

Ferromagnetism observed in pristine SnO₂ thin films

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Room temperature ferromagnetism (FM) was observed in laser ablated undoped SnO₂ thin films grown on LaAlO₃ substrates (the saturated magnetization is about 12 emu/cm³, as half of that of the TiO₂ films with the same thickness). Experiments on Mn-doped SnO₂ films show that a transition-metal doping does not play any key role in introducing FM in the system. Mn doping (even if with a small content), in fact, just degrades the structure of the SnO₂ host and, as a consequence, reduces its magnetic moment. Both oxygen vacancies and confinement effects are assumed to be key factors in introducing magnetic ordering into SnO₂.

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In 2000, Dietl *et al.* theoretically predicted that ferromagnetism (FM) at high temperature could be obtained in many semiconductors if one dopes Mn plus a certain concentration of holes, and the magnetic ordering should be originated from the Ruderman-Kittel-Katsuya-Yoshida interaction via the dopants.¹ After that, experimentalists have tried to dope transition metals (TM) into various semiconducting oxides such as ZnO, TiO₂, SnO₂, and In₂O₃. Actually, room temperature FM was observed in those oxides under the thin film form.²

The finding of unexpected FM in HfO₂ thin films of Venkatesan *et al.* in 2004 has urged researchers in the field to rejudge the real role that a doping may play in tailoring the magnetic properties of semiconducting and insulating oxides.³ Observations of FM in various pristine oxides such as TiO₂, HfO₂, In₂O₃, and ZnO thin films confirmed that magnetism is certainly possible in pure semiconducting and insulating oxide thin films.^{4–6} The report of Sundaresan *et al.* on room temperature FM in nanoparticles of CeO₂, Al₂O₃, ZnO, In₂O₃, and SnO₂ has strongly supported the assumption stated in Refs. 4–6 for FM due to oxygen vacancies in those undoped oxides.⁷ Additionally, x-ray magnetic circular dichroism measurements on TiO₂ films have proved that the detected ferromagnetic signals indeed originated from O-2*p* and Ti-3*d* electrons, so that, finally, the above speculation seems to be logically reinforced.⁸

When we investigated Cr-Ni-V-doped SnO₂ films,⁹ the observed FM was supposed to be introduced due to doping, similarly to what the other groups also claimed.^{10,11} However, after the recent finding of FM in series of pure oxides, we realize that it is important to reverify if the undoped SnO₂ can become ferromagnetic under the thin film form (i.e., a low dimension configuration, with a special environment for oxygen formation), and the real role that a TM doping can play in tailoring the magnetism of this system as well. Therefore, in this Brief Report, we will report our investigations on magnetism of pristine and Mn-doped SnO₂ thin films.

The 220-nm- and 10-nm-thick SnO₂ films, as well as the 170-nm-thick Mn_{0.02}Sn_{0.98}O₂, Mn_{0.05}Sn_{0.95}O₂, and Mn_{0.08}Sn_{0.92}O₂ films, were grown on (001) LaAlO₃ substrates by using the pulsed laser deposition technique (KrF laser with $\lambda=248$ nm) from corresponding ceramic targets made by a solid state reaction method. Note also that the targets are pure with no impurity peaks that could be de-

tected from x-ray diffractions (impurities are of less than 10⁻² wt %). The repetition rate of film deposition was 10 Hz and the energy density was 1.8 J/cm². The substrate temperature was 700 °C. During deposition, the oxygen partial pressure (P_{O_2}) was kept as 10⁻⁴ Torr, and after deposition, films were cooled down to room temperature under the same P_{O_2} as during deposition, with a rate of 20 °C/min. Some films were annealed in oxygen flow with a pressure of 760 Torr at 700 °C for 10 h. The structural study was done by x-ray diffraction. The magnetic moment (M) measurements were performed by a Quantum Design superconducting quantum interference device system under magnetic field (H) from 0 up to 0.5 T under a range of temperatures (T) from 400 down to 5 K. The chemical composition was determined by Rutherford backscattering spectroscopy.

Magnetization as a function of temperature for a 220-nm-thick SnO₂ film is shown in Fig. 1(a). One can see that the film is ferromagnetic for the whole range of temperature below 400 K. The saturated magnetization (M_s) is about 12 emu/cm³, as half of that of the undoped TiO₂ films with the same thickness.⁴ One can clearly see from Fig. 1(b) that the $M(H)$ curve taken at 300 K when H is parallel to the film's plane shows ferromagnetic behavior, while as for H applied perpendicular, it shows nonferromagnetic characteristics. Thus, the magnetic ordering in SnO₂ films is likely in plane (i.e., the c axis seems to be hard axis, and, in fact, spins are aligned basically on the ab plane). One should notice that, very similar to the case of TiO₂, HfO₂, In₂O₃, and ZnO films that was reported before,^{4,6} this amazing feature of FM in pristine SnO₂ could be observed uniquely in the films but not in the bulks. Figure 1(c) shows clearly that the SnO₂ bulk is well diamagnetic. Since there is no reason to attribute the introduction of FM to any dopant, and moreover, in this SnO₂ case, there is no 3*d* electron involved, one cannot think of any interaction that may originate from that. Thus, we must reconsider the possibility that was previously assumed for the other ferromagnetic undoped oxides: FM due to oxygen vacancies and/or defects and confinement effects.^{3–7} As for SnO₂, it seems that both factors are equally important. Some groups reported that their films of SnO₂ are diamagnetic, while ours is certainly ferromagnetic. Hays *et al.* reported that their nanoparticles of SnO₂ are nonferromagnetic,¹² while Sundaresan *et al.*⁷ have confirmed

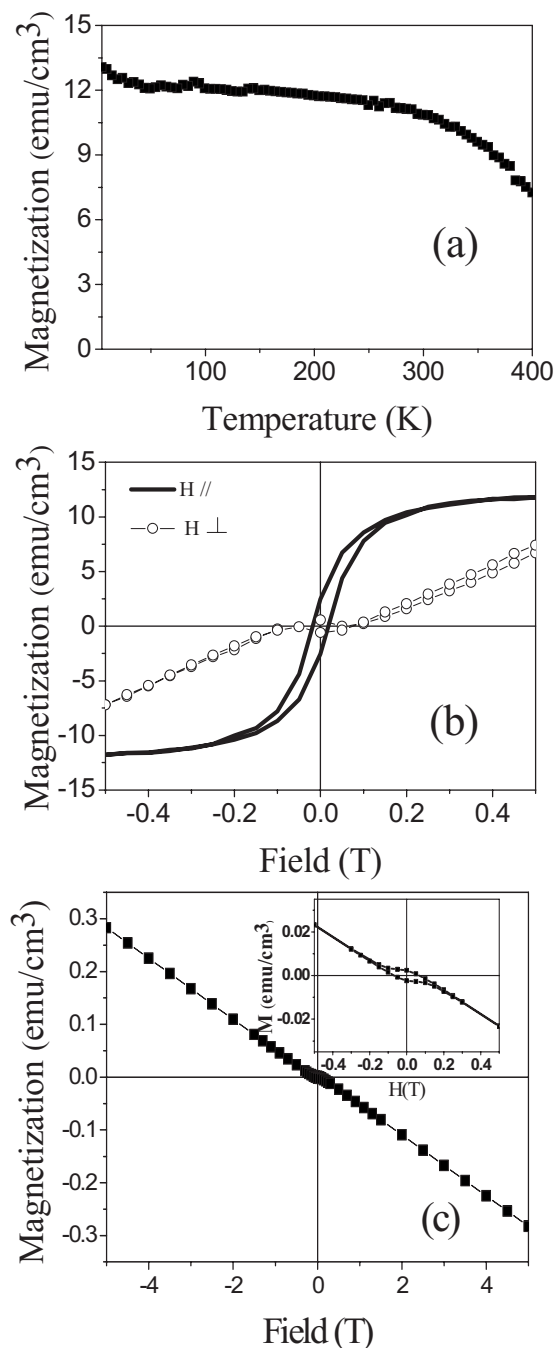


FIG. 1. Magnetization versus (a) temperature at 0.5 T as magnetic field is applied parallel to the film plane for the 220-nm-thick SnO_2 film; (b) magnetic field at 300 K as magnetic field was applied in both configuration, parallel and perpendicular, for the 220-nm-thick SnO_2 film; and (c) magnetic field at 300 K for SnO_2 bulk (a piece cut from the SnO_2 target). The inset in (c) shows the zoom for $M(H)$ of the SnO_2 bulk in the low field region (-0.5 – $+0.5$ T).

that their SnO_2 nanoparticles are weakly ferromagnetic with some paramagnetic component. To explain the observed FM in our films, we must say that most probably, oxygen vacancies formed during the growth are a key factor here, besides the presence of confinements. However, fabrication conditions and how to control them correctly must be a problem to

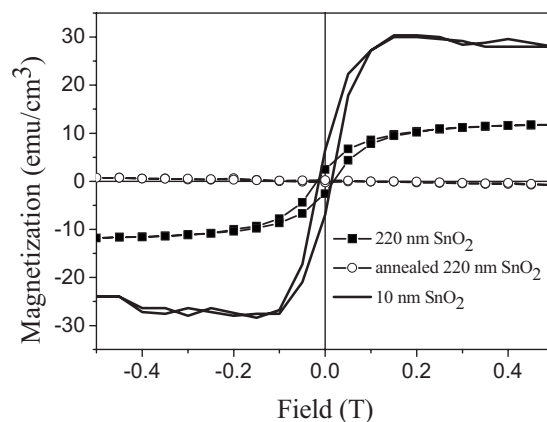


FIG. 2. Magnetization versus magnetic field taken at 300 K as magnetic field is applied parallel to the film's plane for the 10-nm-thick SnO_2 film, the as-deposited 220-nm-thick SnO_2 film, and the 220-nm-thick SnO_2 film annealed in the O_2 atmosphere with P_{O_2} =760 Torr at 700 °C for 10 h after deposition.

be solved in the future. We would like to recall Ref. 7 reporting that heating and sintering at different temperatures could drastically influence the magnetic properties of SnO_2 nanoparticles. This statement explained well why they got weak FM while Hays *et al.*¹² did not. It is also the reason why we could get much more pronounced FM in the SnO_2 films, while in the case of Ref. 7, the paramagnetic phase is still more dominant than the coexisting ferromagnetic one. The assumption about FM due to oxygen vacancies is supported by the data of the SnO_2 film that was annealed in an oxygen atmosphere. One can see from Fig. 2 that after annealing in oxygen for 10 h, the SnO_2 film loses its ferromagnetic ordering and becomes diamagnetic. It appears that filling up oxygen vacancies degrades magnetic ordering of the pristine SnO_2 films. In the case of TiO_2 and HfO_2 films, we found that there is strong thickness dependence (i.e., the thinner films have a much larger magnetization than that of the thick films). Thus, one should interpret that if the FM observed in those films stems from oxygen vacancies and/or defects, then those vacancies and/or defects must be located mostly at the surface and/or interface between the film and the substrate.⁴ Even though there is thickness dependence in SnO_2 films, the difference by only a factor of 2 between the magnitude of magnetization of the 10-nm-thick film and that of the 220-nm-thick one (Fig. 2) suggests that if the FM in pure SnO_2 films comes from oxygen vacancies and/or defects, then those are not just located mainly at the surface and interface but spread more thoroughly in the sample.

Since the other groups reported that the FM could be found only in TM-doped SnO_2 but not in the undoped SnO_2 ,^{12–14} we now carefully investigate the case of Mn-doped SnO_2 films to see how a TM doping could influence the magnetic properties of the SnO_2 host. $M(H)$ curves taken at 300 K of films of $\text{Mn}_x\text{Sn}_{1-x}\text{O}_2$ (where $x=0.02, 0.05, 0.08$) are shown in Fig. 3. One can see that the Mn doping obviously reduces the magnetic moment of the undoped SnO_2 . Upon doping, no matter how much the dopant concentration is, the magnitude of M does not differ very much. However, the degradation of magnetic ordering due to TM doping is

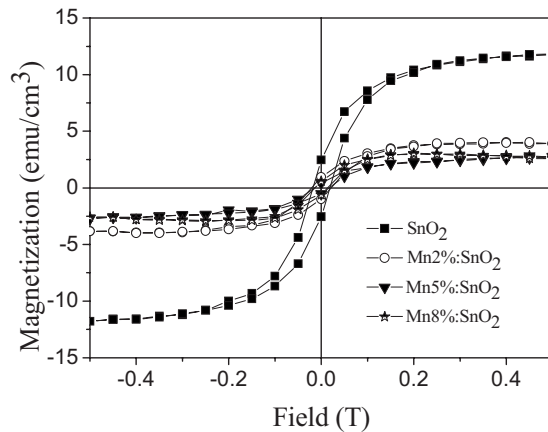


FIG. 3. Magnetization versus magnetic field taken at 300 K as magnetic field is applied parallel to the film's plane for the $\text{Mn}_x\text{Sn}_{1-x}\text{O}_2$ films (where $x=0, 0.02, 0.05, \text{ and } 0.08$).

always present. One should question if there is any relation between structural and magnetic properties leading to this reduction of M . From Fig. 4 showing x-ray diffraction patterns of the $\text{Mn}_x\text{Sn}_{1-x}\text{O}_2$ films, one can see that Mn doping actually degrades the crystallinity of the SnO_2 films. When Mn content is 5%–8%, the (305) peak of Mn_3O_4 clearly appears in the spectra. This formation of Mn_3O_4 clusters and/or particles may be the reason for the magnetic ordering of the SnO_2 host lattice to get degraded. From Ref. 12 reporting on the room temperature FM of the TM-doped SnO_2 , it was found that as for the Co doping, for example, one could not dope more than 1% because it made the lattice expanded enormously. As consequences, it caused a significant disordering that destroyed FM. Thus, perhaps we should understand here that the nanostructured configuration of SnO_2 should be a more important factor in introducing FM than a TM doping. In fact, the FM observed in Co-doped SnO_2 is a hidden feature of the SnO_2 host. This remark would be logical if one looks at the case of Fe-doped SnO_2 with the Fe concentration below 5%.¹³ Fe doping makes the lattice parameter of SnO_2 decreases and magnetic moment increases. However, while being heated at 600 °C, Fe diffused to the surface and destroyed the FM of the SnO_2 . Even though only 24% of Fe content was uniformly incorporated into SnO_2 as Fe^{3+} , there was no evidence of any ion impurity phase in Fe-doped SnO_2 . The authors then interpreted that the magnetic interaction in this system was most likely related to properties of the host SnO_2 and their oxygen stoichi-

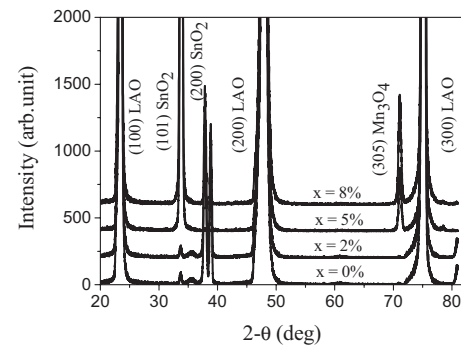


FIG. 4. X-ray diffraction patterns for the $\text{Mn}_x\text{Sn}_{1-x}\text{O}_2$ films.

ometry. This is reinforced by the work of the other group reporting that Fe doping, in fact, just brings more oxygen vacancies into the SnO_2 system. Those vacancies likely play a key role in magnetic interaction (i.e., the Fe doping only acts as a catalyst).¹⁵ As for Mn-doped SnO_2 , Fitzgerald *et al.* reported that they could dope up to 28%, and the M_s obtained was really huge (for Mn content of 1%, M_s was $20\mu_B/\text{Mn}$).¹⁴ The difference between M_s and anisotropy in their Mn-doped SnO_2 films and our films could be explained by the different types of substrates (Al_2O_3 and LaAlO_3). Due to that, strains and confinements must be different. Theoretically, in no case, M_s can be larger than $5\mu_B/\text{Mn}$. Therefore, it is impossible to attribute the source for FM observed in the Mn-doped SnO_2 to only the TM doping. One should suppose that doping of the $3d$ element into SnO_2 actually just helps to stabilize the low-lying magnetic excited state. Or in other words, one must say that the dopant acts as the activation factor of the defect moment.¹⁴ This is absolutely in accord with our finding of FM in pristine SnO_2 films.

In conclusion, FM above room temperature was observed in undoped SnO_2 thin films. This finding suggests that pristine semiconducting oxides could be ferromagnetic if oxygen vacancies and confinement effects could be formed in the compounds. Experiments on Mn-doped SnO_2 films show that a transition-metal doping does not play any essential role in introducing FM, but it just degrades the structure of the SnO_2 host indeed and reduces its magnetic moment. Both oxygen vacancies and confinement effects are supposed to be equally important to shape up the magnetic properties of SnO_2 . This result may open a route to make pure oxides to become potential candidates for applications just by controlling oxygen vacancies and downscaling those compounds to be nanometer sized.

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