

Magnetism in Fe-implanted ZnO

Y.W.Heo*, J.Kelly**, D.P.Norton*, A.F.Hebard**, S.J.Pearnton*, J.M.Zavada*** and Y.D.Park****

Abstract—High dose ($3 \times 10^{16} \text{ cm}^{-2}$) implantation of Fe or Ni ions into bulk, single-crystal ZnO substrates was carried out at substrate temperature of $\sim 350^\circ\text{C}$ to avoid amorphization of the implanted region. The samples were subsequently annealed at 700°C to repair some of the residual implant damage. X-Ray Diffraction did not show any evidence of secondary phase formation in the ZnO. The Ni implanted samples remained paramagnetic but the Fe-implanted ZnO showed evidence of ferromagnetism with an approximate Curie temperature of $\sim 240\text{K}$. Preliminary X-Ray Photoelectron Spectroscopy measurements showed the Fe to be in the 2+ oxidation state. The carrier density in the implanted region still appears to be too low to support carrier-mediated origin of the ferromagnetism and formation of bound magnetic polarons may be one potential explanation for the observed magnetic properties. No evidence of the Anomalous Hall Effect could be found in the Fe-implanted ZnO, but its transport properties were dominated by the conventional or ordinary Hall effect.

I. INTRODUCTION

There is interest in achieving ferromagnetism with Curie temperatures above room temperature in ZnO for applications in the field of spintronic devices, in which

the spin of the carriers is exploited. The control of spin-dependent phenomena in electronic oxides or more conventional semiconductors may lead to devices such as spin light-emitting diodes (spin-LEDs), spin field effect transistors (spin-FETs) and the spin qubits for quantum computers⁽¹⁻¹⁰⁾. A key requirement in realizing most devices based on spins in solids is that the host material be ferromagnetic above room temperature. The incorporation of several atomic percent of the transition metals without creation of second phases appears possible under optimized synthesis conditions, leading to ferromagnetism. Pulsed laser deposition, reactive sputtering, molecular beam epitaxy and ion implantation have all been used to produce the ZnO-based dilute magnetic materials. The mechanism is still under debate, with carrier-induced, double-exchange and bound magnetic polaron formation all potentially playing a role depending on the conductivity type and level in the material.

A major breakthrough in the field came with the theoretical prediction of magnetic ordering temperatures in excess of room temperature for five atomic percent Mn doping in GaN, diamond and ZnO⁽¹¹⁾. Sato and Katayama-Yoshida have covered the first principles design for both semiconductor and oxide spintronics⁽¹²⁾, while reviews have appeared on the experimental status of TiO_2 , SnO_2 , Cu_2O and some ZnO ^(13,14). Ferromagnetism in magnetically doped ZnO has been both predicted^(8,12) and observed⁽¹⁶⁻²⁸⁾. However, in addition to Mn in which the results suggest that ferromagnetic ordering occurs when mediated by hole doping, magnetic indirect exchange through the valence band may produce ferromagnetic ordering without the need of additional charge carriers. This is also suggested to occur for Cr, Fe, Co, and Ni dopants⁽¹⁶⁾.

In this paper we report on the magnetic properties of Fe and Ni implanted bulk ZnO. In the former case, the samples display ferromagnetic properties up to $\sim 240\text{K}$,

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*Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611

**Department of Physics, University of Florida, Gainesville, FL 32611

***US Army Research Office, Research Triangle Park, NC 27709

****CSCMR and School of Physics, Seoul National University, Seoul, 151-747 Korea

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while the Ni-implanted samples are paramagnetic. Higher Curie temperatures may be possible by doping the ZnO during epitaxial growth, to avoid residual implantation damage.

II. EXPERIMENTAL

Bulk n-ZnO crystals from CERMET were used in these experiments and were undoped grade I quality crystals grown by vapor phase. Van der Pauw measurements showed a room temperature electron concentration of $9 \cdot 10^{16} \text{ cm}^{-3}$ and the room temperature electron mobility was $200 \text{ cm}^2/\text{V.s}$. The samples were implanted at $350 \text{ }^\circ\text{C}$ to avoid amorphization by Fe or Ni ions with a dose of $3 \cdot 10^{16} \text{ cm}^{-2}$ and energy of 250 keV . In both cases the projected range of ions was $\sim 0.15 \text{ }\mu\text{m}$ which was confirmed by the secondary ion mass spectrometry (SIMS) measurements. After the implantation the samples were annealed for 5 minutes at $700 \text{ }^\circ\text{C}$ in a N_2 atmosphere to try to remove the ion implantation damage. The magnetic properties were obtained using a commercially available RF-Superconducting Quantum Interface Device (SQUID) (Quantum Design MPMS). None of the films showed any evidence for second phase formation from x-ray diffraction measurements.

III. RESULTS AND DISCUSSION

The temperature dependence of conductivity in the unimplanted control samples showed the activation energy of the dominant donors as 35 meV . The carrier concentration was slightly higher with Ni or Fe implantation ($\sim 2 \cdot 10^{17} \text{ cm}^{-3}$) but remained n-type and the mobilities were distinctly lower ($\sim 35 \text{ cm}^2/\text{V.s}$). This appears to be the result of introducing additional donors and possibly scattering on the high density of neutral centers. If the transition metal ions substitute the Zn they should act as deep donors and would be neutral in n-type material. The slopes observed in the temperature dependences of resistivity were consistent with the 35 meV donors attributed to hydrogen.

The Ni-implanted samples remained paramagnetic, independent of the post-implant anneal temperature used

and will not be discussed further. However the Fe-implanted samples showed more promising results. Figure 1 (top) shows hysteresis present in the Fe-doped sample at 10K . There was no clear evidence of hysteresis at 300K as shown at the bottom of Figure 1.

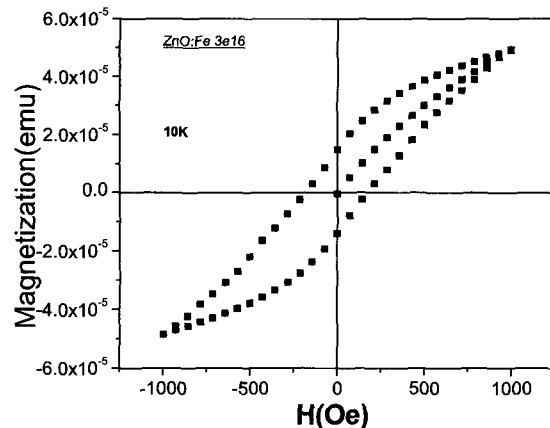


Fig. 1. Hysteresis loops in ZnO implanted with Fe, measured at 10K (top) or 300K (bottom).

This data is consistent with the magnetization versus temperature results. Figure 2 shows the temperature dependence of the difference in magnetization, $\Delta M(T) = M_{FC}(T) - M_{ZFC}(T)$, between the field-cooled and the zero-field-cooled data. The difference between the two plots advantageously eliminates para- and diamagnetic contributions and indicates the presence of hysteresis if the difference is nonzero. Although ferromagnetism is the usual explanation for hysteresis, spin glass effects, cooperative interactions between superparamagnetic clusters, or superparamagnetism below a blocking temperature can also be the cause. All of these effects, however, are magnetic phenomena involving the ordering of spins, and it is in this sense that we refer to the hysteresis measured by the $\Delta M(T)$ data as 'ferromagnetic'. The $\Delta M(T)$ plot of Fig. 2 has a strong positive curvature and approaches zero near room temperature. Identification of T_c from such a plot as the temperature at which $\Delta M(T)$ equals zero is at best a statement about the disappearance of hysteresis at the 250 Oe field in which the data are acquired. Similar data taken at lower fields will have a higher T_c . These rather unconventional shapes in the temperature-dependent magnetization were first seen in $(\text{Ga,Mn})\text{As}$ and are common in most DMS materials. Explanations for this

behavior can be found in theoretical treatments that consider the effect of randomness and disorder on percolating ferromagnetic clusters ^(27,28). The apparent Curie temperature derived from Figure 2 is ~240 K. We did not find any evidence of second phase formation in the Fe-implanted material by x-ray diffraction, as shown in Figure 3. Of course, small Fe clusters might be present, but preliminary X-Ray Photoelectron Spectroscopy (XPS) data indicates that the Fe was predominantly in the 2+ oxidation state, which suggests it is soluble and substitutional in the ZnO lattice.

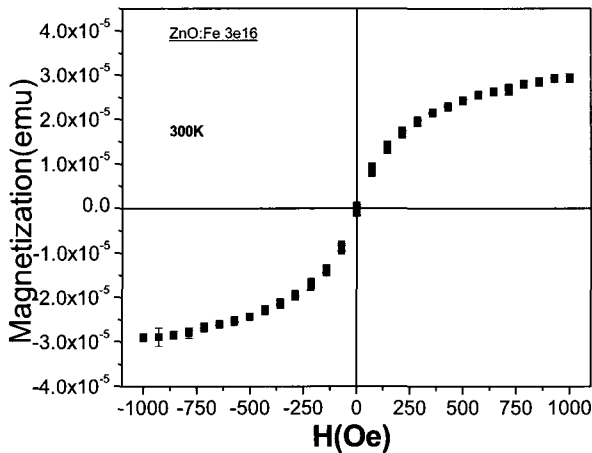


Fig. 2. Temperature dependence of difference in field-cooled and zero-field cooled magnetization in Fe-implanted ZnO.

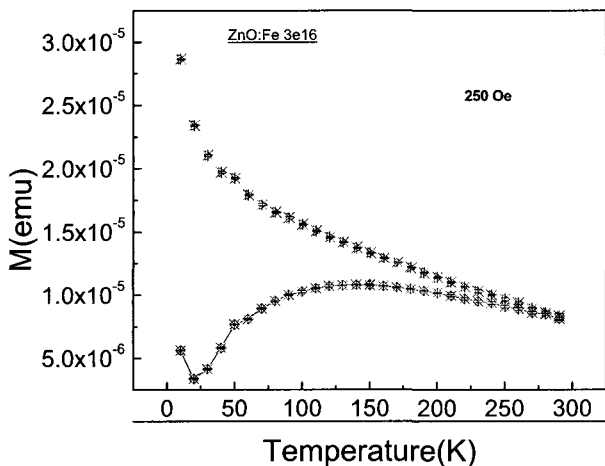


Fig. 3. XRD scans in log form from Fe-implanted ZnO.

The presence of the Anomalous Hall Effect (AHE) is often used as an independent measure of the presence of a polarized carrier population in magnetic systems. The resulting measurement will have a mixture of normal magnetoresistance (MR) and the Hall resistance. Figure

4 shows the transport data. This particular sample shows high negative MR even in the Van der Pauw geometry. Therefore, the real MR can be even larger than the 1% seen in the Figure. We cannot determine whether the sample shows the AHE, due to the large MR dominating even the Van der Pauw geometry of the sample.

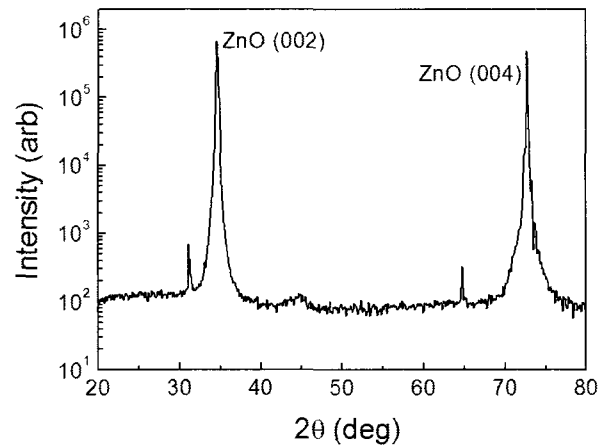


Fig. 4. Magnetoconductance data for Fe-implanted ZnO at 5K. The line corresponds to the Ω_{XX} data while the symmetric plot corresponds to Ω_{XY} .

Dietl et al.⁽⁸⁾ have applied Zener's model for ferromagnetism, driven by exchange interaction between carriers and localized spins, to explain the ferromagnetic transition temperature in III-V and II-VI compound semiconductors. The theory assumes ferromagnetic correlations mediated by holes from shallow acceptors in a matrix of localized spins in a magnetically doped semiconductor. Specifically, transition metal ions substituted on the group II site provide the local spin. High concentrations of holes are believed to mediate the ferromagnetic interactions among transition metal ions. A schematic of this process is shown in Figure 5. In the case of electron doped or heavily transition metal doped materials, no ferromagnetism is detected. Theoretical results suggest that carrier-mediated ferromagnetism in n-type material is relegated to low temperatures, if it occurs at all, while it is predicted at higher temperatures for p-type materials .

Carrier-mediated ferromagnetism in semiconductors is dependent on the magnetic dopant concentration as well as on the carrier type and carrier density. As these systems can be envisioned as approaching a metal-insulator transition when carrier density is increased and

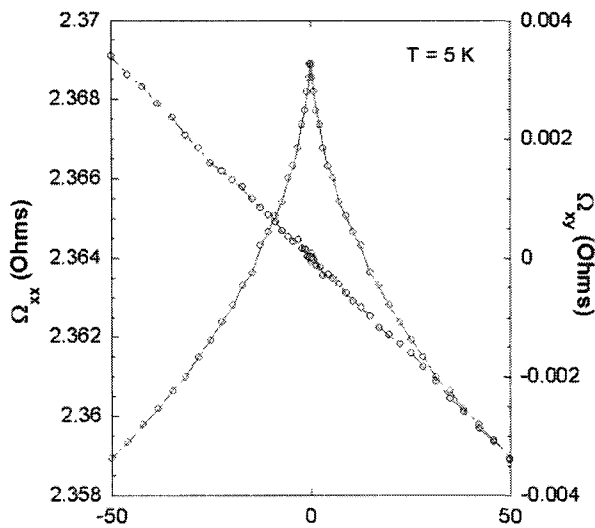


Fig. 5. Schematic of carrier-induced mechanism for ferromagnetism in Fe-doped n-type semiconductors.

ferromagnetism is observed, it is useful to consider the effect of localization on the onset of ferromagnetism. As carrier density is increased, the progression from localized states to itinerant electrons is gradual. On the metallic side of the transition, some electrons populate extended states while others reside at singly occupied impurity states. On crossing the metal-insulator boundary, the extended states become localized, although the localization radius gradually decreases from infinity. For interactions on a length scale smaller than the localization length, the electron wavefunction remains extended. In theory, holes in extended or weakly localized states could mediate the long-range interactions between localized spins. This suggests that for materials that are marginally semiconducting, such as in heavily doped semiconducting oxides, carrier-mediated ferromagnetic interactions may be possible.

Since the carrier density is still low in our samples a more likely mechanism is the bound magnetic polaron model^(29,30). As shown schematically in Figure 6, many localized spins due to the transition metal ions interact with a much lower number of weakly bound carriers, leading to polarons. The extent of these polarons increases as the temperature is lowered and the transition temperature occurs essentially when the polaron size is the same as that of the sample. The overlap of the individual polarons produces long-range interactions and energetically it is favorable for the spin polarization to develop. This model is inherently attractive for low

carrier density systems such as many of the electronic oxides. The polaron model is applicable to both p- and n-type host materials.

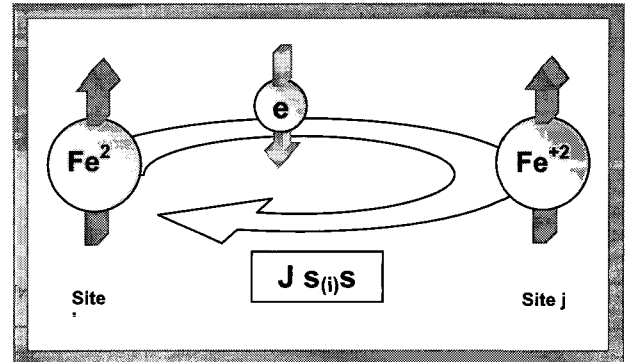
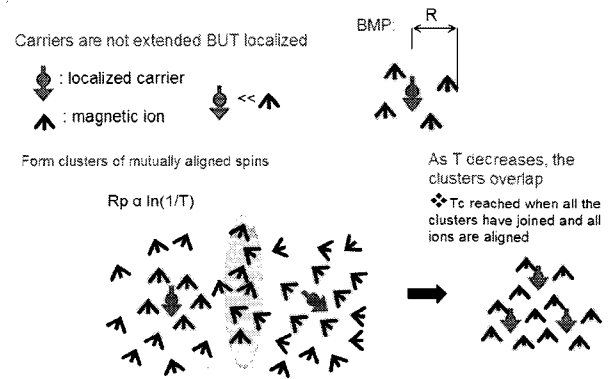


Fig. 6. Schematic of bound magnetic polaron model for ferromagnetism in low carrier density semiconductors (after refs. 29 and 30).



IV. CONCLUSIONS

We have shown that Fe and Ni implanted ZnO crystals remain n-type. Therefore the high Curie temperature (~240K) in the Fe-implanted is not due to hole-mediated spin alignment. Fe-doping during epitaxial growth may be an attractive method for obtaining higher Curie temperature, due to the absence of residual implant damage.

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Y.W.Heo is a post-doctoral researcher in the Department of Chemical Engineering at the University of Florida. His interests are novel wide bandgap devices and in particular on ZnO nanowire sensors and transparent electronics. He has published over 30 journal publications.

J.Kelly is a postdoctoral researcher in the Department of Physics at the University of Florida. His interests are in novel magnetic systems, especially low carrier density dilute magnetic semiconductors.

D.P.Norton is a professor in the Department of Materials Science and Engineering at the University of Florida. He joined UF after being a scientist at Oak Ridge National Labs. His interests are in electronic oxides, quantum computing, novel magnetic systems, especially low carrier density dilute magnetic semiconductors and superconductors. He has published over 150 papers in international journals.

A.F.Hebard is a professor of physics at the University of Florida. He joined UF after 23 years as a member of technical staff at AT&T Bell Laboratories. He received his Ph.D in physics from Stanford University and his interests are across a broad spectrum of condensed matter physics, including the metal-insulator transition, carbon nanotubes, spintronics and superconductors. He is Fellow of the APS.

S.J.Pearton is Distinguished Professor in the Department of Materials Science and Engineering at the University of Florida. After receiving a Ph.D in Physics from the University of Tasmania, he worked as a postdoc at the Australian Atomic Energy Commission and UC Berkeley before spending 10 years at AT&T Bell Laboratories. He is Fellow of IEEE, AVS and ECS and has co-authored over 900 journal publications.

J.M.Zavada is a contract research monitor with the US Army Research Office. His interests are in the optical, electrical and magnetic properties of wide bandgap semiconductors and their application to novel communication and sensor systems.

Y.D.Park graduated from the University of Florida with a Ph.D in materials science and engineering and then spent two years as postdoctoral researcher at the Naval Research Lab in Washington, DC, where he made fundamental contributions to the science of dilute magnetic semiconductors. He is now on the physics faculty at Seoul National University. He has published over 30 papers on magnetic semiconductors and numerous invited talks at international conferences.