Studies on diluted oxide magnetic semiconductors for spin electronic applications

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Studies on diluted oxide magnetic semiconductors for spin electronic applications

A thesis submitted in fulfilment of the requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

GERMANAS PELECKIS, BSc, MSc

Institute for Superconducting and Electronic Materials and Faculty of Engineering

2006
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.

Germanas Peleckis
Wollongong
July 2006
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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, magneto-electronics 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 TiO₂ 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, Ga₂O₃, and In₂O₃. 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$_2$O$_3$ and indium-tin oxide (ITO). In contrast to the reported data, our Fe doped In$_2$O$_3$ samples were paramagnetic. Paramagnetism was also observed in Cr doped In$_2$O$_3$. Mn doped
In$_2$O$_3$ 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$_2$O$_3$ and ITO samples were also found to be ferromagnetic at room temperature. Electrical transport properties, though, were different in nature. Ni doped In$_2$O$_3$ 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$_2$O$_3$ 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 $\mu_B$/($\text{Mn,Fe}$) ions at a temperature of 300 K. (Mn,Fe) co-doped In$_2$O$_3$ samples were insulating at room temperature, while (Fe,Cr) co-doped In$_2$O$_3$ 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$_2$O$_3$ polycrystalline samples were semiconducting and showed giant positive magnetoresistance at 5 K. The obtained magnetoresistance in (Eu,Fe) co-doped In$_2$O$_3$ 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$_2$O$_3$ 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

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

$L$ Distance between voltage contacts
→ $L$ The total orbital angular momentum
LED Light Emitting Diode
LS Low Spin
$m$ Mass
$M$ Magnetization
$	ext{min}$ Minute
$m_i$ The magnetic quantum number
$mm$ Millimetre
MPMS Magnetic Property Measurement System
MR Magnetoresistance
MRAM Magnetic Random Access Memory
$m_s$ The spin quantum number
$n$ The principal quantum number, charge carrier density
$N$ The number of atoms
$N_A$ Avogadro’s number
$N(E_F)$ Density of states at Fermi energy
NNH Nearest Neighbor Hopping
Oe Oersted
PC Personal Computer
PPMS Physical Property Measurement System
$R$ Electrical resistance
$RE$ Rare Earth
$r_{ij}$ Distance between “$i$” and “$j$” in carrier hopping model
$R_s$ Anomalous Hall coefficient
$R_{o}$ Ordinary Hall coefficient
MPMS $\rightarrow s_i$ The spin angular momentum
MR $\rightarrow S$ The total spin angular momentum
$M_{R}$ Magnetoresistance
$S$ Siemens
$M_{RAM}$ Magnetic Random Access Memory
$m_{s}$ The spin quantum number
$n$ The principal quantum number, charge carrier density
$N$ The number of atoms
$N_A$ Avogadro’s number
$N(E_F)$ Density of states at Fermi energy
NNH Nearest Neighbor Hopping
Oe Oersted
PC Personal Computer
PPMS Physical Property Measurement System
$T$ Temperature
$T_C$ Curie temperature
$T_C$ Curie temperature
$T_{CR}$ Temperature Coefficient of Resistivity
$TEM$ Transmission Electron Microscopy
$TM$ Transition Metal
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$T_N$</td>
<td>Néel temperature</td>
</tr>
<tr>
<td>$\Delta \rho$</td>
<td>Difference of electrical resistivity</td>
</tr>
<tr>
<td>$V$</td>
<td>Volt</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Charge carrier mobility, micro</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage, Volume</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Magnetic moment</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Electrical resistivity</td>
</tr>
<tr>
<td>VRH</td>
<td>Variable Range Hopping</td>
</tr>
<tr>
<td>$\mu_B$</td>
<td>Bohr magneton</td>
</tr>
<tr>
<td>$W$</td>
<td>Hopping energy</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>Effective magnetic moment</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percent</td>
</tr>
<tr>
<td>$\mu_t$</td>
<td>Associated magnetic moment of an electron with an orbital angular momentum</td>
</tr>
<tr>
<td>XAFS</td>
<td>X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>$\mu_z$</td>
<td>Projection of magnetic moment along direction of applied magnetic field</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near band edge spectroscopy</td>
</tr>
<tr>
<td>$\mu_s$</td>
<td>Associated magnetic moment of an electron with spin angular momentum</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>Magnetic permeability</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoemission Spectroscopy</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>Curie-Weiss temperature</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Electrical resistivity</td>
</tr>
<tr>
<td>ZFC</td>
<td>Zero Field Cooled</td>
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<tr>
<td>$\rho_H$</td>
<td>Electrical resistivity under applied magnetic field</td>
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<tr>
<td>$\alpha$</td>
<td>Wave function decay factor</td>
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<tr>
<td>$\chi$</td>
<td>Magnetic susceptibility</td>
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<tr>
<td>$\rho_H$</td>
<td>Hall resistivity</td>
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<tr>
<td>$\chi_0$</td>
<td>Electrical resistivity in zero magnetic field</td>
</tr>
<tr>
<td>$\chi_0$</td>
<td>Temperature independent magnetic susceptibility</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Electrical conductivity</td>
</tr>
</tbody>
</table>
Ω
°
ºC
ℏ
Ohm
Degree
Degrees Celsius
Plank constant