Room-temperature ferromagnetism observed in undoped semiconducting and insulating oxide thin films

Nguyen Hoa Hong*
Laboratoire LEMA, UMR 6157 CNRS-CEA, Université F. Rabelais, Parc de Grandmont, 37200 Tours, France

Joe Sakai
School of Materials Science, JAIST, Asahidai 1-1, Nomi Ishikawa 923-1292, Japan

Nathalie Poirot
IUT de Blois, 3 place Jean Jaurès, C.S. 2903, 41029 Blois, France
and Laboratoire LEMA, UMR 6157 CNRS-CEA, Université F. Rabelais, Parc de Grandmont, 37200 Tours, France

Virginie Brizé
Laboratoire LEMA, UMR 6157 CNRS-CEA, Université F. Rabelais, Parc de Grandmont, 37200 Tours, France
(Received 29 November 2005; revised manuscript received 13 March 2006; published 13 April 2006)

Remarkable room-temperature ferromagnetism was observed in undoped TiO_2, HfO_2, and In_2O_3 thin films. The magnetic moment is rather modest in the case of In_2O_3 films on MgO substrates (while on Al_2O_3 substrates, it is negative showing diamagnetism) when the magnetic field was applied parallel to the film plane. In contrast, it is very large in the other two cases (about 20 and 30 emu/cm^3 for 200-nm-thick TiO_2 and HfO_2 films, respectively). Since bulk TiO_2, HfO_2, and In_2O_3 are clearly diamagnetic, and moreover, there are no contaminations in any substrate, we must assume that the thin film form, which might create necessary defects or oxygen vacancies, would be the reason for undoped semiconducting or insulating oxides to become ferromagnetic at room temperature.

DOI: 10.1103/PhysRevB.73.132404 PACS number(s): 75.70.Ak

Following the theoretical prediction of Dietl *et al.*,[1] many research groups have put a lot of effort into searching for high-temperature ferromagnetism (FM) in transition-metal (TM)-doped semiconductors. A lot of studies have been done on TM-doped TiO_2, ZnO, SnO_2,…[2–6] and they have resulted in obtaining FM above room temperature. However, Coey's group reported in 2004 about magnetism observed in HfO_2 thin films on sapphire or silicon substrates. This has really given an alert to researchers in the field about a new phenomenon, so-called d^0 magnetism.[7] In fact, the thin film form might make a big difference, which is assumed to cause defects or oxygen vacancies that might lead to a source of magnetism. This assumption was somewhat supported by the fact that theoretically Mn doping in ZnO alone could not introduce any room temperature FM,[8] but experimental work has proved that under appropriate growth conditions, room temperature FM could be achieved in Mn-doped ZnO films.[9] It turns out that growth conditions might create necessary oxygen vacancies, which could play a role as *n*-type doping. Recently, various experimental reports have given feedback to the present theories with evidence showing that defects certainly could tune the FM in diluted magnetic oxide thin films. For instance, it was found that defects could introduce FM in ZnO. In some other cases, it was obvious that perfect crystallinity could, in fact, destroy the FM. Also it was shown that having more oxygen could degrade the magnetic ordering.[10–13] Recently, Pammaraju and Sanvito have simulated the HfO_2 system to clarify the role that defects might play in introducing magnetism. It was confirmed that isolated cation vacancies in HfO_2 could form high-spin defect states, and therefore, they could be coupled ferromagnetically with a rather short-range magnetic interaction resulting in a ferromagnetic ground state.[14] All of these surprising results have encouraged us to verify experimentally the magnetic properties of various types of undoped semiconducting and insulating oxides. Does transition-metal doping indeed play a very important role in introducing FM in those supposedly nonmagnetic oxide hosts? Or, in other words, could the thin film form turn some nonmagnetic oxides into ferromagnetic? In this Brief Report, we report some surprising results obtained in undoped TiO_2, HfO_2, and In_2O_3 thin films.

Films of TiO_2, HfO_2, and In_2O_3 were deposited by a pulsed-laser deposition system (KrF, 248 nm) from ceramic targets on (100) $LaAlO_3$ (LAO), (100) yttrium stabilized zirconia (YSZ), and (001) MgO or *R*-cut Al_2O_3 substrates, respectively. The targets were 99.99% pure. Iron and nickel impurities are well below 10^{-2} wt. %. The growth conditions for these undoped oxide films are exactly the same as the optimal conditions we had found for TM-doped TiO_2,[2] Ni-doped HfO_2,[15] or Ni-doped In_2O_3 films.[16] The typical thickness of TiO_2 and HfO_2 films is 200 nm, while it is 600 nm for In_2O_3 films on MgO and 650 nm for In_2O_3 films on Al_2O_3. All films of TiO_2, HfO_2, and In_2O_3 are colorless, shiny, and highly transparent. Magnetic moment data were basically taken when the magnetic field was applied parallel to the film plane.

TiO_2 films deposited on LAO substrates are ferromagnetic at room temperature [see Fig. 1(a)] for a magnetization (M) versus field (H) curve taken at 300 K showing a very well-defined hysteresis loop]. Films have T_C higher than 400 K, and the saturated magnetization is rather large, about 20 emu/cm^3 [see the inset of Fig. 1(a)]. This large value of the magnetic moment is hard to attribute to any kind of impurities. A similar feature was observed in HfO_2 films on

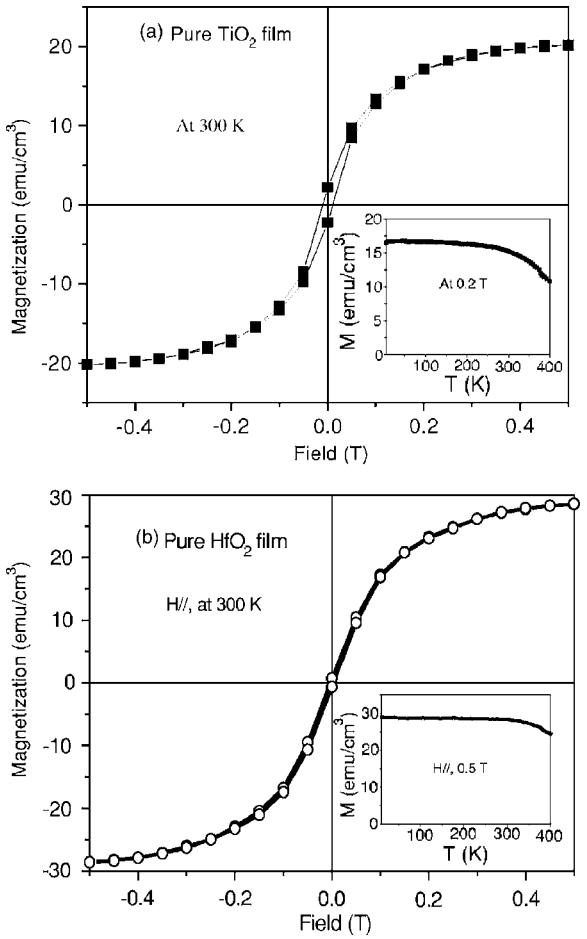

FIG. 1. Magnetization (a) versus magnetic field at 300 K for a pure TiO_2 film grown on a LAO substrate. The inset shows the *M-T* curve taken at 0.2 T and (b) versus magnetic field at 300 K for a pure HfO_2 film grown on an YSZ substrate. The inset shows the *M-T* curve taken at 0.5 T. (Note that the signals of substrates were subtracted already.)

YSZ substrates [see Fig. 1(b)], however the magnetization curve shows a much smaller hysteresis with the remnant magnetization of only about 0.7 emu/cm^3 (this feature is very similar to what was reported in Ref. 17). Not only are the HfO_2 films room-temperature ferromagnetic, but their magnetic moment is also very large (about 30 emu/cm^3). This value seems to be even larger than what Venkatesan *et al.* reported for their HfO_2 films on Al_2O_3 and Si substrate (as of $0.15\mu_B/HfO_2$ formula unit).[7] What can be the source for magnetism here? For the TiO_2 case, neither Ti^{4+} nor O^{-2} is magnetic. Also for the HfO_2 case, neither Hf^{4+} nor O^{-2} is magnetic. An initial assumption is that it is due to impurities. From the viewpoint of the purity of the targets, we must say that such a possibility is very small, since impurities of less than 10^{-2} wt. % could not create such huge magnetic moments. From the viewpoint of the structural properties of the deposited films, it is found that there is no trace of impurities that could be seen from x-ray diffraction (XRD) and films are single phase. One typical example is shown in Fig. 2 for the XRD pattern of the TiO_2 film on LAO. The film is very well crystallized, *c*-axis oriented, and only very strong-

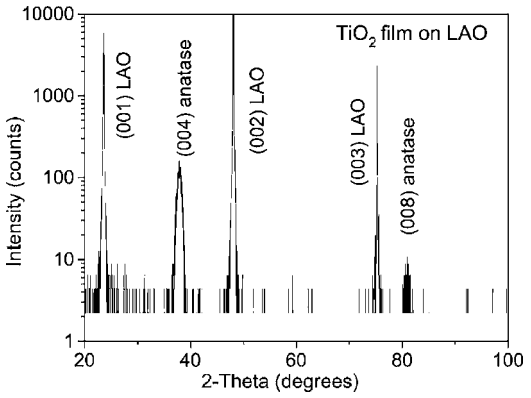

FIG. 2. XRD patterns for the TiO_2 film.

intensity peaks of pure anatase phase appear in the spectra.

Films of In_2O_3 on MgO are also room temperature ferromagnetic. However, these have a rather modest magnetic moment [Fig. 3(a)]. In contrast, from Fig. 3(b), one can see that films fabricated under the same conditions on Al_2O_3 substrates are diamagnetic. There is no report so far about In_2O_3 that could be magnetic, since In^{3+} could not be the source of magnetism. Even though In_2O_3 tends to create oxygen vacancies,[18] the fact that FM is observed on only one

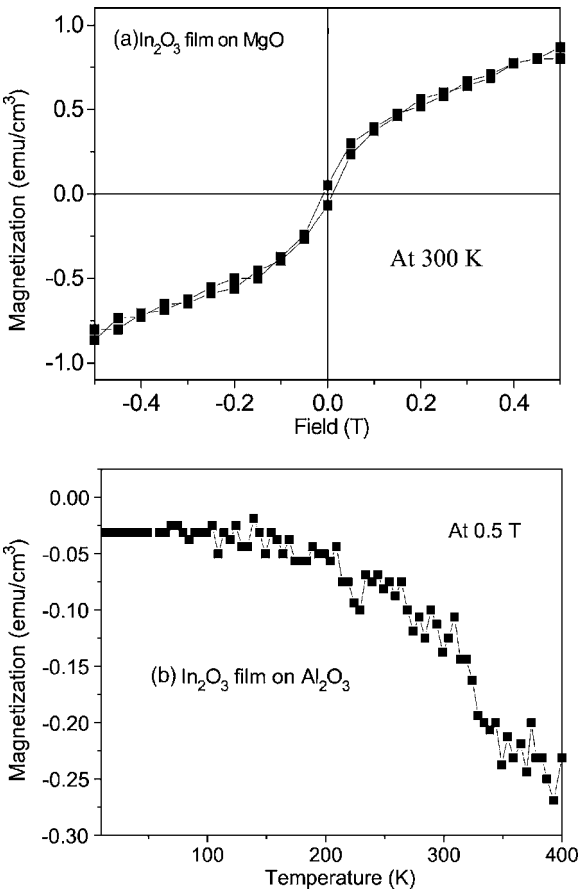

FIG. 3. Magnetization (a) versus magnetic field at 300 K for an In_2O_3 film grown on a MgO substrate and (b) versus temperature for an In_2O_3 film grown on an Al_2O_3 substrate. (Note that the signals of substrates were subtracted already.)

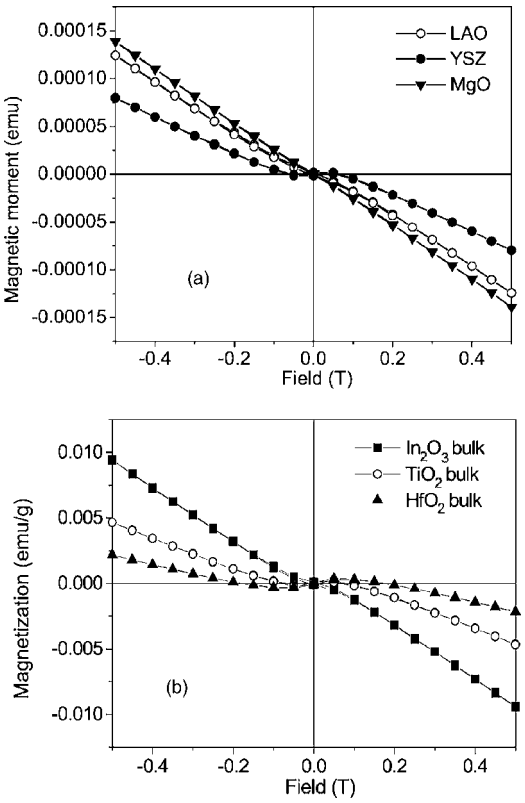

FIG. 4. Magnetization versus magnetic field taken at 300 K for (a) LAO, YSZ, and MgO substrates with the size of 5 mm $\times$5 mm$\times$0.5 mm and (b) for TiO_2, HfO_2, and In_2O_3 bulks (pieces cut from the ceramic targets).

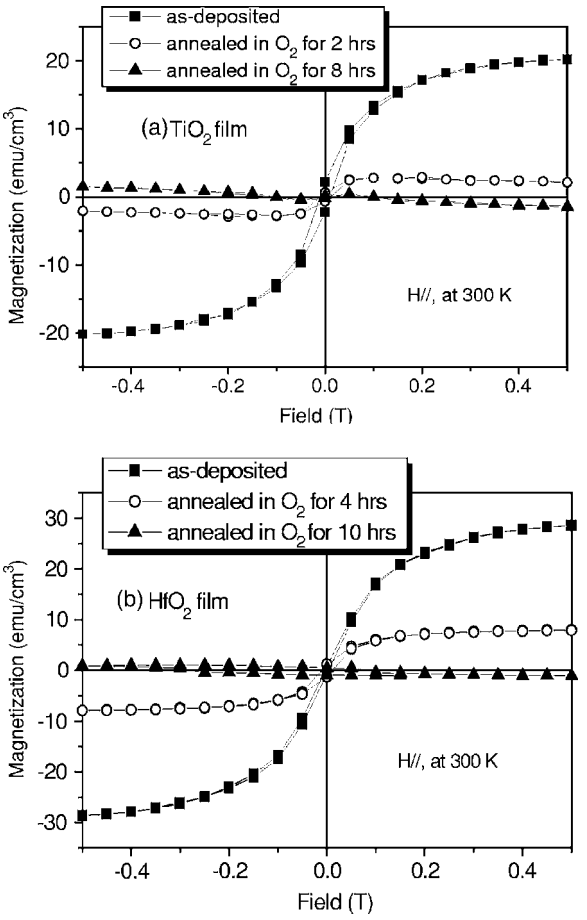

FIG. 5. Magnetization versus magnetic field taken at 300 K for (a) TiO_2 films as-deposited, annealed in O_2 at 650 °C for 2 h and for 8 h and (b) HfO_2 films as-deposited, annealed in O_2 at 800 °C for 4 h and for 10 h. (Note that the signals of substrates were subtracted already.)

type of substrate but not on the other implies some sort of defects that might cause such magnetism. We must assume that the origins for magnetism observed in In_2O_3, TiO_2, or HfO_2 films must be the same. In these families of compounds, magnetism should be d^0 magnetism. In other words, defects and/or oxygen vacancies might be the main source for the observed ferromagnetism as suggested in Ref. 7.

In order to check if there is any contamination of the substrates that might contribute to the observed FM, all the substrates were measured under the same sequences as for the films. All the bare substrates showed diamagnetic behavior as expected [Fig. 4(a)]. (We note here that all the pieces of straws that we used during the measurements were also checked carefully and all gave no magnetic signals.) Additionally, data of bulks likely support the assumption for FM due to the thin film form only. As one can see from Fig. 4(b), all bulk TiO_2, HfO_2, and In_2O_3 (i.e., pieces cut from the corresponding targets) are diamagnetic, or in other words, we must say that the room-temperature FM observed in TiO_2, HfO_2, and In_2O_3 films are very unique for the film form. At the moment, it is not possible to claim precisely that such remarkable FM at such high temperatures is due to defects on the Ti site. Similarly, it could not be claimed for the Hf site as the calculations in Ref. 14; or on In site. In addition, it is not possible at the moment to confirm the cause as due to defects at the interface between the films and the substrates (as in the case of Co:TiO_2 that Pradhan *et al.* reported in Ref. 19); or oxygen vacancies.[13] However, this surprising discovery makes us aware of a special class of compounds that urgently demands a different theory to explain.

In order to check if the magnetism in these systems is due to defects and/or oxygen vacancies, oxygen-annealing tests were done. Data of the oxygen annealed films of TiO_2 and HfO_2 are shown in Fig. 5 along with the data of as-deposited films in order to be able to compare directly. One can clearly see that annealing in the oxygen atmosphere for few hours can reduce the magnetic moments of those systems enormously. When we increase the duration of annealing up to 8–10 h, it is certainly possible to turn the samples from a ferromagnetic state to a diamagnetic state as that of the bulks. This evidence has clearly proved that the magnetism in those systems of undoped oxides really originates from oxygen vacancies: filling up vacancies could degrade magnetic moments, and could even destroy the ferromagnetic ordering completely. There is another small piece of evidence that can support this: Normally after several months of fabrication, samples tend to lose oxygen. As for TiO_2, HfO_2, and In_2O_3 films, after a few months, if we measured the samples again, we found an increase in magnetic moments. It is likely that those two features go along when supposing that magnetism is due to oxygen vacancies: since there are

more oxygen vacancies in the samples, the magnetic moment could be increased. On the other hand, if defects and/or oxygen vacancies are a possible source for magnetism in those types of films, a strong anisotropy is also well expected.[17] The data that we have shown above are for magnetic fields that were applied parallel to the film plane. We must say that basically in TiO_2 and HfO_2, FM is in-plane, since as magnetic fields applied perpendicular to the film plane, magnetic moments are much smaller (i.e., paramagnetism for TiO_2 films and a mixed state of diamagnetism and a small component of paramagnetism for HfO_2 films). In the case of In_2O_3 films, no anisotropy was found for films on MgO, however, for films on Al_2O_3, while there is no FM if magnetic field parallel to the film plane (as seen in Fig. 3), it is ferromagnetic in the perpendicular configuration.[20] In a good agreement with the authors of Ref. 17, we must say that the sign of anisotropy depends very much on the composition and the texture of each type of compound as well as the growth conditions. We also found that there is a strong thickness dependence of the magnetic moment in undoped oxide thin films: As for TiO_2 and HfO_2 films, the 10-nm-thick films have a magnetization of about 20–15 times (respectively) larger than that of the 200-nm-thick films.[20] Thus, the observed magnetism is certainly due to defects, but we must assume that those defects are localized mostly near the interface between films and the substrates. Since the compounds are wide band-gap semiconductors and/or insulators, a question would arise: if defect centers are expected to be far apart, how could a coupling mechanism be possible? The issue of whether defect centers are placed widely apart or not should be the key point here. Since the M in our case is huge (for 200-nm-thick films, it is $20-30\ \mathrm{emu/cm^3}$, for 10-nm-thick films it could be even more than $400\ \mathrm{emu/cm^3}$). If the observed FM is due to defects, then defects in the films fabricated by our conditions must be, in fact, very close to each other (the defect density should be very large), so that a direct coupling has become possible.

The finding of room-temperature FM in various types of undoped semiconducting and insulating oxide thin films grown on different types of substrates has called our attention to a new but common phenomenon: d^0 magnetism, or magnetism due to defects and/or oxygen vacancies. We must re-judge carefully the role that $3d$ element doping indeed could play in introducing FM in semiconducting hosts: Does the doping really introduce FM? Or, in fact, does it just enhance the magnetism that already exists in the oxide hosts under a thin film form? Could the doping of a transition metal contribute any paramagnetic component to the net moment of a pure oxide? Furthermore, the actual role that the temperature and oxygen pressure during the growth process could play in creating necessary defects and/or oxygen vacancies must be well clarified.

The authors sincerely thank A. Barla and N. Q. Huong for fruitful discussions, and P. Degenaar for a careful reading of the manuscript.

*Author to whom correspondence should be addressed. Email address: hoahong@delphi.phys.univ-tours.fr or nguyen.hoahong@univ-tours.fr

[1] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).
[2] N. Hoa Hong, J. Sakai, W. Prellier, A. Hassini, A. Ruyter, and F. Gervais, Phys. Rev. B **70**, 195204 (2004).
[3] M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, Phys. Rev. Lett. **93**, 177206 (2004).
[4] S. B. Ogale, R. J. Choudhary, J. P. Buban, S. E. Lofland, S. R. Shinde, S. N. Kale, V. N. Kulkarni, J. Higgins, C. Lanci, J. R. Simpson, N. D. Browning, S. Das Sarma, H. D. Drew, R. L. Greene, and T. Venkatesan, Phys. Rev. Lett. **91**, 077205 (2003).
[5] J. M. D. Coey, A. P. Douvalis, C. B. Fitzgerald, and M. Venkatesan, Appl. Phys. Lett. **84**, 1332 (2004).
[6] N. H. Hong, J. Sakai, W. Prellier, and A. Hassini, J. Phys.: Condens. Matter **17**, 1697 (2005).
[7] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, Nature (London) **430**, 630 (2004).
[8] N. A. Spaldin, Phys. Rev. B **69**, 125201 (2004).
[9] N. H. Hong, V. Brizé, and J. Sakai, Appl. Phys. Lett. **86**, 082505 (2005).
[10] D. A. Schwartz and D. R. Gamelin, Adv. Mater. (Weinheim, Ger.) **16**, 2115 (2004).
[11] P. V. Radovanovic and D. R. Gamelin, Phys. Rev. Lett. **91**, 157202 (2003).
[12] K. R. Kittilstved, N. S. Norberg, and D. R. Gamelin, Phys. Rev. Lett. **94**, 147209 (2005).
[13] N. H. Hong, J. Sakai, N. T. Huong, N. Poirot, and A. Ruyter, Phys. Rev. B **72**, 045336 (2005).
[14] C. Das Pammaraju and S. Sanvito, Phys. Rev. Lett. **94**, 217205 (2005).
[15] N. H. Hong, J. Sakai, N. Poirot, and A. Ruyter, Appl. Phys. Lett. **86**, 242505 (2005).
[16] N. H. Hong, J. Sakai, N. T. Huong, and V. Brizé, Appl. Phys. Lett. **87**, 102505 (2005).
[17] J. M. D. Coey, M. Venkatesan, P. Stamenov, C. B. Fitzgerald, and L. S. Dorneles, Phys. Rev. B **72**, 024450 (2005).
[18] *Semiconducting Transparent Thin Films*, H. L. Hartnagel, A. L. Daar, A. K. Jain, and C. Jagadish (IOP Publishing, Bristol and Philadelphia, 1995).
[19] A. K. Pradhan, D. Hunter, J. B. Dadson, T. M. William, K. Zhang, K. Lord, J. Zhang, D. J. Sellmyer, U. N. Roy, Y. Cui, A. Burger, C. Hopkins, N. Pearson, and A. L. Wilkerson, Appl. Phys. Lett. **86**, 222503 (2005).
[20] J. Sakai and N. H. Hong (unpublished).