International Journal of Emerging Research in Management &Technology
ISSN: 2278-9359 (Volume-4, Issue-7)

Research Article | **July 2015**

ZnO Based Diluted Magnetic Semiconductors for Spintronic Device Applications: A Review

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Abstract—

Spintronics i.e. spin transfer electronics is a new research field, which studies possible applications of both spin and charge of the electrons. ZnO based diluted Magnetic Semiconductor may lead to devices with new and enhanced functionality, such as polarized solid state optical components, Non-Volatile storage devices, sensitive biological and chemical sensors and Spin-based solid-state approaches for quantum computation, Spin Transistors. In this paper, we review the latest experimental results on transition metal doping of ZnO on the basis of magnetic characterization. It has been observed that researchers have different opinion regarding origin of ferromagnetism. Further, inconsistencies regarding the ferromagnetic ordering in transition metal doped ZnO indicate that these materials are very sensitive to the fabrication and processing conditions. High Curie temperature (T_C above room temperature) DMS is required for practical applications and it is still challenging.

Keywords— ZnO, Diluted Magnetic Semiconductor, Spintronic

I. INTRODUCTION

Spintronics i.e. spin transfer electronics is a new research field, which studies possible applications of both spin and charge of the electrons. According to Moore's law the number of transistors in a chip doubles every eighteen to twenty two months. At this rate, very soon, the size of a transistor will not exceed several atoms. Thus, our ability to make faster processors is limited by the transistor size. In order to overcome the shortcoming of conventional electronics the idea of spintronics was proposed. Spintronics utilizes both charge and spin of the electrons to process and store data. Spintronics based transistors have several major advantages over today's transistors, among them are their ability to integrate data process and storage in a single step and controlling of spin currents with an external magnetic field. In fact, the idea of using electron spin has already revolutionized data storage device technology as we use giant magneto-resistant (GMR) devices everyday such as hard-disks and RAM memories. One should keep in mind that these memory devices are based on static spin as opposed to data processing units which are based on spin currents.

Recently, ferromagnetic semiconductors have become a major focus in both academia and industry as these materials might form the base of spintronics. As conventional electronics, semiconductors are more appropriate than normal metals, since metal devices do not amplify current. Moreover, mixed devices (based on metal and semiconductors) have problems with spin injection due to the large scattering cause by the conductivity mismatch at the interface between the ferromagnetic metal and semiconductor. Magnetic semiconductors that act as spin-injectors might be the solution for the above problems.

Therefore, Diluted magnetic semiconductors (DMS) are promising candidates for spintronic applications. This class of materials has been discovered because of their property of exhibiting room temperature ferromagnetism or well above it, since they have the potential of being used in optoelectronic, magneto electronic or other devices using both spin and charge of the electrons. Two major criteria are considered to select the most promising materials for semiconductor spintronics. First, the ferromagnetism should be retained to practical temperatures namely room temperature. Second, it would be a major advantage if there were already an existing technology base for the material in other applications.

II. DILUTE MAGNETIC SEMICONDUCTOR MATERIALS

In order to satisfy the need for a magnetic semiconductor for spin injection where none exist naturally, extrinsic magnetic doping of semiconductors using transition metals has been used for decades. These materials, also referred to as dilute magnetic semiconductors (DMS), can be formed by uniformly doping a semiconductor with a small concentration of a metal throughout the lattice in order to attain an intrinsically ferromagnetic material, ideally with room temperature functionality. With an initial influx of interest in the realm of spintronics, novel materials such as GaAs doped with Mn **[1]**, ZnO doped with Ni **[2]** and Mn **[3]**, GaN doped with Mn **[4]**, and Mn doped InP **[5]** have been fabricated. However, in order for these materials to be of use in spintronic devices, room temperature ferromagnetism is a necessity. Theoretical predictions made by Dietl *et al.* **[6]** have indicated that both GaN as well as ZnO have the potential to be ferromagnetic at room temperature as shown in figure 1.

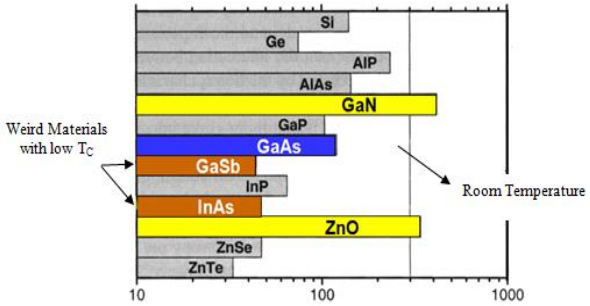

Fig.1: Theoretical predictions made by Dietl *et al.* [6]

III. MATERIAL CONSIDERATION FOR SPINTRONICS DEVICE APPLICATIONS

Nominally highly spin-polarized materials could provide both effective spin injection into nonmagnetic materials and large magneto-resistance effects which is important for nonvolatile applications. Examples include half-metallic oxides such as CrO_2, Fe_3O_4 etc. **[8]**

A high Curie temperature ($T_{C)}$ and almost complete spin polarization in bulk samples are alone not sufficient for successful applications. Spintronic devices typically rely on inhomogeneous doping, structures of reduced dimensionality, and/or structures containing different materials. Interfacial properties, as discussed in the previous sections, can significantly influence the magnitude of magneto-resistive effects and the efficiency of spin injection. Doping properties and the possibility of fabricating a wide range of structures allow spintronic applications beyond magneto-resistance effects, for example, spin transistors, spin lasers, and spin-based quantum computers. **[8]**

A. Spin field-effect Transistors

Datta and Das (1990) proposed what became the prototypical spintronic device scheme shown in figure 2; the Datta-Das spin field-effect transistor (SFET). The device is based on spin injection and spin detection by a ferromagnetic source and drain. The attractive feature of the Datta-Das SFET is that spin-dependent device operation is controlled not by external magnetic fields, but by gate bias, which controls the spin precession rate.

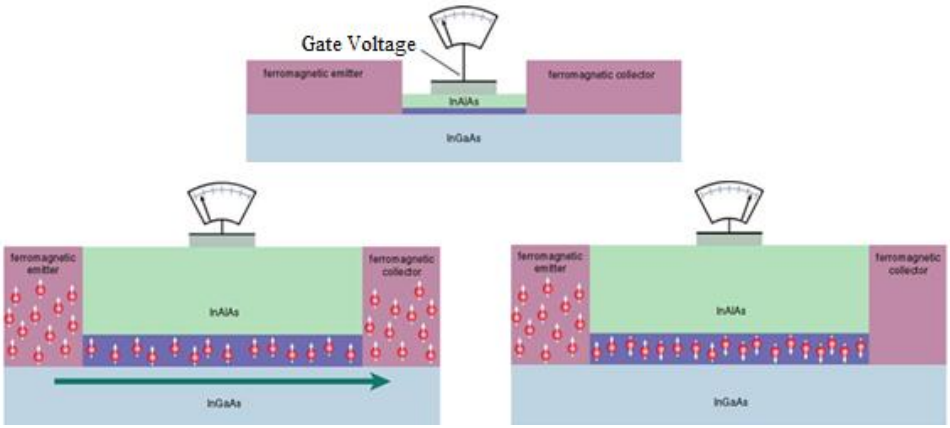

Fig.2: Datta-Das Spin field-effect Transistor

B. Quantum Computation

Spin-based solid-state approaches for quantum computation provide the potential for fixing isolated quantum degrees of freedom in space, by embedding quantum dots or ions within a solid matrix, and then addressing those degrees of freedom with small electrical contacts. Progress in understanding the coupling between spin degrees of freedom and electrical fields [9, 10–12], principally through the spin-orbit interaction but also through nano magnetic Fabrication [13], avoid some of the problems with producing highly localized a.c. magnetic fields. Extremely long room-temperature spin-coherence times, such as 350 μs for nitrogen vacancy centres in diamond [14], and short gate times [15], provide ratios of coherence times to gate times that exceed.

Through the coupling of the spin degree of freedom of an electron to optical fields there is a clear method of coupling photons into and out of a spin-based quantum computer [16], and those photons can have wavelengths compatible with current communications.

IV. ZNO BASED DILUTE MAGNETIC SEMICONDUCTOR

Because of the materialistic advantages of oxide-based systems; ZnO has become one of the most widely studied DMS based systems. ZnO belongs to the list of most promising candidates for spintronics application due to friendly nature and also due to its potential as a suitable optoelectronic with a wide band gap (-3.3ev) and high exciton binding energy of 60meV. Early reports of a ZnO:Co were given by Ramachandran *et al.* in 2004 **[7]**. They reported the formation of phase pure thin films grown by pulsed laser deposition which showed room temperature ferromagnetism. The critical formation of phase pure materials was supported by high resolution TEM (HRTEM) and X-ray diffraction measurements. By

illustrating the formation of a pure ferromagnetic semiconductor and providing a delineation of the mechanism behind its ferromagnetic behaviour, it has been made possible to further research and study DMS systems for spintronics application. Table 1, summarizes few recent researches and their findings in detail.

TABLE I LIST OF ZNO-BASED DMS RECENTLY REPORTED

S. No.	Compound	TM Content	Substrate	Year	Fabrication Technique	Growth Temperature	Results	Origin of Ferromagnetism	Reference No.
1	ZnO:(Fe, Co)	0.02 – 0.10	Bulk ZnO	2012	Homogeneous Precipitation	400 ^{0}C	RTFM	Secondary spinal Phase	17
2	ZnO: (Fe, Cu, Ni)	0.01 – 0.06	Bulk ZnO	2013	Co-precipitation	200 ^{0}C	RTFM	Electron exchange interaction	18
3	ZnO: Fe	0.01<=x<=0.05	Bulk ZnO	2012	Solution Combustion	400 +/- 20 ^{0}C	Ferromagnetic State for the 5% Fe doping	Exchange Interaction	19
4	ZnO: Ni	0.02 – 0.08	Bulk ZnO	2012	Sol-gel Auto combustion	800 ^{0}C	Ferromagnetic State for the 4% Ni doping	Exchange Interaction between Ni^{2+} ions	20
5	ZnO: Co	0.01 – 0.05	Bulk ZnO	2012	Co-precipitation	200 ^{0}C	RTFM	Additional phases at higher doping	21
6	ZnO: Ni	0 <=x<= 0.05	Bulk ZnO	2007	Ultrasonic Assisted Sol-gel	500 ^{0}C	Ferromagnetic only for x <= 0.02 else Paramagnetic	Long range Ni^{2+} - Ni^{2+} ferromagnetic coupling mediated by shallow donor electrons	22
7	ZnO: Mn	2 * 10^{19} cm^{-1}	Bulk ZnO	2012	Molecular Beam Epitaxy	800 ^{0}C	RTFM	Isolated ions with long range carrier mediated spin-spin coupling	23
8	ZnO: Cu	0.06 – 0.23	Bulk ZnO	2012	Co-precipitation	200 ^{0}C	RTFM	Intrinsic property	24
9	ZnO: Fe	0.011 – 0.20	AI2O3 (0001) Substrate	2009	Magnetron Co-sputtering	400 ^{0}C	RTFM	Electron double exchange mechanism	25
10	ZnO: Co	0.03	Bulk ZnO	2011	Ball Milling	500 ^{0}C	RTFM	Intrinsic defects and magnetic impurities	26
11	ZnO: Ni	3.9, 8.3 & 12.4 %	Bulk ZnO	2012	Solvo thermal through oxalate precursor	450 ^{0}C	Paramagnetic		27

V. CONCLUTION

It has been observed that ZnO doped with transition metals has been extensively investigated for Diluted Magnetic Semiconductor applications. Ferromagnetism with Curie temperature higher than room temperature has been observed in Fe-doped, Mn-doped, Cu-doped, Ni-doped and Co-doped ZnO nanoparticles. There are few reports which deny ferromagnetic behavior for above doping. Also, several codoped ZnO have been studied in order to further enhance the magnetic properties of materials. Doping of two different kinds of transition ions simultaneously in a host material produces magnetic property that can be different from the magnetic property with single transition metal ions. ZnO doped with Fe ions without any modification of the structure has been the most considerable interest. It is well established from many reports, that Co with ZnO has shown high Curie value than the other transition metal ion in the same ZnO system.

Despite the considerable amount of data a great deal of controversy remains, especially regarding the fundamental issue of whether the system actually exhibits room temperature ferromagnetic at all; and in the case where it does, whether the effect is intrinsic to the material or it originate due to formation of secondary phases, metallic clusters and defects such as oxygen or zinc vacancies. From the literature, it has been observed that researchers have different opinion regarding origin of ferromagnetism. Further, inconsistencies in the literature regarding the ferromagnetic ordering in transition metal doped ZnO indicate that these materials are very sensitive to the fabrication and processing conditions. High Curie temperature (T_C above room temperature) DMS is required for practical applications and it is still challenging.

Therefore, clear understanding of the room temperature ferromagnetic ordering can provide us with new experimental approaches to an opportunity to develop spintronic devices.

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