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# Ferromagnetism in laser ablated ZnO and Mn-doped ZnO thin films: A comparative study from magnetization and Hall effect measurements

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ABSTRACT

Room temperature FM was observed in pristine ZnO thin films grown by pulsed laser deposition on $Al_2O_3$ substrates. It seems to originate from other defects but not oxygen vacancies. Magnetization of thinner films is much larger than that of the thicker films, indicating that defects are mostly located at the surface and/or the interface between the film and the substrate. Data on the Fe:ZnO and Mn:ZnO films show that a transition-metal doping does not play any essential role in introducing the magnetism into ZnO. In the case of Mn doping, the magnetic moment could be very slightly enhanced. Hall effect measurements reveal that an incorporation of Mn does not change the carrier type, but decreases the carrier concentration, and increases the Hall mobility, resulting in more resistive Mn:ZnO films. Since no anomalous Hall effect was observed, it is understood that the observed FM is not due to the interaction between the free-carrier and the Mn impurity.



## 1. Introduction

In 2000, Dietl et al. theoretically predicted that high temperature ferromagnetism (FM) can be obtained in ZnO, GaN, etc., if one dopes 5% of Mn into those systems, and make them *p*-type with a carrier concentration of about $3.5\times10^{20}\,cm^{-3}$. The magnetic ordering in those semiconductors was supposed to originate from the Ruderman–Kittel–Katsuya–Yoshida (RKKY) interaction via delocalized charge carriers [1]. Following this direction, experimentalists have tried to incorporate transition-metals (TM) into many semiconducting oxides such as ZnO, $TiO_2$, $SnO_2$, $In_2O_3$ [2]. Room temperature FM was observed in thin films grown by some special methods [3], and not in samples prepared by some other techniques [4–6]. The origin of the observed FM remains unclear, since most of these doped compounds are found to be *n*-type.

In 2004, the first observation of FM in pristine $HfO_2$ thin films has urged researchers in the field to re-judge the real role that a dopant can play in tailoring the magnetic properties of semiconducting and insulating oxides [7]. Recently, experimental results of various groups have confirmed that magnetism would certainly be observed in pristine oxides [8–12]. As for the $TiO_2$, $HfO_2$ and $SnO_2$ films, it was shown that the FM is most probably due to oxygen vacancies. The assumption for FM due to oxygen vacancies/defects in $TiO_2$ thin films is confirmed by the X-ray magnetic circular dichroism (XMCD) measurements [13]. Concerning ZnO system, some groups have also reported that defects could tune the FM [14,15], and having more oxygen could degrade the magnetic ordering [16]. Since ZnO is a potential semiconductor for applications in spin and opto-electronics, it is interesting to know whether the pristine ZnO can be ferromagnetic or not, and what should be the mechanism that governs it? Additionally, we aim to verify the role of a transition-metal doping. In order to elucidate these issues, we have investigated the magnetic and transport properties of pristine ZnO, Fe- and Mn- doped ZnO thin films.

## 2. Experiment

ZnO, $Fe_{0.01}Zn_{0.99}O$ and $Mn_{0.01}Zn_{0.99}O$ thin films were deposited by a pulsed-laser deposition (PLD) system (KrF-248 nm, 5 Hz, 2 J/cm$^2$) from ceramic targets on (0 0 0 1) $Al_2O_3$ substrates. As for ZnO and Mn-doped ZnO, the substrate temperature was kept constantly at 650 °C and an oxygen partial pressure ($P_{O_2}$) of $10^{-6}$ Torr was used during deposition. As for Fe-doped ZnO, the substrate temperature was 600 °C and $P_{O_2}$ was $5\times10^{-6}$ Torr. For ZnO, films with different thickness such as 10, 50, 375 nm, were made. As for $Fe_{0.01}Zn_{0.99}O$ and $Mn_{0.01}Zn_{0.99}O$ films, the thickness is 306 and 400 nm, respectively. Magnetic moment ($M$) was measured by a SQUID magnetometer in the range of temperature ($T$) from 5 up to 400 K and magnetic field ($H$) from 0 to 0.5 T. $H$ was applied parallel to the film plane. Transport properties have been studied by temperature dependent Hall effect set-up in Van der

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Pauw configuration. Resistivity and carrier concentration were measured in the temperature range of 5–300 K.

## 3. Results and discussions

Magnetization versus magnetic field at 300 K for a 375 nm-thick as-grown and post-annealed ZnO, Fe-doped ZnO, and Mn-doped ZnO films is shown in Fig. 1(a). One can see that the pristine ZnO film is room temperature ferromagnetic. However, the saturated magnetization ($M_s$) of ZnO films is rather modest (about 1 order smaller than that of $TiO_2$ and $HfO_2$ films with the same thickness [8]). The observed FM in ZnO films is surprising, since neither $Zn^{2+}$ nor $O^{2-}$ is magnetic. Different from the cases of $TiO_2$, $HfO_2$ and $SnO_2$ films, where one could find a strong relation between oxygen vacancies and magnitude of magnetic moment, the oxygen post-annealing does not give any obvious effect on the magnetism of the undoped ZnO films. From Fig. 1(a), one also can see that after annealing in an $O_2$ atmosphere for 10 h, the magnetic moment of the undoped ZnO films does not change. This suggests that the magnetism in ZnO films is governed by another mechanism, and nothing is directly related to oxygen vacancies. This assumption is in agreement with a theoretical model for FM due to oxygen vacancies in oxide films that concluded that the case of pristine ZnO is completely different from that of $TiO_2$, $HfO_2$, or $In_2O_3$ [17]. Most probably for laser ablated films, by depositing on a substrate under some specific conditions, new defects or/and impurities are induced, so that it results in the observed FM.

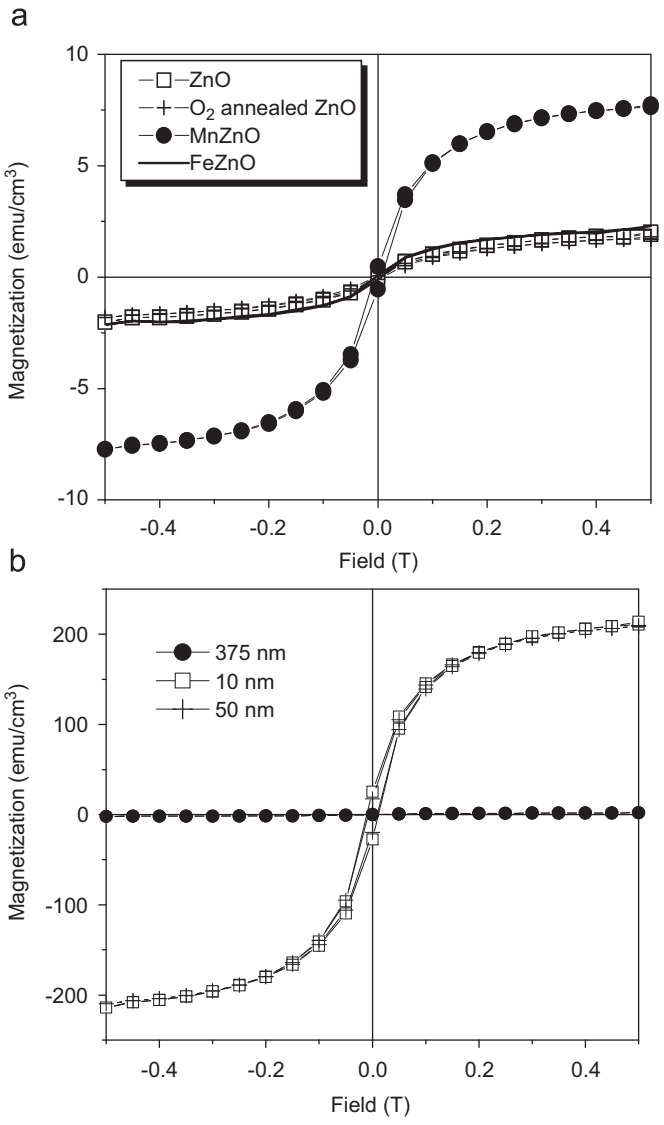


**Fig. 1.** Magnetization versus magnetic field taken at 300 K for (a) as-grown ZnO, $O_2$-annealed ZnO, Fe-doped ZnO, and Mn-doped ZnO films, and (b) ZnO films with various thicknesses. Field was applied parallel to the film plane.

In order to verify the real role of magnetic impurities, we have investigated two examples of doping: Fe- and Mn-doped ZnO films. From Fig. 1(a), one can see that the $Fe_{0.01}Zn_{0.99}O$ film has the same magnetization as that of the pristine ZnO film. We must say that the Fe doping indeed does not play any important role in tailoring the magnetic properties of the ZnO host. Concerning Mn doping, it is known that the case should be more complicated. Some theoretical work suggested that doping Mn alone could not result in any FM in n-type ZnO, and in order to obtain FM, one must co-doped Mn with Cu in order to have additional carriers [18]. However, experimentally, it was shown that doping with 10% of Mn alone in ZnO films could result in FM due to oxygen vacancies that were formed during the film growth [19]. In this work, we investigated the case of doping with only 1% of Mn. The $M(H)$ curve for a $Mn_{0.01}Zn_{0.99}O$ film taken at 300 K was shown in Fig. 1(a). The film is obviously ferromagnetic at room temperature with the $M_s$ of about 7 emu/cm$^3$, which is about 3 times larger than that of the pristine ZnO films. Different from the Fe doping case, doping with 1% of Mn can certainly enhance the magnetic moment of the ZnO host (i.e. Mn doping brings some additional contribution). The assumption for a different mechanism that Mn doping can bring into ZnO is supported by the different behavior of its anisotropy. When the magnetic field was applied perpendicular to the film plane, the Mn-doped ZnO film has a smaller magnetic moment, but certainly it is still well ferromagnetic (not diamagnetic as in the ZnO and Fe-doped ZnO cases) [3]. In Mn-doped ZnO films, there must be two different sources for magnetism: a major one comes from the Mn situated on the Zn sites of the ZnO host, and another one related to the ZnO matrix with undetermined defects. From Fig. 1(b), one also should notice that very thin films of ZnO (i.e. 10–50 nm-thick) are room temperature ferromagnetic, and they have the magnetization of about 2 orders of magnitude larger than that of the 375 nm-thick one. It implies that if the magnetism in ZnO films comes from defects, then those defects must be mostly located near the interface between the film and the substrate, or at the film's surface. Therefore, the observed FM is kind of "skin effect" but not any bulk's property. This is very similar to what observed for $TiO_2$ and $HfO_2$ films [8,9].

To verify the relation between magnetization and spin carrier polarization, anomalous Hall effect (AHE) measurements should be performed. Viewing the two cases of Fe and Mn dopings, one may expect to see some difference in the carriers in those compounds. Hall effect and resistivity measurements, therefore, were carried out to correlate transport properties and the observed FM.

All the undoped ZnO, Fe and Mn-doped ZnO films are $n$-type. At room temperature, while in the case of Fe-doped ZnO film, resistivity, electron concentration and mobility ($\rho = 1.88 \times 10^{-1}$ Ω cm, $n = 2.43 \times 10^{18}$ cm$^{-3}$ and $\mu = 13.7$ cm$^2$ V$^{-1}$ s$^{-1}$) are found not much different from those of the pure ZnO film ($\rho = 7.58 \times 10^{-1}$ Ω cm, $n = 8.25 \times 10^{18}$ cm$^{-3}$ and $\mu = 15.1$ cm$^2$ V$^{-1}$ s$^{-1}$), as for $Zn_{0.99}Mn_{0.01}O$, they are very different with $\rho = 4 \times 10^{-1}$ Ω cm, $n = 9.2 \times 10^{17}$ cm$^{-3}$ and $\mu = 29.3$ cm$^2$ V$^{-1}$ s$^{-1}$, indicating that Mn doping makes the carriers decreased while it increases the resistivity and Hall mobility. Since Fe does not seem to be electrically active in ZnO, and behaves like $Fe^{2+}$, it is surprising that the Mn is electrically active regarding to ZnO, and