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A key to room-temperature ferromagnetism in Fe-doped ZnO: Cu

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Successful synthesis of room-temperature ferromagnetic semiconductors, $Zn_{1-x}Fe_xO$, is reported. The essential ingredient in achieving room-temperature ferromagnetism in bulk $Zn_{1-x}Fe_xO$ was found to be additional Cu doping. A transition temperature as high as 550 K was obtained in $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$; the saturation magnetization at room temperature reached a value of $0.75\mu_B$ per Fe. A large magnetoresistance was also observed below 100 K. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1525885]

Diluted magnetic semiconductors (DMSs) have attracted a great deal of attention because of the possibility of incorporating the magnetic degrees of freedom in traditional semiconductors.[1,2] DMSs combine their transport and/or optical properties with magnetism, and thereby carry an enormous potential of opening up a path to entirely new devices. Until recently, (Ga,Mn)As has been a representative DMS with its moderately high Curie point (maximum $T_C \approx 110$ K).[3] However, an essential task in a realization of the potential is to find a DMS with the Curie point above room temperature.[4–6]

Recent theoretical works predicted ferromagnetism above room temperature in a II–VI semiconductor ZnO, normally *n*-type, when doped with magnetic impurities.[7,8] Since ZnO is optically transparent, ferromagnetic ZnO would be a transparent magnet as well. Despite intensive efforts on transition metal-doped ZnO *thin films*, the experimental results did not converge on a definite conclusion; there are, for instance, contradicting reports on Co-doped ZnO thin films.[9,10] Even the successful report, in which Co-doped ZnO thin films showed T_C of about 300 K, was attached with the reservation that the reproducibility was less than 10%.[10] Surveying the current situation with transition metal-doped ZnO, one naturally comes to a suspicion that the inconsistent results in thin film DMSs, within a group or among different groups, might be due to sensitive dependence of thin films on detailed process conditions such as target qualities, substrates, growing temperatures, oxygen pressure, etc. These thoughts motivated us to probe *bulk* samples rather than thin films.

In this letter, we concentrate on Fe-doped ZnO bulk samples. As described later, Fe-doping alone turned out to be not sufficient for room temperature ferromagnetism in ZnO, and a third element was required. As one member of the transition metal group, Cu substitution may be considered as magnetic doping if Cu substitutes for Zn^{2+} as Cu^{2+}. Cu-doping, however, did not induce a significant change in the magnetic property of ZnO films.[9] On the other hand, Cu may be used as an additional *p*-type dopant into naturally *n*-type ZnO samples.[11] The idea of additional Cu-doping in $Zn_{1-x}Fe_xO$ was highly successful and led us to a room-temperature ferromagnetic DMS. In view of the inconsistent film results, reproducibility was ascertained by measuring several samples synthesized by the same procedures.

Polycrystalline samples were fabricated with the standard solid state reaction method in Ar-filled quartz tubes. High purity ZnO(99.99+%), FeO(99.9+%), and CuO(99.99+%) powders were mixed thoroughly and processed at 1170 K for 24 h. The single phase nature of samples was checked by θ–2θ x-ray diffraction (XRD) using a Cu K_α source; substantial amount of exposure time was allowed in the XRD scans to check even a minute amount of a secondary phase. Magnetization, resistivity, Hall coefficient, and thermopower were measured by employing two pieces of equipment, a magnetic property measurement system (MPMS) and a physical property measurement system (PPMS), manufactured by Quantum Design. The superconducting quantum interference device magnetometer (MPMS) was equipped with a high temperature oven facility. X-ray absorption spectroscopy (XAS) was carried out at the Dragon beamline of the Synchrotron Radiation Research Center in Taiwan.

Figure 1(a) shows a typical powder XRD pattern of $Zn_{1-x}Fe_xO$ for $x=0.07$. All the peaks belong to the hexagonal lattice of ZnO, and no indication of a secondary phase is found. A shift of XRD peak positions related to lattice spacing changes was clearly observed when the concentration of Fe was varied; the data refinement revealed that the shift was caused by a variation of lattice spacing *a* as displayed in Fig. 1(b). The linear expansion of the *a*-axis lattice spacing with increasing *x* indicates that doped Fe atoms substitute for Zn atoms in the lattice up to $x=0.07$ under the current processing condition. The incorporation of Fe atoms into the lattice was also evidenced from the XAS measurements, which yielded the oxidation state of Fe to be mostly Fe^{2+}. On further doping of Fe above $x \approx 0.1$, the system enters a coexistence region of the dominant hexagonal phase (Fe-doped ZnO) and a minor cubic phase (FeO). It should be noted here that the Fe solubility of bulk ZnO found in this work is

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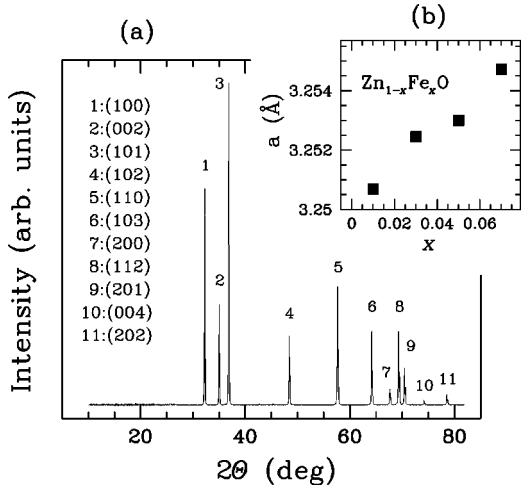

FIG. 1. (a) Intensity of XRD vs 2θ, from a polycrystalline $Zn_{1-x}Fe_xO$ sample with $x=0.07$. All the peaks belong to the hexagonal structure of ZnO. (b) Variation of the lattice constant a vs Fe concentration x.

higher than that of thin films.[9] The low solubility of the films seems to be related to the fact that it is the c-axis lattice constant, not the a-axis which is constrained by a substrate, that varies as the contents of Fe changes. This is a manifestation of the difference between bulk and thin films, which will be discussed elsewhere.[12]

We now turn to the magnetic properties of $Zn_{1-x}Fe_xO$. When measured at room temperature, a sample with $x=0.05$ showed a maximum saturation magnetization (M_s). However, the measured M_s of $Zn_{0.95}Fe_{0.05}O$ ($0.025\mu_B$/Fe, μ_B=Bohr magneton) was far too small to be considered as a room temperature ferromagnet. The situation is evident in Fig. 2(a), showing the magnetization–field ($M-H$) curve of $Zn_{0.95}Fe_{0.05}O$ sample at 300 K. We then attempted additional Cu-doping into $Zn_{0.95}Fe_{0.05}O$ as a means of rendering respectable ferromagnetism to the system. According to Dietl *et al.*, hole doping is most effective in achieving carrier-mediated ferromagnetism in semiconductors.[7] Jun and Choi showed that introduction of CuO into n-type ZnO increases resistivity up to 1% mixture,[11] which suggests that Cu can play the role of a p-type dopant. Cu-doping into $Zn_{0.95}Fe_{0.05}O$ via the standard ceramic method neither caused any structure change nor induced a secondary phase up to 1% incorporation. A small amount of additional Cu-doping, however, brought about drastic changes in M as illustrated in

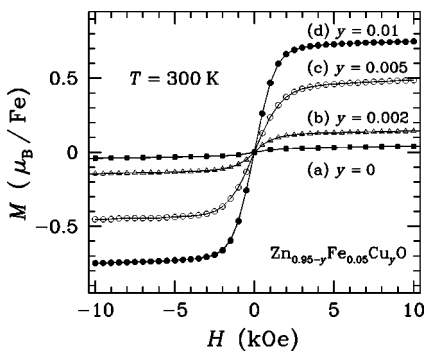

FIG. 2. Room temperature $M-H$ curves of bulk $Zn_{0.95-y}Fe_{0.05}Cu_yO$: (a) $y=0$, (b) 0.002, (c) 0.005, and (d) 0.01. The vertical scale (magnetic moment/Fe) was converted from measured values, assuming homogeneous magnetic states.

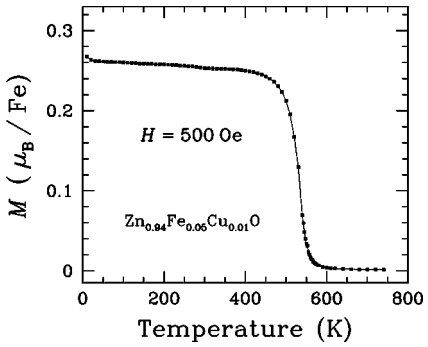

FIG. 3. The magnetization of $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$ is plotted as a function of temperature. The strength of the applied field was 500 Oe.

Figs. 2(b), 2(c), and 2(d). The magnetization is greatly enhanced with Cu-doping, so that M_s at room temperature of the sample with 1% Cu ($0.75\mu_B$/Fe) becomes 30 times larger than that of the sample without Cu. The fact that M_s increases systematically only with Cu contents virtually eliminates the possibility of Fe (or iron oxide) clusters being responsible for magnetization. The saturation occurs at 2 kOe, while the coercive field is about 20 Oe at room temperature. The small coercivity of a polycrystalline sample indicates the intrinsically soft nature of this material.

Now that we have established ferromagnetism in $Zn_{0.95-y}Fe_{0.05}Cu_yO$ at room temperature, its Curie temperature is of interest. In order to determine T_C of $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$, which shows the largest M_s at 300 K in Fig. 2(c), its M was measured as a function of temperature at a small field (500 Oe). The measured M, presented in Fig. 3, clearly shows that a transition to a paramagnetic state occurs near 550 K. It is noted that the transition is rather sharp and appears to deviate from a mean field description. The transition temperature of 550 K is considerably higher than the Curie temperature of most DMSs. More importantly, it is high enough for the purpose of device applications at room temperature.

In addition to ferromagnetism, transport properties are of exceeding importance in DMS. Figure 4(a) is the plot of the resistivity of $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$ at zero field as a function of temperature. The resistivity displays a typical semiconducting behavior. At room temperature the resistivity has a value of 0.1 Ω cm. Magnetoresistance {MR≡[$\rho(H)$

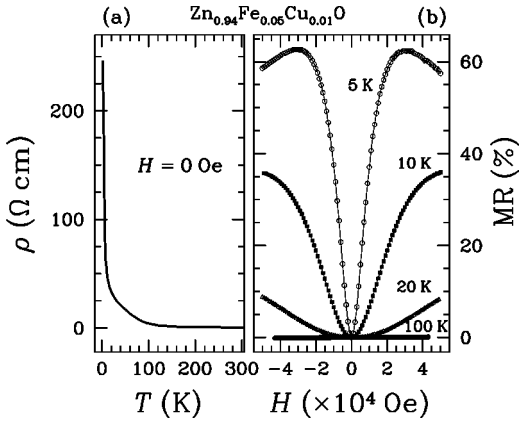

FIG. 4. Transport properties of $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$: (a) The resistivity vs temperature. (b) Magnetoresistance (MR) at various temperatures. MR is defined as $[\rho(H)-\rho(0)]/\rho(0)$. At 100 K, the MR is insignificant.

$-\rho(0)]/\rho(0)\}$ was also measured at various temperatures. The measured MR of a bulk sample is very large and positive, as shown in Fig. 4(b). However, the MR of $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$ becomes insignificant above 100 K, even if the system is still ferromagnetic. At present, we have no understanding on this peculiar behavior.

In order to elucidate the origin of ferromagnetism, we also measured the thermopower and the Hall coefficient of $Zn_{0.95}Fe_{0.05}O$ and $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$. Both samples yielded negative values for thermopower as well as Hall coefficient, and no anomalous Hall effect was observed. These results, first of all, indicate that electrons are major carriers in the samples. The number of carriers at room temperature estimated from the Hall coefficients are $4.2\times10^{17}/cm^3$ and $5.0\times10^{17}/cm^3$ for $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$ and $Zn_{0.95}Fe_{0.05}O$, respectively. XAS measurements also showed that the valence state of Cu in $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$ is Cu^{1+}, rather than Cu^{2+}. Thus, Cu ions play the role of acceptors and reduces the number of electron carriers, although they are not able to change the *n*-type character itself. It is then evident that the ferromagnetism in $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$ (which appears with reduction in the number of electrons) is not mediated by electrons. As Sato *et al.* suggested, it is very likely that a $3d$ band is formed by doped Fe atoms, and ferromagnetism occurs within this band via double exchange.[8] The lack of anomalous Hall effect is probably due to a weak coupling of the conduction electrons, which dominate transport, to magnetic degrees of freedom.

In conclusion, we achieved ferromagnetism in $Zn_{1-x}Fe_xO$ by Cu-doping, and the Curie temperature of 550 K and the saturation magnetization of $0.75\mu_B$/Fe were obtained for $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$.

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[1] J. K. Furdyna, J. Appl. Phys. **64**, R29 (1988).
[2] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488 (2001).
[3] H. Ohno, J. Magn. Magn. Mater. **200**, 110 (1999).
[4] G. A. Medvedkin, T. Ishibashi, T. Nishi, K. Hayata, Y. Hasegawa, and K. Sato, Jpn. J. Appl. Phys. **39**, L949 (2000).
[5] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, and H. Koinuma, Science **291**, 854 (2001).
[6] M. L. Reed, N. A. El-Masry, H. H. Stadelmaier, M. K. Ritums, M. J. Reed, C. A. Parker, J. C. Roberts, and S. M. Bedair, Appl. Phys. Lett. **79**, 3473 (2001).
[7] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).
[8] K. Sato and H. Katayama-Yoshida, Jpn. J. Appl. Phys. **39**, L555 (2000).
[9] Z. Jin, T. Fukumura, M. Kawasaki, K. Ando, H. Saito, T. Sekiguchi, Y. Z. Yoo, M. Murakami, Y. Matsumoto, T. Hasegawa, and H. Koinuma, Appl. Phys. Lett. **78**, 3824 (2001).
[10] K. Ueda, H. Tabata, and T. Kawai, Appl. Phys. Lett. **79**, 988 (2001).
[11] S.-T. Jun and G.-M. Choi, J. Am. Chem. Soc. **81**, 695 (1998).
[12] J. W. Song, C. H. Yang, S-J. Han, and Y. H. Jeong (unpublished).