

Fe clusters as origin of ferromagnetism in hydrogenated $Zn_{1-x}Fe_xO$ ($x= 0.02$ & 0.05) samples

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ABSTRACT

Bulk samples of $Zn_{1-x}Fe_xO$ ($x=0.02$ and 0.05) were synthesized via solid state reaction route by sintering in air at $800^\circ C$. Some sintered samples were annealed in Ar/H_2 at $800^\circ C$ for ~ 5 hrs. X-ray diffraction results reveal that the basic crystal structure of the as sintered and hydrogenated (Ar/H_2) samples corresponds to ZnO wurtzite structure together with some traces of $ZnFe_2O_4$ in the as sintered and Fe metal in the hydrogenated samples. The as sintered samples of both compositions show paramagnetic behaviour and after hydrogenation they exhibit ferromagnetic interactions at room temperature. Increase in the electrical conductivity has also been observed in the hydrogenated samples. The presence of small Fe clusters in the hydrogenated samples are expected to be responsible for the observed room temperature ferromagnetism. Copyright © 2012 VBRI Press.

Keywords: Annealing; magnetization; hydrogenation; ferromagnetism.



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Introduction

The theoretical prediction of room temperature ferromagnetism (RTFM) in transition-metal doped ZnO diluted magnetic semiconductors by Dietl et al. [1] and K. Sato et al. [2] led to much attention in these materials due to their possible use in new spin based devices [3-4]. Lot of experimental work have been carried out to explore the magnetic properties of transition metal doped ZnO, particularly, Mn and Co doped ZnO. Regarding RTFM

both positive [5-7] and negative [8-9] results have been reported. It appears from the results of various groups that the ferromagnetism in the sample rely very much on the growth conditions such as synthesis temperature and gaseous environment during synthesis. The ferromagnetic interactions in these materials are explained by Ruderman-Kittel-Kasuya-Yosida (RKKY) [10] or double exchange mechanism. In this mechanism, concentration of free carrier is vital to determine whether the material is paramagnetic or ferromagnetic. Experimental results show enhanced ferromagnetism in ZnO based diluted magnetic semiconductors by hydrogenation [11-12] and co-doping of various ions, such as Li, Cu, Al etc. [13-15]. Although, RTFM has been reported by several groups in the hydrogenated Fe doped ZnO, there is no consensus on the origin of this. G Y. Ahn et al. [16] reported RTFM in the hydrogen treated samples of $Zn_{1-x}Mn_xO$ ($x=0.00 - 0.10$), synthesized by sol-gel route having pure ZnO crystal structure. In another paper [17], they reported enhanced ferromagnetic properties of diluted Fe doped ZnO with hydrogen treatment. They argued that in the hydrogenated samples carrier concentration got increased leading to enhanced ferromagnetism in the sample. Kunming et al. [18] observed no ferromagnetic interactions in the as grown Fe doped ZnO by sol-gel route having pure ZnO structure and after hydrogen treatment the samples exhibited RTFM due to formation of Fe_3O_4 phase. Soumahoro et al. [19] studied the effect of Fe concentration on the magnetic properties in $Zn_{1-x}Fe_xO$ films prepared by spray pyrolysis method. The magnetic properties indicated the presence of a dominant paramagnetic (PM) behavior with small

ferromagnetic (FM) and antiferromagnetic (AFM) fractions and the AFM fraction was found to increase with the increase in Fe concentration. Recently, Xue et al. [20] studied the magnetic properties of Fe and C implanted ZnO films synthesized by the radio frequency magnetron sputtering technique. They found that simultaneous incorporation of Fe and C results in the enhancement of ferromagnetism in ZnO films in comparison single Fe or C implanted ZnO films. Thus, there is no consensus on the magnetic properties of Fe doped ZnO diluted magnetic semiconductors.

In the light of above the present investigations on the effect of hydrogenation on magnetic and structural characteristics of Fe doped ZnO have been undertaken. The bulk samples of Fe doped ZnO have been synthesized with nominal compositions $Zn_{1-x}Fe_xO$ ($x=0.02$ & 0.05) via solid state reaction route. The effect of hydrogenation on the structural and magnetic properties of the synthesized materials has been explored. RTFM with enhanced value of magnetization has been observed in the hydrogenated samples. Increase in the conductivity and evidence of formation of Fe metal clusters have been found after hydrogenation of the samples.

Experimental

Bulk samples with nominal compositions of $Zn_{1-x}Fe_xO$ ($x=0.02$ and 0.05) were synthesized by the standard solid-state reaction route, where first of all appropriate amounts of ZnO and Fe_2O_3 were mixed and ground in an agate mortar. The resulting powder was heated at $450^\circ C$ for 15 hrs in air followed by furnace cooling. After this, the resulting material was reground and pelletized. Finally, the pellets were sintered at $800^\circ C$ in air for 12 hrs followed by furnace cooling. Thereafter, some sintered samples were annealed in Ar/H_2 (90 % Ar + H_2 10%) atmosphere at $800^\circ C$ for ~5 hrs.

We are comparing the structural, magnetic and electric properties of air sintered samples with Ar/H_2 annealed samples of Fe doped ZnO. The crystal structure of the samples was studied using an X-ray diffractometer (BRUKER D8 ADVANCE) employing $Cu-K\alpha$ radiation. The temperature dependence of the magnetization (M-T) and magnetic hysteresis (M-H) loops were measured using Vibrating Sample Magnetometer (VSM - Model 155 Princeton Applied Research). Resistivity of the samples was measured by standard four-probe method employing *van der Pauw* geometry. The contacts were made on the samples using conducting silver paste.

Results and discussion

The X-ray diffraction patterns of as sintered and hydrogenated samples synthesized with nominal compositions of $Zn_{1-x}Fe_xO$ ($x=0.02$ & 0.05) are shown in Fig. 1. The diffraction pattern show majority of diffraction peaks corresponding to ZnO wurtzite structure. There are few weak peaks in the patterns of as sintered samples that correspond to $ZnFe_2O_4$. These peaks have been marked by ● in Fig. 1. The diffraction patterns of the hydrogenated samples show a peak (marked by ■) corresponding to Fe metal and there is no evidence of $ZnFe_2O_4$. Thus X-ray diffraction investigation reveals that in the as sintered

samples there is $ZnFe_2O_4$ as minority phase together with major ZnO wurtzite structural phase. After hydrogenation the $ZnFe_2O_4$ impurity phase disappears and a new peak corresponding to Fe appears. This is due to the fact that Ar/H_2 is a reducing atmosphere; and there is a lot of probability that the oxygen from the air sintered samples is removed when annealed in Ar/H_2 atmosphere.

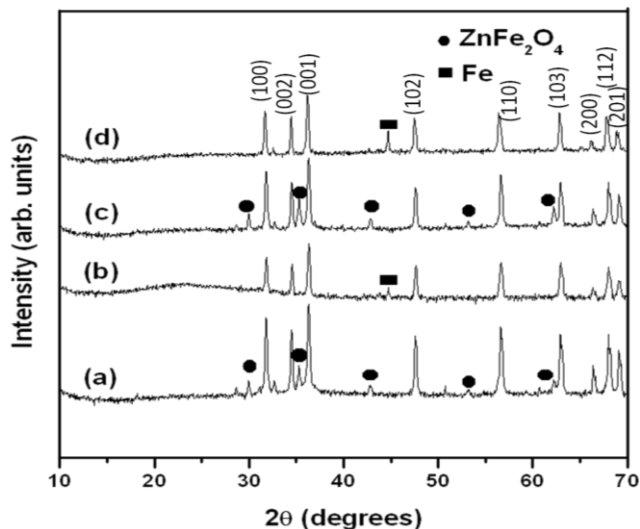


Fig. 1. X-ray diffraction pattern (logarithmic scale) of $Zn_{1-x}Fe_xO$: (a) as sintered $Zn_{0.98}Fe_{0.02}O$, (b) hydrogenated $Zn_{0.98}Fe_{0.02}O$, (c) as sintered $Zn_{0.95}Fe_{0.05}O$ and (d) hydrogenated $Zn_{0.95}Fe_{0.05}O$.

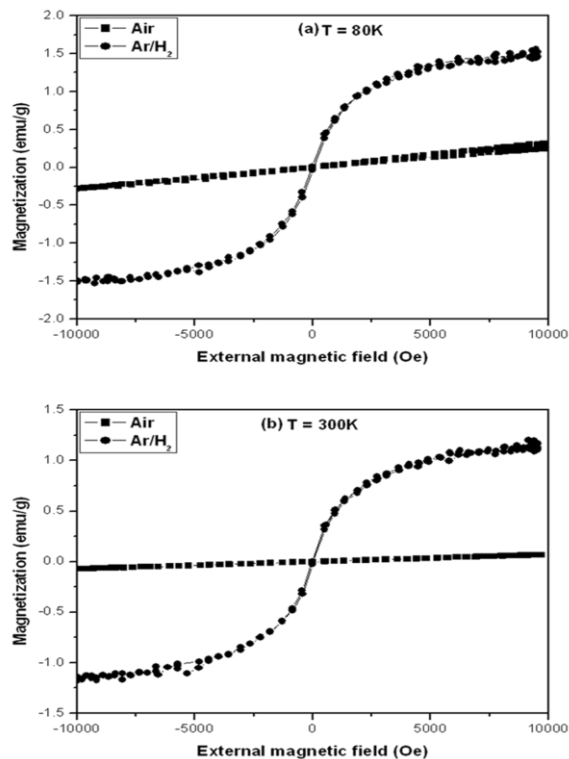


Fig. 2. (a) Magnetization vs. applied field (M-H) curves recorded at 80 K of as sintered and hydrogenated $Zn_{0.98}Fe_{0.02}O$. (b) M-H curves recorded at 300 K of as sintered and hydrogenated $Zn_{0.98}Fe_{0.02}O$.

Fig. 2 shows the magnetization versus magnetic field (M-H) curves measured at 80 K and 300 K of the as

sintered and hydrogenated $\text{Zn}_{0.98}\text{Fe}_{0.02}\text{O}$ samples. From the **Fig. 2** it is clear that as sintered sample does not show formation of hysteresis loop at both temperatures and M varies almost linearly with H , which is typical behaviour of paramagnetism. On the other hand, the M - H curve of the hydrogenated sample with same composition shows clear hysteresis loops at 80 and 300 K with almost same value of coercive field ($H_C \sim 25$ Oe), confirming the ferromagnetic interactions in the sample. The M - H curves measured at 80 and 300 K of the as sintered and hydrogenated $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$ samples are shown in **Fig. 3**. The M - H curve of the as sintered sample again shows paramagnetic behavior and the hydrogenated sample clearly shows formation of hysteresis loop with coercive field (H_C) ~ 90 Oe. Above results show that as sintered samples show paramagnetic behaviour and after hydrogenation they show ferromagnetism at room temperature. The value of magnetization is more in the $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$ samples as compared to $\text{Zn}_{0.98}\text{Fe}_{0.02}\text{O}$ at each magnetic field. The variation of magnetization with temperature (M - T) for hydrogenated samples of compositions $\text{Zn}_{0.98}\text{Fe}_{0.02}\text{O}$ and $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$ recorded at 5 kOe is shown in **Fig. 4**. This (M - T) curve indicates that magnetization appears to be almost independent of temperature in the range 80-300 K, which is also evident from the M - H curves of hydrogenated samples.

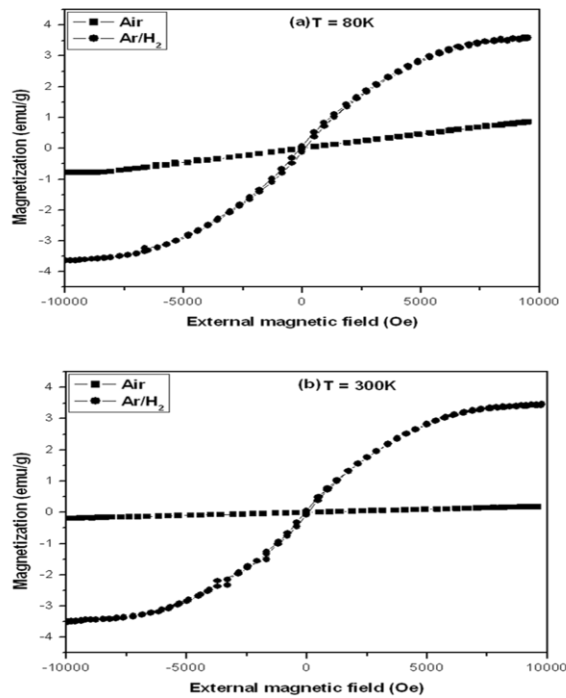


Fig. 3. (a) Magnetization vs. applied field (M - H) curves recorded at 80 K of as sintered and hydrogenated $\text{Zn}_{0.98}\text{Fe}_{0.05}\text{O}$. (b) M - H curves recorded at 300 K of as sintered and hydrogenated $\text{Zn}_{0.98}\text{Fe}_{0.05}\text{O}$.

The measurement of electrical resistance of the as sintered samples shows high resistance, typically of the order of few mega ohms. The same measurement of the hydrogenated sample shows resistance of the order of few ohms. The variations of electrical resistivity with temperature in the range 80-300 K of the hydrogenated samples of compositions $\text{Zn}_{0.98}\text{Fe}_{0.02}\text{O}$ and $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$ are shown in **Fig. 5**. Both samples show semiconducting behaviour. The decrease in resistivity may be accounted

for; increase in carrier concentration in the sample or precipitation of Fe metal in the sample or both. In order to confirm whether the increase in conductivity is due to increase in carrier concentration or due to precipitation of Fe in the hydrogenated samples, we annealed the pure ZnO samples in the hydrogenated argon at 800°C for ~ 5 hrs and measured its resistance. In this case decrease in resistance was very small as compared to Fe doped ZnO. This result suggests that large decrease in resistivity of the hydrogenated Fe doped ZnO is mainly due to formation of small Fe clusters in the samples. It has also been observed that decrease in resistivity after hydrogenation is more for the sample $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$ as compared to $\text{Zn}_{0.98}\text{Fe}_{0.02}\text{O}$.

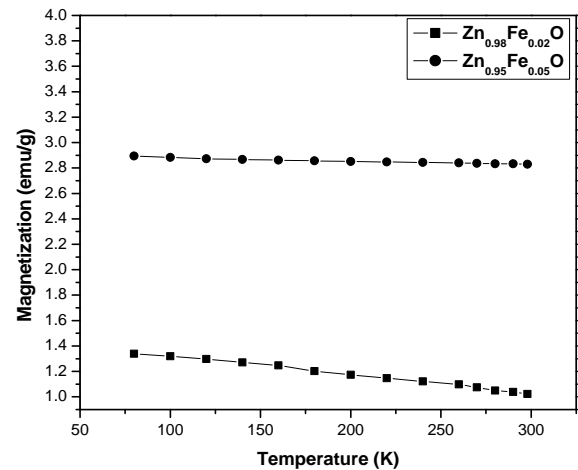


Fig. 4. Magnetization of hydrogenated samples as a function of temperature (M - T) in the applied field of 5 kOe.

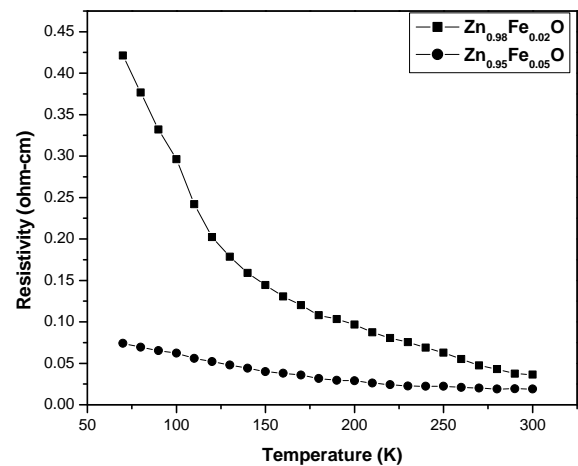


Fig. 5. Variation of resistivity with temperature of hydrogenated $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ ($x=0.02$ and 0.05).

In the present case there may be two possible origin of the observed ferromagnetism in the hydrogenated samples of Fe doped ZnO. One origin is due to the small Fe metal clusters in the samples as detected by the X-ray diffraction technique. The other one is the carrier-mediated ferromagnetism (RKKY or double exchange mechanism). Hydrogenation of the samples results in large decrease in resistance. This large decrease in resistance may be due to introduction of carriers in the sample through

hydrogenation as reported by G. Y. Ahn [17]. However, hydrogenation of pure ZnO under similar conditions showed small decrease in the resistivity. Therefore, it can be concluded that large decrease in resistivity of the samples after hydrogenation is mainly because of formation of Fe clusters in the samples. Hence, in the present case the observed RTFM in the hydrogenated samples is mainly due to formation of Fe clusters in the samples. The value of saturation magnetization (M_s) of the sample $Zn_{0.95}Fe_{0.05}O$ (~3.5 emu/g) is more as compared to $Zn_{0.98}Fe_{0.02}O$ (~1.2 emu/g) sample at room temperature. Thus, the hydrogenated samples investigated in the present work show RTFM together with semiconducting behavior, i.e. materials are magnetic semiconductors and may be useful for spintronic devices. Further investigations to estimate the size of Fe particles and their distribution in the samples, and how much Fe is substituted for Zn, are under progress.

Conclusion

In summary, we have observed RTFM in the hydrogenated bulk samples of nominal compositions $Zn_{1-x}Fe_xO$ ($x=0.02$ and 0.05). It has been argued that the observed room temperature ferromagnetic interactions are mainly due to dispersion of Fe particles in the hydrogenated samples.

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