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# Observation of ferromagnetism at room temperature in ZnO thin films

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## Abstract

Room-temperature ferromagnetism (FM) has been observed in laser-ablated ZnO thin films. The FM in this type of compound does not stem from oxygen vacancies as in the case of TiO<sub>2</sub> and HfO<sub>2</sub> films, but from defects on Zn sites. Magnetization of very thin films is much larger than that of the thicker films, showing that defects must be located mostly at the surface and/or the interface between the film and the substrate. Results on Fe-doped ZnO and Mn-doped ZnO films reveal clearly that the metal-transition doping does not play any essential role in introducing the magnetism in ZnO.

Since 2000, many research groups have tried to look for room-temperature ferromagnetic compounds, which can be obtained by doping transition-metals into semiconducting and insulating oxides such as ZnO, TiO<sub>2</sub>, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>, and the main cause was supposed to be the doping [1–5]. However, very recently, reports of Coey's group about the magnetism observed in HfO<sub>2</sub> thin films [6, 7], our findings for ferromagnetism (FM) in laser-ablated HfO<sub>2</sub>, TiO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> thin films [8], and results on TiO<sub>2</sub> films of Yoon *et al* [9] have raised a serious question if a transition-metal doping indeed plays any key role in introducing FM in those oxides. In fact, results on TiO<sub>2</sub> and HfO<sub>2</sub> systems suggest that magnetism originates from oxygen vacancies and/or defects [8, 10]. As for ZnO system, some groups have also reported that defects could also tune FM [11, 12], and a perfect crystallinity might destroy the FM, or having more oxygen could degrade the magnetic ordering [13]. Since ZnO is a semiconductor that has been widely used in spintronics applications, it is important to know whether the undoped ZnO can be ferromagnetic or not. Additionally, we need to re-judge carefully the role that a transition-metal indeed can play in introducing FM in this specific system. In order

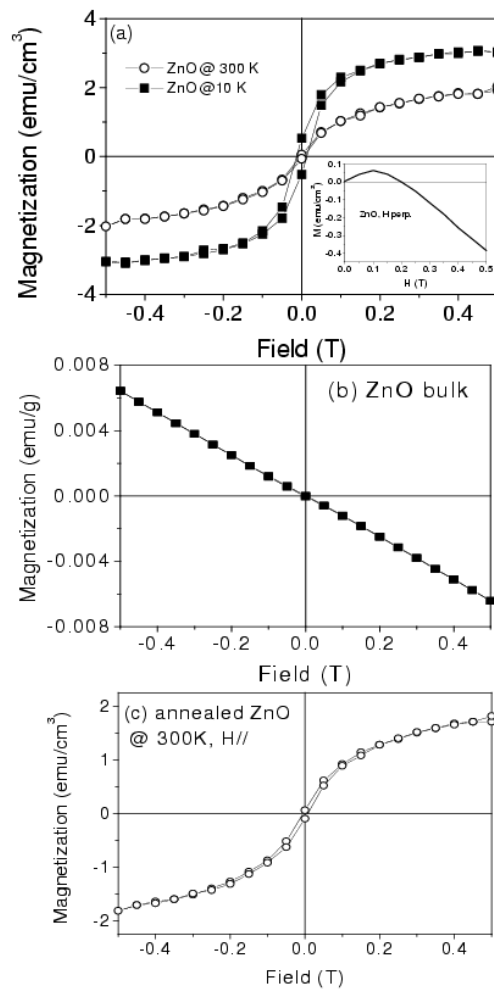
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to elucidate these issues, we have investigated the magnetic properties of undoped ZnO, as well as Fe- and Mn-doped ZnO thin films.

ZnO, Fe<sub>0.01</sub>Zn<sub>0.99</sub>O and Mn<sub>0.01</sub>Zn<sub>0.99</sub>O thin films were deposited by a pulsed-laser deposition (PLD) system (KrF-248 nm, 5 Hz, 2 J cm<sup>-2</sup>) from ceramic targets on (0001) Al<sub>2</sub>O<sub>3</sub> 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<sup>-6</sup> Torr was used during deposition. As for Fe-doped ZnO, three different sets of conditions were applied: at 600 °C and  $P_{O_2}$  of 5 × 10<sup>-6</sup> Torr; at 350 °C and  $P_{O_2}$  of 40 mTorr; at room temperature (without any heating) and  $P_{O_2}$  of 40 mTorr. For ZnO, films with different thicknesses were made to clarify the thickness dependence of magnetic properties. After deposition, some ZnO films were annealed at 600 °C for 10 h in an oxygen atmosphere with a  $P_{O_2}$  of 760 Torr. Some other films were annealed at 800 and 1000 °C for 10 h in a nitrogen atmosphere with a pressure of 760 Torr. Structural properties of films were checked using an x-ray diffractometer. The thickness was determined by Rutherford backscattering spectroscopy (RBS) measurements. The magnetic moment ( $M$ ) was measured by a SQUID (superconducting quantum interference device) magnetometer in the ranges of temperature ( $T$ ) from 5 K up to 400 K and magnetic field ( $H$ ) from 0 T to 0.5 T.  $H$  was applied basically parallel to the film plane.

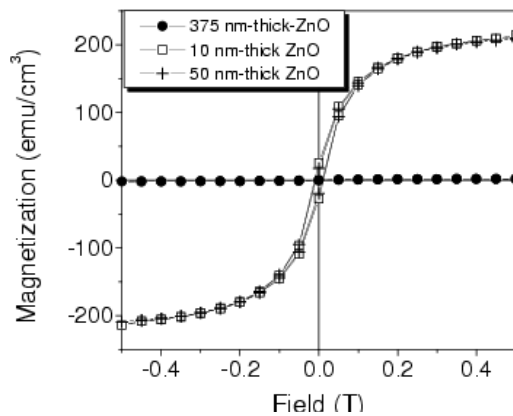
Except for the Fe-doped films fabricated at low temperatures, which have bad crystallinity, all the undoped ZnO films, the Mn-doped ZnO films, and the Fe-doped ZnO films fabricated at 600 °C, are well crystallized in the wurtzite structure. The thickness is determined by the RBS measurement to be in the range of 240–400 nm for most of the films. A few films with a thickness of 10–50 nm were also made in particular to verify the thickness dependence. All films are colourless and transparent.

The magnetization versus magnetic field at 10 and 300 K for a 375 nm-thick pure ZnO film is shown in figure 1(a). One can see that the film is ferromagnetic, not only at low  $T$  but also at room temperature. Comparing the magnitudes of  $M$  for the TiO<sub>2</sub> and HfO<sub>2</sub> systems of about 20–30 emu cm<sup>-3</sup> [8], the magnetization of ZnO films is rather modest, or we must say that the FM is much weaker (about one order smaller). The zoom for the magnetic moment measured in the perpendicular configuration shown in the inset reveals that the magnetism of the ZnO films has a large anisotropy: along the  $c$ -axis, the film basically shows a diamagnetic behaviour with a small mixture of a paramagnetic phase. This large anisotropy strongly implies that the magnetism in this system might come from defects [7, 8]. From figure 2, one can see that very thin films of ZnO (i.e. 10–50 nm-thick) are room-temperature ferromagnetic too, and they have a magnetization of about two orders larger than that of the 375 nm-thick magnetization. This strongly implies that if the magnetism in ZnO films comes from defects, then those defects must be located mostly at or near the interface between the film and the substrate, or at the film's surface. The main point here is that those defects are in a thin layer, as a 'skin effect', not a bulk property. This is very similar to what is observed for TiO<sub>2</sub> and HfO<sub>2</sub> films [8]. The observed magnetism in ZnO films is unexpected, because neither Zn<sup>2+</sup> nor O<sup>2-</sup> is magnetic, thus, in principle, there is no source for magnetism in undoped ZnO. Suspecting that we have results which are similar to those of TiO<sub>2</sub> and HfO<sub>2</sub> films (where FM is found in thin-film form only), the magnetic properties of the ZnO bulk were also checked. One can see from figure 1(b) that the ZnO bulk (i.e. a piece cut from the corresponding target) is perfectly diamagnetic. We must say that the room-temperature FM observed in ZnO films is unique for films only. In contrast to what we expected to see, the oxygen post-annealing does not give any effect on the magnetism of the undoped ZnO films. From figure 1(c), one can see that, after annealing in an O<sub>2</sub> atmosphere for 10 h, the magnetic moment of the undoped ZnO films does not change at all (compare figures 1(c) and (a)). This implies that the magnetism in ZnO films is different from that of TiO<sub>2</sub> and HfO<sub>2</sub>, and has another source rather than oxygen vacancies. Most probably

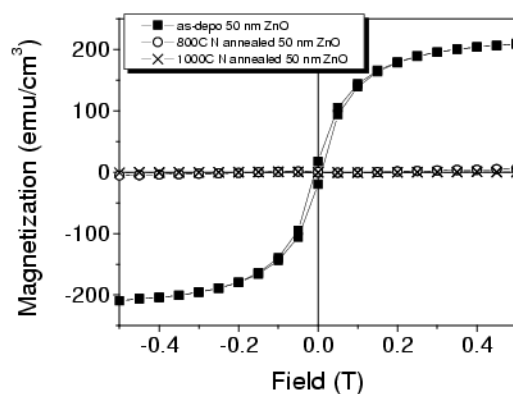


**Figure 1.** (a) Magnetization versus magnetic field at 10 and 300 K for a 375 nm-thick ZnO film.  $H$  was applied parallel to the film plane. The inset shows the zoom for  $M$  from 0 to 0.5 T when  $H$  was applied perpendicular to the film plane. (b) Magnetization versus magnetic field at 300 K for the ZnO bulk (piece cut from the corresponding target).  $H$  was applied parallel to the film plane. (c) Magnetization versus magnetic field at 300 K for a ZnO film with the same thickness, which was post-annealed in an  $O_2$  atmosphere at 600 °C for 10 h.  $H$  was applied parallel to the film plane. Signals from the substrates were subtracted.

in our case, by depositing on a substrate under some specific conditions, defects on the Zn site could occur, resulting in the observed FM. Treatment of the films in an nitrogen atmosphere was performed in order to have more evidence. The  $M(H)$  curves taken at 300 K for the as-deposited 50 nm-thick ZnO film and the N-annealed 50 nm-thick ZnO films at two different temperatures are shown in figure 3. In this range of temperature (800–1000 °C), we do not see an enhancement of magnetic moment but an enormous decrease instead: after annealing in nitrogen atmosphere at high  $T$ , films of ZnO become basically paramagnetic (in fact, it is a mixture of a small amount of diamagnetic phase and a dominant paramagnetic phase). It seems that to use nitrogen to control how it enters the structure of ZnO is a delicate matter



**Figure 2.** Magnetization versus magnetic field at 300 K for the 375 nm-thick, 50 nm-thick, and 10 nm-thick ZnO films.

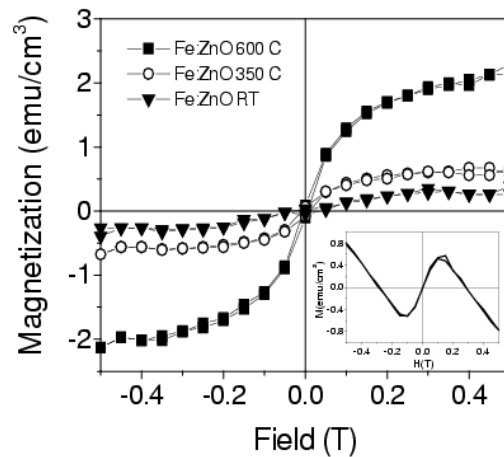


**Figure 3.** Magnetization versus magnetic field at 300 K for the as-deposited, 800 °C N annealed and 1000 °C N annealed 50 nm-thick ZnO films.

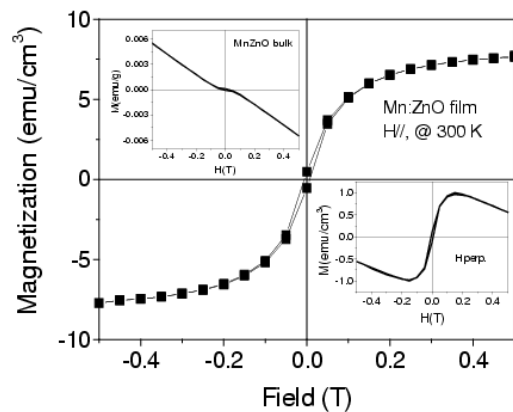
to deal with, and it needs more efforts to find out the appropriate and controllable conditions. However, because a nitrogen annealing basically disturbs Zn sites, and as a consequence a drastic change in magnetic moment appears, we can say affirmatively from these tests that the defects that cause magnetic ordering in ZnO must certainly take place on the Zn sites, not the oxygen site. This assumption is in accord with a theoretical model for ferromagnetism due to oxygen vacancies in oxide films stating that the mechanism for magnetism in ZnO must have a different origin [14].

So far, there have been no papers that have discussed profoundly the magnetism in Fe-doped ZnO films. It appears that this type of compound requires careful handling of the growth conditions, for both target preparation and film deposition.  $M(H)$  curves taken at 300 K for films of Fe-doped ZnO films fabricated at different conditions are shown in figure 4. One can see that only the film fabricated at 600 °C has a rather large  $M$ . However, even in this case, the FM is very modest. Referring to the magnetization data of the ZnO films taken at the same sequence from figure 1(a), one can see that the  $\text{Fe}_{0.01}\text{Zn}_{0.99}\text{O}$  film has the same  $M$  as that of the undoped ZnO film. We must say that the Fe doping does not influence the magnetism of the host matrix. Additionally, the  $M(H)$  taken in the perpendicular configuration (see the inset of figure 4) also supports the earlier remark: the Fe-doped ZnO film has exactly the same origin for anisotropy as that of the ZnO films. It is likely that the Fe doping does not play any important role in tailoring the magnetic properties of this compound.

Mn-doped ZnO has been known as a rather delicate case. Some theoretical work suggested that doping Mn alone could not result in any FM in ZnO, since the antiferromagnetism should



**Figure 4.** Magnetization versus magnetic field at 300 K for the  $\text{Fe}_{0.01}\text{Zn}_{0.99}\text{O}$  films fabricated at 600, 350 °C, and room temperature.  $H$  was applied parallel to the film plane. The inset shows  $M(H)$  at 300 K in the perpendicular configuration. Signals of the substrates were subtracted.



**Figure 5.** Magnetization versus magnetic field at 300 K for an  $\text{Mn}_{0.01}\text{Zn}_{0.99}\text{O}$  film. The upper inset shows the  $M(H)$  curve, taken at 300 K, of the  $\text{Mn}_{0.01}\text{Zn}_{0.99}\text{O}$  bulk (a piece cut from the corresponding target).  $H$  was applied parallel to the film plane. The bottom inset shows the  $M(H)$  curve of the film taken at 300 K in the perpendicular configuration. Signals of the substrates were subtracted.

be the ground state of Mn-doped ZnO [15, 16], and in order to obtain FM, one must co-dope Mn with Cu to have additional carriers [17]. However, it was shown experimentally that doping with 10% of Mn alone in ZnO films could result in FM, because oxygen vacancies might be created during film growth [18]. However, from the Mn:TiO<sub>2</sub> case, it was found that there is a drastic change in the magnetic properties of the compounds over some cut-off concentration of Mn, and the dopant content must be kept well below 5%, in order to possibly enhance the magnetic moment of the host [19]. Thus, in this work on ZnO, we simultaneously investigated the case of doping with only 1% of Mn. The  $M(H)$  curve for a  $\text{Mn}_{0.01}\text{Zn}_{0.99}\text{O}$  film taken at 300 K was shown in figure 5. The film is obviously room-temperature ferromagnetic, with a saturated magnetic magnetization of about  $7 \text{ emu cm}^{-3}$ , which is about three times larger than

that of the undoped ZnO films. Different from the Fe doping case, doping with 1% of Mn can certainly enhance the magnetic moment of the ZnO host. Since the ZnO films themselves are ferromagnetic, as we discussed earlier, in fact Mn doping does not create magnetism in this oxide. However, it can bring about some additional ferromagnetic component via the double exchange interaction, so that it eventually contributes to the total magnetic moment of the host. The assumption for a different mechanism that Mn doping can bring into ZnO is supported by the different behaviour of its anisotropy. In the bottom inset of figure 5, one can see that, 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. Therefore, in Mn-doped ZnO films, there must be two different sources for magnetism: one comes from the defects that may occur on the Zn sites in the ZnO base, and another is due to Mn doping. Note that the FM is the characteristic of the Mn-doped films only, but not of the bulk (see the top inset of figure 5, the Mn-doped ZnO bulk is highly diamagnetic at room temperature). Viewing the two cases of Fe and Mn doping, one should be very careful when judging the role of transition-metal doping. The roles that dopants play in the host matrices are certainly different from one case to the other. Most probably this depends on the carrier type being n-type or p-type, which may form in each host compound [20].

In conclusion, undoped ZnO thin films can be room-temperature ferromagnetic, and it is a particular characteristic of the films only, but not of the bulk. The source for magnetism cannot be oxygen vacancies but defects on Zn sites. The transition-metal doping indeed does not play any key role in tailoring the magnetic properties of the ZnO host. However, the dopant can participate in tuning the FM of the ZnO films. Depending on each case, it may either leave the magnetic moment unchanged or remarkably enhance it via another mechanism.

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