L	Distance between voltage contacts	PC	Personal Computer
$\vec{L}$	The total orbital angular momentum	PPMS	Physical Property Measurement System
LED	Light Emitting Diode	R	Electrical resistance
LS	Low Spin	*RE*	Rare Earth
m	Mass	r_{i}	Ionic radius
M	Magnetization	r_{ij}, R	Distance between "i" and "j" in carrier hopping model
min	Minute	R_s	Anomalous Hall coefficient
m_l	The magnetic quantum number	RT	Room Temperature
mm	Millimetre	R_O	Ordinary Hall coefficient
MPMS	Magnetic Property Measurement System	$\vec{s}_i$	The spin angular momentum
MR	Magnetoresistance	S	Siemens
MRAM	Magnetic Random Access Memory	$\vec{S}$	The total spin angular momentum
m_S	The spin quantum number	sec	Second
n	The principal quantum number, charge carrier density	SEM	Scanning Electron Microscopy
N	The number of atoms	SRRC	Synchrotron Radiation Research Centre
N_A	Avogadro's number	T	Temperature
$N(E_F)$	Density of states at Fermi energy	T	Tesla
NNH	Nearest Neighbor Hopping	T_C	Curie temperature
Oe	Oersted	TCR	Temperature Coefficient of Resistivity
PC	Personal Computer	TEM	Transmission Electron Microscopy
PPMS	Physical Property Measurement System	TM	Transition Metal

T_N	Néel temperature	$\Delta\rho$	Difference of electrical resistivity
V	Volt	μ	Charge carrier mobility, micro
V	Voltage, Volume	$\vec{\mu}$	Magnetic moment
VRH	Variable Range Hopping	μ_B	Bohr magneton
W	Hopping energy	μ_{eff}	Effective magnetic moment
wt%	Weight percent	$\vec{\mu}_l$	Associated magnetic moment of an electron with an orbital angular momentum
XAFS	X-ray Absorption Fine Structure	μ_{lz}	Projection of magnetic moment along direction of applied magnetic field
XANES	X-ray absorption near band edge spectroscopy	$\vec{\mu}_s$	Associated magnetic moment of an electron with spin angular momentum
XAS	X-ray absorption spectroscopy	μ_0	Magnetic permeability
XPS	X-ray Photoemission Spectroscopy	2θ	Diffraction angle in x-ray diffraction
XRD	X-ray Diffraction	Θ	Curie-Weiss temperature
ZFC	Zero Field Cooled	ρ	Electrical resistivity
α	Wave function decay factor	ρ_H	Electrical resistivity under applied magnetic field
χ	Magnetic susceptibility	ρ_{xy}	Hall resistivity
χ^{-1}, $(1/\chi)$	Reciprocal magnetic susceptibility	ρ_0	Electrical resistivity in zero magnetic field
χ_0	Temperature independent magnetic susceptibility	σ	Electrical conductivity

Ω	Ohm
º	Degree
ºC	Degrees Celsius
$\hbar$	Plank constant