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| 14. ABSTRACT In this project, the properties of transition metal (TM) -doped ZnO will be investigated. The project focuses on two activities. First, the properties of ZnO doped with transition metals (Mn, Co, or Cr) and deep level impurities (Cu, As, Sn) is explored. The primary interest will be on elucidating the origin of magnetism in the TM-doped material, including understanding the role of deep level co-dopants in mediating ferromagnetism. Experiments will focus on correlating magnetic properties (Curie temperature, moment/TM dopant) with the TM and deep level dopant concentrations. Epitaxial film growth and ion implantation of single crystals will be used in these studies. Second, for the dilute magnetic semiconducting compounds, there appears to be a correlation of Curie temperature with semiconductor bandgap. In an effort to increase the Curie temperature to greater than 300 K, the properties of TM-doped (Zn,Mg)O will also be investigated, as the addition of Mg to ZnO increases the bandgap. The epitaxial films will be grown by pulsed-laser deposition. Temperature-dependent Hall and resistivity measurements will be used to determine conduction mechanisms, carrier type, and doping. SQUID magnetometry will be used to characterize the magnetic properties of transition metal doped materials. | | | | | |
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87. "ICP Dry Etching of ZnO and Effects of Hydrogen," K. Ip, M.E. Overberg, K. Baik, R. Wilson, S. Kucheyev, J.S. Williams, C. Jagadish, F. Ren, Y. Heo, D. Norton, J. Zavada and S.J. Pearton, *Solid-State Electron.* **47**, 2289 (2003).

1b. Papers published in non-peer-reviewed journal

1. none

1c. Book Chapters

1. K. Ip, S. J. Pearton, D. P. Norton, and F. Ren, "Advances in Processing of ZnO," in *Zinc Oxide Bulk, Thin Films, and Nanostructures*, C. Jagadish and S. J. Pearton, Ed., Elsevier, pp. 313-338, 2006.
2. D.P. Norton, S. J. Pearton, J. M. Zavada, W. M. Chen, and I. A. Buyanova, "Ferromagnetism in ZnO doped with transition metal ions," in *Zinc Oxide Bulk, Thin Films, and Nanostructures*, C. Jagadish and S. J. Pearton, Ed., Elsevier, pp. 555-576, 2006.

1d. Papers presented at meetings, but not published in proceedings:

Invited Presentations

1. "ZnO Thin Films and Nanowires for Photonics, Spintronics, and Sensors Meeting:" 5th International Symposium on Transparent Oxide Thin Films for Electronics and Optics, Kanagawa, Japan, May 2007
2. "Transition metal doped ZnO for spintronics," 2007 Spring Meeting of the Materials Research Society, San Francisco, CA, April 2007
3. "Charge Carrier And Spin Doping In ZnO Thin Films For Device Applications", 2006 Fall MRS Meeting, Boston, MA December 2006
4. "P-type doping and electroluminescence for ZnO," SPIE Meeting , San Diego, CA, August 2006
5. "Charge- and Spin-Based Devices in ZnO Thin Films and Nanostructures," American Physical Society March Meeting, Baltimore, MD, March 2006
6. "Ferromagnetism in ZnO:Mn Epitaxial Films: Dependence on Carrier Density," AFOSR Wide Band Gap Ferromagnetic Semiconductors Workshop, Edinburgh, Scotland, May 2005
7. "Pulsed laser deposition of acceptor doped ZnO," European-MRS, E-MRS, Strasbourg, France, May 2005
8. "Charge carrier and spin doping in ZnO thin films," 4th International Symposium on Transparent Oxide Thin Films for Electronics and Optics, Tokyo, Japan, April 2005
9. "Ferromagnetism in ZnO:Mn Epitaxial Films: Dependence on Carrier Density," ARO Workshop on Spintronics in Wide Bandgap Semiconductors, Gainesville, FL, February 2005
10. "ZnO Spintronics and Nanowire Devices," 2004 Fall MRS Meeting, Materials Research Society, Boston, Massachusetts, December 2004
11. "Charge and Spin-Based Electronics using ZnO Thin Films," 206nd ECS Meeting, The Electrochemical Society, Honolulu, Hawaii, October 2004
12. "Dielectric Response Of K(Ta,Nb)O₃ Thin Films And Asymmetric KNbO₃/KTaO₃ Superlattices," XIII International Materials Research Congress 2004, Cancun, Mexico, August 2004.
13. "Growth of the Anatase Polymorph of TiO₂ Doped with Co using Epitaxial Stabilization: Do we have a 300 K DMS?," ONR Workshop on Frontiers of Epitaxial Engineering, Moab, Utah, May 2004
14. "Charge and Spin Doping in Epitaxial ZnO Thin Films and Nanostructures," 202nd ECS Meeting, The Electrochemical Society, Orlando, Florida, October 2003
15. "Wide Bandgap Semiconductors for Semiconductor Spintronics," 2003 Fall MRS Meeting, Materials Research Society, Boston, Massachusetts, December 2003

16. "Doping ZnO for charge and spin electronics," 10th International Workshop on Oxide Electronics, Augsburg, Germany, September, 2003.

Contributed Presentations

1. "Thermally Stable Novel Metal Contacts on Bulk, Single-Crystal n-type ZnO," 211th Meeting of the Electrochemical Society, Chicago, IL, May 2007
2. "Magnetic And Magneto-Transport Properties In ZnO Films Heavily Doped With Cobalt," Florida Chapter American Vacuum Society Meeting, Orlando, FL, March 2007
3. "Carrier Type Conversion In Post Annealed ZnO:P Thin Films," Florida Chapter American Vacuum Society Meeting, Orlando, FL
4. March 2007
5. "Investigation of carrier type conversion of post annealed ZnO:P thin films as a function of the substrate temperature," TMS 2007 Annual Meeting & Exhibition, Orlando, FL, February 2007
6. "High-density Plasma Etching of Zinc-Oxide and Indium-Zinc-Oxide in Cl₂/Ar and CH₄/H₂/Ar Chemistries," 2006 Fall Meeting of the Materials Research Society, Boston, MA, November 2006
7. "Magnetic Properties and Observation of Anomalous Hall Effect in
8. Cobalt-Doped ZnO," TMS Electronic Materials Conference, State College, PA, June 2006
9. "Investigation of W-Ge-N Deposited on Ge as a Diffusion Barrier for Cu Metallization", 2006 Spring MRS Meeting, San Francisco, CA, April 2006.
10. "Examination Of Thiol Adsorption On Zn-Terminated And O-Terminated Substrates" Florida Chapter American Vacuum Society Meeting, Orlando, FL, March 2006
11. "Determination Of MgO/GaN And Zn_{0.95}Cd_{0.05}O/ZnO Heterojunction Band Offsets By X-Ray Photoelectron Spectroscopy" Florida Chapter American Vacuum Society Meeting, Orlando, FL, March 2006
12. "Properties of (Ba_xSr_{1-x})FeO₃ Thin Films and Multilayers" Florida Chapter American Vacuum Society Meeting, Orlando, FL, March 2006
13. "Highly Selective Hydrogen Sensing at Room Temperature with Platinum-Functionalized ZnO Thin Films and Nanorods" Florida Chapter American Vacuum Society Meeting, Orlando, FL, March 2006
14. "Magnetic Properties and Observation of Anomalous Hall Effect in Cobalt-Doped ZnO", Florida Chapter American Vacuum Society Meeting, Orlando, FL, March 2006
15. "Properties of W-Ge-N Deposited on Ge as a Diffusion Barrier for Cu", Florida Chapter American Vacuum Society Meeting, Orlando, FL, March 2006
16. "Enhanced Hydrogen Sensing at Room Temperature by Pd-Functionalized ZnO Nanorods" 2005 Fall MRS Meeting, Boston, Massachusetts, December 2005
17. "Properties of (Ba_xSr_{1-x})FeO₃ thin films and multilayers" Southeast Section of the American Physical Society Meeting, Gainesville, FL, November 2005
18. "Hydrogen-Selective Sensing at Room Temperature with Pt-Coated ZnO nanorods" Southeast Section of the American Physical Society Meeting, Gainesville, FL, November 2005
19. "Properties of W-Ge-N as a diffusion barrier material for Cu" Southeast Section of the American Physical Society Meeting, Gainesville, FL, November 2005
20. "Simulation of ZnO-based UV and Visible Light-Emitting Diode Structures" Southeast Section of the American Physical Society Meeting, Gainesville, FL, November 2005
21. "Synthesis and characterization of P-doped ZnO and (Zn,Mg)O thin films for optoelectronic applications" Southeast Section of the American Physical Society Meeting, Gainesville, FL, November 2005
22. "Electrical, optical and structural properties of Arsenic-doped (Zn,Mg)O films" 52nd American Vacuum Society Meeting, Boston, MA, November 2005
23. "Improved Pt /Au and W/Pt/Au Schottky Contacts on n-type ZnO Using Ozone Cleaning", 2005 Annual Joint Symposium of Florida Chapter of the AVS and Florida Society for Microscopy, Florida AVS, Orlando, FL, March 2005
24. "Fabrication of ZnO-based P-N junction diodes", 2005 Annual Joint Symposium of Florida Chapter of the AVS and Florida Society for Microscopy, Florida AVS, Orlando, FL, March 2005
25. "Thermal Stability of Tungsten-Based Schottky Contacts to N-Type ZnO", 207nd ECS Meeting, The Electrochemical Society, Quebec City, Canada, May 2005
26. "Fabrication of ZnMgO:P/ZnO p-n Junctions on ZnO Substrates", 2005 Electronic Materials Conference (EMC), TMS, Santa Barbara, CA, June 2005
27. "Realization of phosphorus-doped p-type (Zn,Mg)O thin films via pulsed laser deposition", 2005 Electronic

Materials Conference (EMC), TMS, Santa Barbara, CA, June 2005

28. "(La,Sr)TiO₃ as a Conductive Buffer for High Temperature Superconducting Coated Conductors", Applied Superconductivity Conference 2004, Jacksonville, FL, October 2004
29. "Nanodevices using Single ZnO Nanowire", 2004 Fall MRS Meeting, Materials Research Society, Boston, Massachusetts, December 2004
30. "ZnO Spintronics and Nanowire Devices", 2004 Fall MRS Meeting, Materials Research Society, Boston, Massachusetts, December 2004
31. "The Dependence Of Ferromagnetism On Sn Concentration in ZnMnO:Sn Epitaxial Films", 2004 Fall MRS Meeting, Materials Research Society, Boston, Massachusetts, December 2004
32. "Effect of Ozone Cleaning on Pt /Au and W/Pt/Au Schottky Contacts to n-type ZnO", 27th Int. Conf. Physics of Semiconductors, Flagstaff, AZ, July 2004
33. "Carrier Concentration Dependence of Ti/Al/P+/Au Ohmic Contacts to p-doped ZnO Thin Films", 2004 MRS Spring Meeting, Materials Research Society, San Francisco, California, April 2004
34. "Sensitivity of Pt/ZnO Schottky Diode Characteristics to Hydrogen", 203rd Meeting of ECS, The Electrochemical Society, San Antonio, Texas, May 2004
35. "Ferromagnetism in Mn- and Co-implanted ZnO Nanorods", IEEE Nano-2003, IEEE, San Francisco, August 2003
36. "Ion Implantation for Creating Room Temperature Ferromagnetism in Wide Bandgap Semiconductors", ISCS-2003, IEEE, La Jolla, California, August 2003
37. "Annealing Temperature Dependence of Contact Resistance and Stability for Ti/Al/Pt/Au Ohmic Contacts from Bulk n-ZnO", ISCS-2003, IEEE, La Jolla, California, August 2003
38. "Thermal Stability and Magnetic Properties of Mn- and Co-Implanted ZnO Nanorods", 11th Intl. Cong. On II-VI Compounds, IEEE, Niagara Fall, NY, September 2003
39. "Dielectric Response of Asymmetric KNbO₃/KTaO₃ Superlattices", 2003 Annual Meeting of the American Vacuum Society, AVS, Baltimore, MD, November 2003
40. "Properties of p-Doped ZnMgO Thin Films", 2003 Fall MRS Meeting, Materials Research Society, Boston, Massachusetts, December 2003
41. "Transparent Transistors Based On Semiconducting Oxides", 2003 Fall MRS Meeting, Materials Research Society, Boston, Massachusetts, December 2003
42. "Modification of MBE Grown ZnO Nanorods with Mn and Co Effects on Microstructure and Properties", 2003 Fall MRS Meeting, Materials Research Society, Boston, Massachusetts, December 2003
43. "Dielectric Response of K(Ta,Nb)O₃ Thin Films", 202nd ECS Meeting, The Electrochemical Society, Orlando, Florida, October 2003
44. "Growth and Microstructure of Cored (Zn_{1-x}Mg_x)O Nanorods," 202nd ECS Meeting, The Electrochemical Society, Orlando, Florida, October 2003
45. "Ferromagnetism In Mn- And Sn-Codoped ZnO Films Grown By Pulsed Laser Deposition," 202nd ECS Meeting, The Electrochemical Society, Orlando, Florida, October 2003
46. "Transition metal doped TiO₂ thin films grown by reactive sputtering deposition," 202nd ECS Meeting, The Electrochemical Society, Orlando, Florida, October 2003
47. "Leakage Current Behavior for HfO₂ Thin Films," 202nd ECS Meeting, The Electrochemical Society, Orlando, Florida, October 2003
48. "Electric Field Modulation of ZnO Film Conductance in ZnO-Based FET Structures," 202nd ECS Meeting, The Electrochemical Society, Orlando, Florida, October 2003
49. "Transparent ZnO-Based FET Structures for Displays," 202nd ECS Meeting, The Electrochemical Society, Orlando, Florida, October 2003

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3. Report of Inventions:

None

4. Scientific progress and accomplishments

Detailed descriptions can be found in the published papers cited above. An overview of the research project is given below.

Ferromagnetism in Transition-Metal Doped ZnO

ABSTRACT

ZnO is an attractive candidate for spintronics studies because of its potential for exhibiting high Curie temperatures and the relative lack of ferromagnetic second phases in the material. In this paper we review experimental results on transition metal doping of ZnO and the current state of theories for the ferromagnetism. It is important to re-examine some of the earlier concepts for spintronics devices, such as the spin field-effect transistor, to account for the presence of the strong magnetic field which has deleterious effects. In some of these cases, the spin device appears to have no advantage relative to the conventional charge-control electronic analog. We have been unable to detect optical spin polarization in ZnO.

Introduction

There is strong interest in the development of dilute magnetic semiconductors (DMS) that are ferromagnetic at room temperature for devices such as spin-based light-emitting diodes, sensors and transistors that utilize electron spin in addition to charge⁽¹⁻¹¹⁾. The ferromagnetism is induced by incorporation into substitutional sites of large concentrations of transition metal (TM) or rare earth ions into the semiconductor. Both types of ions have partially filled *d* and *f* shells, respectively, which give rise to unpaired electrons. The resulting magnetic behavior is found to be a strong function of a number of parameters, including the concentration of the TM ions in the crystal, the carrier density and the crystal quality. A major challenge is to prevent formation of second phases that may dominate the magnetic properties of the doped semiconductor, since the concentrations of transition metal ions is usually well above the solid solubility. The usually small amount of magnetization induced by the transition metal doping and difficulty in maintaining a single-phase material have led to many conflicting reports in the literature.

The more conventional DMS materials such as GaMnAs, InMnAs, and GaMnSb, show relatively low magnetic ordering temperature (~ 170 K for GaMnAs). These materials provide a rich environment for basic studies of magnetism in semiconductors but the low Curie temperatures limit their potential applications. The wide bandgap materials GaMnN and ZnMnO appear promising for obtaining robust room temperature ferromagnetism⁽⁴⁻⁸⁶⁾. Figure 1 shows that the wider bandgap semiconductors, which tend to have smaller lattice constants, large *p-d* hybridization and small spin-orbit interaction, are predicted to have higher Curie temperatures⁽¹²⁾. Even though the theories are still under development and there is disagreement between groups, there is some consensus that the wider bandgap materials have the most promise for achieving high Curie temperatures.

Summary of Current Understanding

The standard mean field theory that is applicable to carrier-driven magnetism in systems such as GaMnAs in which the transition metal doping also creates shallow acceptor states predicts that the Curie temperature will be dependent on the concentration of uncompensated Mn spins, the coupling constant between localized Mn spins and the free holes (*p-d* coupling), the effective mass of the holes and the free hole concentration^(1,3,12). For low carrier density systems such as ZnO, mechanisms other than carrier-induced ferromagnetism are more likely. An example is shown in Figure 2, which shows a schematic of the formation of bound magnetic polarons (BMP) in a system that also has direct anti-ferromagnetic coupling between closely spaced transition-metal ions⁽⁵⁾. As the sample temperature is lowered, the polarons increase in radius and eventually overlap at the Curie temperature.

The work of Sato and Katayama-Yoshida suggests that the ferromagnetic state is predicted to stabilize for most of the transition metal dopants in ZnO except Mn, as shown in Figure 3. Some of the theoretical predictions suggest that only *p*-type (Zn,Mn)O can lead to ferromagnetism^(6,13,33-37) (Figure 4). Experimentally however, it is difficult to obtain robust *p*-type doping of ZnO in the presence of high concentrations of transition metals and observations of ferromagnetism have been for insulating (Zn,Mn)O, *n*-type (Zn,Mn)O, and undoped (Zn,Mn)O. Values of T_C above room temperature have been reported for Mn, Co, Sc, Ti and V-doped *n*-type ZnO powders and films deposited on many different types of substrates methods such as sintering and pulsed laser deposition. Mn doping is attractive since the only potential second phase that contributes to the magnetism is Mn_3O_4 with a Curie temperature below 50K. By sharp contrast, Co-doping is a more complicated case, since Co itself is ferromagnetic. The data in the literature on Co-doping show a wide variety of results. Bulk $Zn_{1-x}Co_xO$ has been found to be antiferromagnetic in polycrystalline powder samples prepared by both solid-state and liquid-phase reactions. This antiferromagnetic behavior may result from Co clusters observed in the $Zn_{1-x}Co_xO$ powder, together with a population of interstitial Co atoms instead of substitutional Co⁽⁷¹⁾. Some experimental data show that homogeneous films of $Zn_{1-x}Co_xO$ exhibit spin-glass behavior, whereas inhomogeneous $Zn_{1-x}Co_xO$ films are more likely to demonstrate room-temperature ferromagnetism^(6-8,71). This is evidence that Co clusters might be the source of the high T_C ferromagnetism in some $Zn_{1-x}Co_xO$. Norton et al. observed such an effect for ZnO films implanted with high doses of Co ions⁽⁵⁷⁾. Table I summarizes many of the recent reports of the magnetic properties of transition metal doped ZnO^(8,9). There is still a wide variation reported for the magnetic properties of transition metal doped ZnO^(8,9,71-86). The exact growth conditions are crucial in determining the magnetic properties of the material at these high impurity concentrations^(8,9,70,71). A key issue in many of the published reports is whether the resulting material is indeed an alloy of transition-metal elements with the host material or whether it remains as the host material with clusters, precipitates or second phases that are responsible for the observed magnetic properties. A relatively complete characterization of the DMS would involve magnetic hysteresis measurements as well as field-cooled and zero field-cooled magnetization, magneto-transport, high resolution transmission electron microscopy, chemical bonding information obtained from X-Ray Photoelectron Spectroscopy (XPS) and lattice location measurements by ion channeling or Extended X-Ray Absorption Fine Structure (EXAFS). In most cases, such a detailed characterization is not carried out. The ZnO system provides an

excellent platform for studying such effects, since most of the secondary phases that could form cannot explain the observed magnetism.

The recent model of Coey et al.⁽⁵⁾, the so-called spin-split-orbit model, is shown schematically in Figure 5. The ferromagnetic exchange is mediated by shallow donor electrons that form BMPs, which in turn overlap to create a spin-split impurity band. Magnetic ions in different charge states couple by virtual hopping of the 'extra' electron from one ion to the other⁽⁵⁾. The 3d electrons in the partially occupied 3d-orbitals are allowed to hop to the 3d-orbitals of the neighboring TM, if neighboring TM ions have parallel magnetic moments. The ferromagnetic exchange is mediated by charge carriers in a spin-split impurity band formed by extended donor states. The impurity states hybridize with the d-orbitals of the transition metal elements.

It should also be noted that there is also a school of thought that suggests the observed ferromagnetism is not intrinsic to the transition-metal doped ZnO, but may originate from small clusters of contaminants^(72,77). This controversy points out the need to use a variety of different characterization methods to establish the lattice position, charge state and oxidation state of the transition metal in the ZnO lattice. Some of the more useful methods are the observation of the Anomalous Hall Effect (AHE)^(70,71) or the observation of polarized light emission from a quantum well using the DMS material as a spin injector. The latter has not yet been demonstrated for the ZnO system. To be considered a true DMS, it is necessary to show that the carrier population is polarized. In the case of Zn_{1-x}Co_xO magneto-optical effects measured by magnetic circular dichroism (MCD) indicate this is a true DMS material with polarized carrier population^(24,27). The MCD spectra of ZnO films doped with Sc, Ti, V, Cr, Mn, Co, Ni, and Cu using pulsed laser deposition were measured, as shown in Figure 6. Those doped with Mn, Fe, Co, Ni and Cu showed clear MCD structures near 3.4 eV. The films doped with Sc, Ti, V, and Cr did not exhibit any magneto-optical effect and were paramagnetic. Results from other methods that determine the half-metallicity (such as X-ray magnetic circular dichroism, a difference spectrum of two x-ray absorption spectra (XAS), one taken with left circularly polarized light, and one with right circularly polarized light. By closely analyzing the XMCD spectrum, information can be obtained on the magnetic properties of the atom, such as its spin and orbital magnetic moment) or can determine the oxidation state (XPS) or the lattice position (EXAFS, Ion Channeling) are needed.

Theory for Ferromagnetism in DMS

The mean-field Zener model proposed by Dietl et al.⁽¹²⁾ has been successful in explaining the transition temperatures observed for III-V DMS such as *p*-(Ga,Mn)As and II-VI DMS such as (Zn,Mn)Te. The mean-field Zener theory is based on the original model of Zener and the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction^(5,70,71). In the Zener model, the direct interaction between *d* shells of adjacent Mn atoms (super-exchange) leads to an antiferromagnetic configuration of the *d* shell spins because the Mn-*d* shell is half-filled. By contrast, the indirect coupling of spins through the conduction electrons tends to align the spins of the incomplete *d* shells in a ferromagnetic manner. It is only when this coupling dominates over the direct super-exchange coupling between adjacent *d* shells that ferromagnetism is present^(12,71). Accordingly, the mean-field approach assumes that the ferromagnetism occurs through interactions between the local moments of the Mn atoms mediated by free holes in the material. This approach works well for materials in which the transition metal dopants introduces a shallow level in the bandgap and therefore the material achieves a near-metallic conductivity when percent levels of the TM dopant are introduced on substitutional sites within the host.

The spin-spin coupling in the Zener approach is also assumed to be a long-range interaction, allowing the use of a mean-field approximation^(12,71). The mean-field model calculates the effective spin-density due to the Mn ion distribution within the host material. The direct Mn-Mn interactions are antiferromagnetic (AF) so that the Curie temperature T_C , for a given material with a specific Mn concentration and hole density (derived from Mn acceptors and/or intentional additional shallow level acceptor doping), is determined by a competition between the ferromagnetic and antiferromagnetic interactions^(12,71). As compared to the RKKY interaction, the mean-field Zener model takes into account the anisotropy of the carrier-mediated exchange interaction associated with the spin-orbit coupling in the host material. In the process it reveals the important effect of the spin-orbit coupling in the valence band in determining the magnitude of the T_C and the direction of the easy axis in DMS⁽⁷¹⁾. Based on this model, it was predicted that TM-doped *p*-type GaN and ZnO, as shown in Figure 1, are the most promising candidates for ferromagnetic DMS with high Curie temperature⁽¹²⁾. However, one aspect of these predictions that is usually overlooked is that they assumed very high hole concentrations ($>10^{20} \text{ cm}^{-3}$) and large Mn contents (5 at.%). While the latter is possible in ZnO, the former is not possible and indeed the relatively low carrier densities in most wide bandgap semiconductor-based DMS precludes the achievement of the classical carrier-induced ferromagnetism.

To overcome the limitations of the Zener-type carrier-induced models for low carrier density materials where the TM dopant may not necessarily introduce additional carriers, Sato and Katayama-Yoshida^(6,13,33-37) performed first principles *ab initio* calculations of the electronic structures of TM-doped ZnO and proposed the double exchange mechanism for the ferromagnetism. In the double exchange mechanism, also originally proposed by Zener, magnetic ions in different charge states couple with each other by virtual hopping of the extra electron from one ion to the other. In the DMS material, if neighboring TM magnetic moments are in the same direction, the TM-*d* band is widened by the hybridization between the spin-up states. Therefore, in the ferromagnetic configuration the band energy can be lowered by introducing carriers in the *d* band. In these cases, the 3d electron in the partially occupied 3d-orbitals of the TM is allowed to hop to the 3d-orbitals of the neighboring TM, if neighboring TM ions have parallel magnetic moments. As a result, the *d*-electron lowers its kinetic energy by hopping in the ferromagnetic state, or the so-called double exchange mechanism.

Sato and Katayama-Yoshida have reviewed their first principles approaches to theory of magnetism in DMS previously^(6,13,33-37). The basic approach is to calculate the total energy and electronic structures for the TM-doped material using density functional theory (DFT). The magnetic state of the DMSs can be investigated by calculating the electronic structure of a ferromagnetic DMS in which all the magnetic moments of the substitutional ions are parallel to each other and that of a spin-glass like state in which there are

at least two components of transition metal ions whose magnetic moments are anti-parallel^(6,13,33-37,71). The total energy of the ferromagnetic state minus that of the spin-glass state is calculated as a function of transition-metal composition. This approach was used to predict that the TM-doped ZnO is a candidate for high- T_C ferromagnetic DMS^(6,13,33-37). The first principle calculations predicted that transition metals V, Cr, Fe, Co, and Ni-doped ZnO would exhibit ferromagnetism at TM concentrations from 5% to 25%, whereas the Mn-doped ZnO would be antiferromagnetic in the ground state because of the exact half-filled d^5 state of Mn ions. In these calculations, the ferromagnetic state in Mn-doped ZnO was found to be stabilized by hole doping due to the double exchange mechanism as shown in Figure 4. It is important to realize that T_C values well in excess of room temperature, which would be needed since devices operate in excess of this temperature due to self-heating, were only predicted for high TM concentrations where it is expected to be difficult to reproducibly incorporate such large dopant fractions.

The first-principle calculations also suggested that the n -type doping in ZnO can increase the Curie temperature of Fe-, Co- and Ni-doped samples when the effects of disorder are taken into account by what is called the coherent potential approximation^(6,13,33-37). Considering that n -type ZnO is readily available and the intrinsic defects such as O-vacancies and Zn-interstitials form donor states, it was concluded that (Zn, Fe)O, (Zn, Co)O and (Zn, Ni)O are promising candidates for high- T_C ferromagnets. It was also suggested that (Zn,Mn,Fe)O, (Zn,Mn,Co)O, or (Zn,Mn,Ni)O may show carrier-induced ferromagnetism under electron doping by tuning the ratio of Mn to Fe, Co or Ni^(6,13,33-37).

Spin Relaxation in ZnO

Time-resolved magneto-PL results from undoped and Mn-doped ZnO structures have recently been performed in an effort to detect polarized light emission. In an applied magnetic field, the ZnO PL becomes polarized to about 10% at 6T. The polarization degree decreases with increasing emission energy. The behaviour is similar for both undoped and doped ZnO. Data for Zn(Mn,Mg)O/ZnO/AlGaIn spin LEDs grown on sapphire is shown in Figure 7. No transient PL polarization was noticeable by monitoring the high-energy side of the PL emission. This may be attributed to very fast spin relaxation between the Zeeman split spin levels, faster than the experimental resolution about 20 ps, even near $k=0$. By monitoring the low-energy side of the PL band, on the other hand, a polarization rising (though weak) with time seems to occur indicating a slower spin relaxation process associated with the monitored emission. This energy dependence is opposite to what we observed in InGaIn quantum wells⁽⁸⁷⁻⁸⁹⁾. If one can design a resonant tunnelling diode (RTD) such that the polarized spins carried by either electrons or holes can be injected directly to the ground state of the corresponding carriers in a spin detector without involving energy and momentum relaxation, there may have a hope to preserve the spin polarization much better. Spin relaxation within the spin sublevels of the ground state seems to be within the range that is detectable, based on past results from InGaIn⁽⁸⁷⁻⁸⁹⁾. Viewing from the observed 50 ps spin relaxation time for the exciton ground state in InGaIn QW, a spin LED or a device that utilizing ZnO-based materials for spin transport has to operate on a similar or shorter time scale to be effective even with a RTD-type of spin injection. For example, a pulsed operation mode should be employed.

In recent work, spin-dependent tunneling between two ferromagnetic films separated by an insulating (I) film shows junction magnetoresistance (JMR) of better than 20%⁽⁹⁰⁻⁹³⁾. This suggests that tunneling may be a more effective way of achieving spin injection than diffusive transport. A large magnetoresistance can also be obtained if the tunnel barrier is also ferromagnetic. A prototype device, shown in Figure 7, comprises a non-magnetic electrode, a ferromagnetic insulating tunnel barrier (the polarizer), and a ferromagnetic counterelectrode (the analyzer). Below T_c of the ferromagnetic insulator, the tunnel barrier is spin split, giving a highly polarized tunnel current as indicated in the schematic. If the moments of the ferromagnetic counterelectrode analyzer are parallel (antiparallel) to the moments of the spin polarized tunnel current, then the resistance is low (high). Magnetoresistance exceeding 100% has been obtained in an Al-EuS-Gd device⁽⁹⁴⁾, where EuS, the ferromagnetic insulator, has a $T_c = 16.8K$ and Gd, the analyzer, a T_c near room temperature.

One key objective in the future will be to find materials that enable operation of these novel spin filter devices at room temperature. Promising barrier materials might be transition metal doped ZnO, insulating ferrites ($CoFe_2O_4$), or insulating DMS materials with localized carriers to provide the necessary magnetic interactions. For satisfactory operation the localization length ξ_L must be less than the sample size (barrier thickness) but greater than the length characterizing the magnetic interactions. An example of such a device based on ZnO is shown at the bottom of Figure 8.

A number of initial device configurations for GaMnAs have already been demonstrated at low temperatures and this might be possible in ZnO. This list includes exchange-biased samples, spin-dependent resonant tunnelling diodes, magnetic tunnel junctions and spin-polarized light-emitting diodes ('spin LEDs')⁽⁸⁷⁻⁹⁸⁾. The presence of tunable wavefunction overlap between magnetic ions and carriers confined to quantum structures has also been reported⁽⁹⁷⁾. More controversial are reports of very large magneto-transport effects, the so-called "giant planar Hall effect"⁽⁹⁸⁾. There are also numerous theoretical analyses of new bipolar device configurations combining n -doped semiconductors with GaMnAs.

One of the main device concepts envisioned for spintronics has been the spinfet which has been suggested to be able to operate at lower powers and higher speeds than conventional charge-controlled transistors. However, recent reexamination of the spinfet concept has revealed serious potential shortcomings. Cahay and Bandyopadhyay⁽⁹⁹⁻¹⁰²⁾ modelled phase-coherent spin transport in the weakly disordered quasi-one-dimensional channel of a gate-controlled electron spin interferometer. When the effects of an axial magnetic field in the channel of the interferometer (caused by the ferromagnetic contacts), a Rashba spin-orbit interaction, and elastic (nonmagnetic) impurity scattering are all considered, it was shown that in the presence of an axial magnetic field, nonmagnetic impurities can cause spin relaxation in a manner similar to the Elliott-Yafet mechanism. Bandyopadhyay and Cahay⁽⁹⁹⁻¹⁰²⁾ suggest that is generally untrue that spin-based devices will be faster and consume less power than their electronic counterparts. They did an analysis of the switching voltages in a one-dimensional spinfet relative to a Si-based MOSFET and found that the former is actually not a lower power device. Their main conclusion was that unless materials with extremely strong spin-orbit interaction can be developed, the spintronic devices

will not measure up to their electronic analogs. Several other manifestations of the spinfet have recently been proposed, but in each case, doubts have been raised whether these present versions show any advantage over the original Datta-Das design. Bandyopadhyay and Cahay⁽⁹⁹⁻¹⁰²⁾ concluded that it is unlikely that currently proposed spinfets will play a significant role in digital, analog or mixed signal circuits but may be more suited to applications in memory, where high gain, high frequency, etc. are not necessary. They also concluded that spintronic devices may also have better noise margin since spin does not easily couple to stray electric fields (unless the host material has very strong spin-orbit interactions). Thus they concluded that it is also possible that spintronics may be able to outpace electronics in nonconventional applications such as single spin logic, spin neurons and using spin in a quantum dot to encode qubits. There is still hope that integration of spintronic devices with existing electronic and photonic devices and circuits may offer new functionalities and that this is where the DMS materials may have the most impact.

FUTURE WORK

The status of transition metal doped ZnO is still in a state of controversy. More work is needed to establish both lattice location or chemical state and the origin of the observed magnetism. Methods that detect or manipulate spin polarized injection, transport and detection in ZnO or ZnCdO/ ZnMgO heterostructures are definitely needed.

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Table I List of ZnO-based DMS recently reported(after refs . 8 and 9)

| Compound | TM content | Substrate | Fabrication method | Growth temperature (°C) | Oxygen pressure (Torr) | Post-annealing | T_c (K) | Notes | Ref |
|-------------------------------------|-----------------|----------------------|----------------------|-------------------------|---------------------------------|-----------------------------------------|-----------|--------------------------------------|-----|
| ZnO:Mn | <0.35 | c-Sapphire | PLD | 600 | 5×10^{-5} | | N/A | | 15 |
| ZnO:Mn | 0.36 | c-Sapphire | PLD | 600 | 5×10^{-5} | | N/A | Spin-glass | 14 |
| Zn _{1-x} TM _x O | | c-Sapphire | PLD | 500-600 | 1×10^{-9} to 10^{-6} | | N/A | | 16 |
| ZnO:Co | 0.02-0.5 | c-Sapphire | PLD | 300-700 | 1×10^{-6} to 10^{-1} | | | Spin-glass | 17 |
| ZnO:Mn | 0.01-0.36 | c-Sapphire | PLD | 610 | 5×10^{-5} | | | Paramagnetic | 18 |
| ZnO:Mn | 0.07 | a-sapphire | sputtering | 400 | 0.06 | | | Paramagnetic | 20 |
| ZnO:Mn | 0.03-0.2 | GaAs(100) | sputtering | 500-600 | 8×10^{-4} | | | | 63 |
| ZnO:(Co, Mn, Cr, or Ni) | 0.05-0.25 | r-Sapphire | PLD | 350-600 | $2-4 \times 10^{-5}$ | | 280-300 | $2 \mu_B/\text{Co}$ | 28 |
| ZnO:Ni | 0.01-0.25 | c-Sapphire | PLD | 300—700 | 1×10^{-3} | | | Superpara- or ferro-magnetic | 55 |
| ZnO:V | 0.05-0.15 | r-Sapphire | PLD | 300 | 10^{-5} to 10^{-3} | | >350 | $0.5 \mu_B/\text{V}$ | 56 |
| ZnO:(Co, Fe) | <0.15 | SiO ₂ /Si | Magnetron sputtering | 600 | 2×10^{-3} | 600°C, 10 min, 1.0×10^{-5} Ton | >300 | $12-15 \text{ emu/cm}^3$ | 30 |
| ZnO:Co | 0.03-0.05 | Bulk ZnO | Ion implantation | | | 700C, 5 min under O ₂ | >300 | Oriented Co precipitates | 57 |
| ZnO:Co | 0-0.25 | c-Sapphire | Sol—gel | <350 | | 700°C, 1 min | >350 | $0.56 \mu_B/\text{Co}$ | 58 |
| ZnO:Mn | 0-0.3 | c-Sapphire | PLD | | | | >30-45 | $0.15-0.17 \mu_B/\text{Mn}$ | 23 |
| ZnO:Mn | <0.04 | | Sintered pellets | 500-700C | Air, atmospheric pressure | | >425 | $0.006 \text{ emu/gm, single phase}$ | 38 |
| ZnO:Mn | 0.02 | Fused quartz | PLD | 400C | | | >425 | $0.05 \text{ emu/gm, single phase}$ | 38, |
| ZnO:(Fe, Cu) | 0-0.1 | Solid state reaction | 897 | | | | 550 | $0.75 \mu_B/\text{Fe}$ | 50 |
| ZnO:Co | 0.015 | | PLD | 650C | 5×10^{-5} | | >300 | ferromagnetic | 60 |
| ZnO:(Co, Al) | 0.04-0.12 | Glass | RF sputtering | | 1×10^{-2} in Ar | | >350 | $0.21 \mu_B/\text{Co}$ | 61 |
| ZnO:Mn | 0.04-0.09 | c-sapphire | Reactive sputtering | 200-380 | | | >400 | $3 \mu_B / \text{Co}$ | 62 |
| ZnO:(Mn, Sn) | 0-0.3 | | Implantation | | | 5 min, 700°C | 250 | ferromagnetic | 26 |
| ZnO:Mn and Sn | Mn 0.03, Sn<0.1 | c-sapphire | PLD | 400-600 | 0.02 | | >300 | ferromagnetic | 64 |

| | | | | | | | | | |
|--------------------------|-----------|----------------------|-----------------------------------------|----------|--------------------|------------------------------------|------|--------------------------------------------------------------------------|------|
| ZnO:Mn and Co | 0.05-0.15 | | Crystalline precursor | | | | | antiferromagnetic | 65 |
| ZnO:Mn and Co | <0.05 | bulk | Melt growth | 1000C | | | | paramagnetic | 66 |
| ZnO:Co | 0.1 | O-face ZnO | PLD | | | | | antiferromagnetic | 67 |
| ZnO:Co | <0.35 | r-sapphire | MOCVD | 350-600C | 40 | 20 min, 500C in vacuum | >350 | ferromagnetic | 68 |
| ZnO:Co and Fe | <0.15 | SiO ₂ /Si | Magnetron sputtering | 600C | 2X10 ⁻³ | 10 min 600C, 10 ⁻⁵ Torr | >300 | Ferromagnetic, 12-15 emu/cm ³ | 69 |
| ZnO:Mn | 0.1 | r-sapphire | PLD | 650C | 0.1 | | >300 | 0.075 μ _B /Mn | 41 |
| ZnO:Mn and Cu | 0.05-0.1 | r-sapphire | PLD | 650C | 0.1 | | 400 | 0.1 μ _B /Mn | 41 |
| ZnO:Sc,Ti,V,Fe, Co or Ni | 0.05 | r-sapphire | PLD | 600C | 0.1-750 | | >300 | 0.5 μ _B /Ti, 5.9 μ _B /Co 0.3 μ _B /Sc | 5,50 |
| ZnO:Mn | 0.02 | Bulk pellets | Powder, pellets and laser-ablated films | 500C | | | >300 | 0.16 μ _B /Mn | 38, |
| ZnO:Cr | | STO | PLD | | | | >400 | ferromagnetic | 40 |
| ZnO: Mn | 0.08 | tetrapods | evaporation | 600C | | | 43 | (Zn,Mn)Mn ₂ O ₄ phases | 54 |
| ZnO:Mn | 0.05 | ZnO sub | PLD | 200-600C | | | 250 | High T _C fpr lower T _G | 51 |

Figure Captions

Figure 1. Predicted Curie temperature as a function of lattice constant for a variety of semiconductors (after S.C. Erwin (Naval Research Laboratory)). The materials predicted to have high T_C 's have large p-d hybridization and small spin-orbit interaction.

Figure 2. Representation of magnetic polarons. A donor electron in its hydrogenic orbit couples with its spin antiparallel to impurities with a 3d shell that is half-full or more than half-full. The figure is drawn for $x = 0.1$, $\gamma = 12$. Cation sites are represented by small circles. Oxygen is not shown; the unoccupied oxygen sites are represented by squares. (After Coey et al.⁽⁵⁾)

Figure 3. The stability of the ferromagnetic states in ZnO-based DMSs. V, Cr, Mn, Fe, Co or Ni is doped as a magnetic impurity. The vertical axis is the energy difference per one formula unit between the ferromagnetic and the spin-glass state. A positive energy difference indicates that the ferromagnetic state is more stable than the spin-glass state (after K. Sato and H. Katayama-Yoshida^(34,37)).

Figure 4. Stability of the ferromagnetic ordering of Mn magnetic moments in ZnO. The energy difference of $\Delta E = TE$ (anti-ferromagnetic ordering) - TE (ferromagnetic ordering) is plotted as a function of carrier concentration. The carrier concentration means N (hole doping) and Ga (electron doping) concentration in the supercell. The inset shows the simple orthorhombic supercell used in the preset calculations (after K. Sato and H. Katayama-Yoshida^(34,37)).

Figure 5. Schematic and structure of oxide with 3d impurities and spin-split donor impurity band. In (a) we show the position of the 3d level for low T_C when the splitting of the impurity band is small. In (b) and (c), respectively, we show the positions of the minority or majority spin 3d bands which lead to high T_C . (after Coey et al.,⁽⁵⁾)

Figure 6. Transmission MCD spectra of ZnO and ZnO: transition metal (after Ando et al.⁽²⁷⁾).

Figure 7. PL spectra at 2K from Zn(Mn,Mg)O/ZnO/AlGaIn spin LEDs grown on sapphire, as well as their polarization properties at 300K.

Figure 8. Spin tunnel device in which the insulating tunnel barrier is ferromagnetic (top) and possible embodiment in the ZnO materials system (bottom).













