Journal of Magnetism and Magnetic Materials 324 (2012) 3013–3016

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

High temperature ferromagnetism in cubic Mn-doped ZrO_2 thin films

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ARTICLE INFO

Article history:
Received 13 February 2012
Received in revised form
20 April 2012
Available online 15 May 2012

Keywords:
Mn-doped ZrO_2
Ferromagnetic semiconductor/insulator
Spintronic
Thin film

ABSTRACT

Theory has predicted that high temperature ferromagnetism (FM) should be found in cubic fake-diamonds, Mn-doped ZrO_2. Experimentally, it is shown that Mn-doped ZrO_2 ceramics are not ferromagnetic, but the nanosized Mn-doped ZrO_2 thin films grown on $LaAlO_3$ substrates can be ferromagnets with T_C above 400 K. The largest saturated magnetic moment (M_s) is huge as of about 230 emu/cm^3 for the $Mn_{0.05}Zr_{0.95}O_2$ films, and it decreases as the Mn content increases. The intrinsic FM is strongly associated with the cubic structure of Mn-doped ZrO_2, and the Mn–Mn interactions via oxygen intermediates are important. No electrical conductivity is observed. Mn-doped ZrO_2 thin films can be truly considered as excellent candidates for spintronic applications.

1. Introduction

Materials that can be used for spintronics must have both charge and spin that can be manipulated at room temperature. Thus, many research groups have tried to modify semiconductors in order to make them simultaneously room temperature ferromagnetic. After the theoretical suggestion of Dietl in 2000 [1] for doping Mn into ZnO in order to create magnetic *p*-type semiconductors with magnetic interaction via dopants, many experimentalists have investigated various oxides such as ZnO, TiO_2, SnO_2 and HfO_2 [2]. Even though they can be made ferromagnetic, the mechanism seems to be very different from what was expected: in most of the cases, it is proved that transition-metal doping does not play any key role, and the defects/oxygen vacancies should be the source for magnetism [3–8]. But the problem is, if the observed ferromagnetism (FM) is due to defects, then it is very difficult to control and manipulate for the purpose of applications. Therefore, we still look for a more certain and stable candidate.

Since the requirement for a good spintronics material is a big difference between the majority and minority spin density of states at the Fermi level, Ostanin et al., based on their *ab* initio electronic structure calculations, have suggested that Mn-doped cubic zirconia, which is known as synthetic diamond, might be a promising candidate for spintronics [9]. They predicted that Mn-doped ZrO_2 ceramics could be ferromagnetic above 500 K. This material is half-metallic with the majority and minority spin Mn impurity states lying in the wide gap of zirconia. The Mn concentration can exceed 40 at%, and the high-T_C FM is robust to oxygen vacancy defects, and thus facilitates the Mn impurities to distribute on the Zr *fcc* sublattice [9]. Theoretically, Mn-stabilized ZrO_2 is considered as a promising future spintronic material. Since 2007, some groups have tried, but not achieved: results of non-ferromagnetic phase in Mn-doped ZrO_2 were reported [10,11]. In some other cases, ferromagnetic phase was found, but the observed FM was supposed to be due to defects, since the pristine ZrO_2 films were found also ferromagnetic [12]. It seems that Mn doping does not play any big role in such a case. From that report, it looks like ZrO_2 should be classified as all other oxides (TiO_2, ZnO, SnO_2, and HfO_2) where one can manipulate its FM by controlling defects and oxygen vacancies. If it is really the case, then again, Mn-doped ZrO_2 should not be an ideal candidate for spintronics as it is hoped. However, nothing is very certain about this yet.

Our aim is to realize the intrinsic room temperature ferromagnetic Mn-doped ZrO_2 in order to verify if they can be indeed useful for the device market. In this paper, we will report about our systematic investigations.

2. Experiment

$Mn_xZr_{1-x}O_2$ targets (where $x = 0$, 0.05, 0.1, and 0.3) were prepared by a sol–gel method. 12- and 80 nm-thick-Mn-doped ZrO_2 films were deposited by the pulsed laser deposition (PLD) technique (248 nm KrF excimer laser, repetition rate of 10 Hz) on

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http://dx.doi.org/10.1016/j.jmmm.2012.04.047

(001) $LaAlO_3$ (LAO) substrates. The partial oxygen pressure (P_{O_2}) was 10^{-4} Torr, and the energy density was 2 J/cm^2. The substrate temperature was kept as 600 °C. After deposition, all films were annealed at 450 °C with the same P_{O_2} for 30 min, and then cooled down slowly to room temperature under a P_{O_2} of 20 mTorr. All films were deposited on substrates with the same size (3.5 mm × 3.5 mm or 5 mm × 5 mm, depending on each purpose) to be able to compare quantitative values directly. The structural analysis was done by X-ray diffraction (XRD) with Cu Kα radiation. The magnetic measurements were performed by a Vibrating Sample Magnetometry (VSM) in Quantum Design Inc. PPMS under a magnetic field from 0 to 2 T in the range of temperature from 380 K down to 5 K and a magnetic force microscope (MFM-Solver LS (NT-MDT)) operated at room temperature in zero field). For VSM measurements, magnetic moment of films and bare $LaAlO_3$ substrates of exactly the same dimensions were measured at the same conditions, in order to get rid of systematic error while subtracting.

3. Results and discussions

XRD data of Mn-doped ZrO_2 films are shown in Fig. 1. One can see that 5% Mn-doped ZrO_2 film has the best XRD pattern with *c*-axis orientation and shows clearly the ZrO_2 cubic structure, while the crystallinity becomes worse when the Mn concentration surpasses 10%.

Fig. 2 shows magnetization as a function of magnetic field applied parallel to the film plane at room temperature for all 80-nm-thick films with different concentrations of Mn. One can see that, except the undoped ZrO_2 film that is paramagnetic, all other films are ferromagnetic. The largest magnetic moment, and actually very huge, is obtained in the film with a very modest Mn

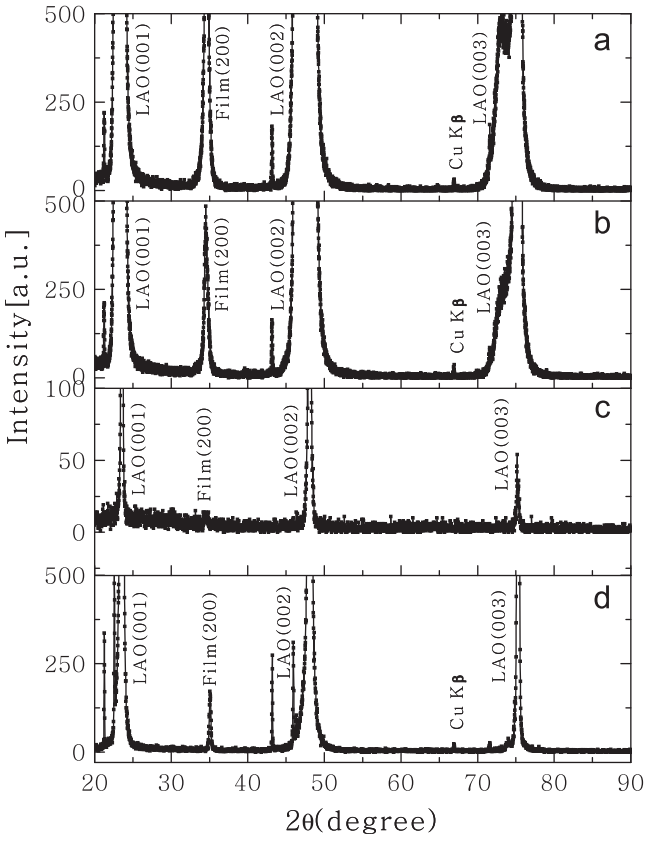

Fig. 1. XRD patterns of (a) ZrO_2, (b) 5% Mn-doped ZrO_2, (c) 10% Mn-doped ZrO_2, and (d) 30% Mn-doped ZrO_2 thin films (with the same thickness of 80 nm).

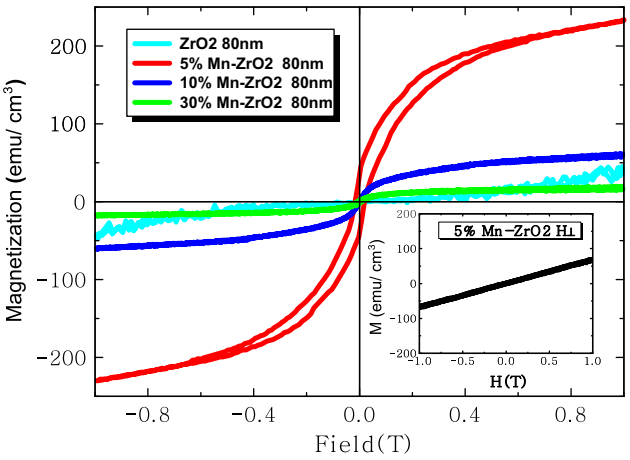

Fig. 2. Magnetization versus magnetic field (applied parallel to the film plane) taken at 300 K for 80-nm-thick $Mn_xZr_{1-x}O_2$ films (where $x = 0$; 0.05, 0.1 and 0.3). The inset shows *M*–*H* curve measured in magnetic field perpendicular to the film plane for the 5% Mn-doped ZrO_2 film taken at 300 K.

concentration of 5% (saturated magnetization, $M_s = 230$ emu/cm^3). As the Mn concentration increases, the magnetic moment enormously decreases. When Mn content reaches 30%, it loses 1 order of magnitude. From the inset for *M*–*H* curve (taken at 300 K) with magnetic field applied perpendicular to the film plane for the 5% Mn-doped ZrO_2 film, it is seen that at room temperature, in that configuration, the film shows a linear behavior without any saturation even up to 9 T (not shown in figure). It means that there is a strong anisotropy in the film (in-plane should be easy-axis). This observation is quite surprising since ZrO_2 crystal structure is cubic, but manganese valence states are 4^+ or 3^+ substituted in zirconium site that should have a non-zero orbital moment. However, it can be understood in terms of the texture of the film growth.

Ostanin et al. [9] predicted that Mn concentration can excess 40%, and even the Curie temperature (T_C) will increase and become much higher. But experimentally, it is proved not to be true. Seeing the degradation of magnetization as Mn concentration increases, it is not possible to think that T_C can be improved in such a case. More likely, once Mn is heavily doped, it cannot be incorporated well in the lattice, and its cubic structure is distorted. Look back at the XRD data for films (Fig. 1) that at a high concentration of Mn, the peak of ZrO_2 phase is very weak and vague, implying an amorphous structure, in the contrary with the case of slightly doped as Mn = 5%, film is very well oriented, showing clearly ZrO_2 phase with cubic structure ($a = 5.101$ Å for the undoped ZrO_2 case, and reduced when Mn concentration increases, $a = 5.09$ Å for Mn of 5%).

In contrast to the result reported in Ref. [12]that their undoped ZrO_2 films would be ferromagnetic, our result firmly shows that if the phase is well cubic, our laser ablated undoped ZrO_2 film is paramagnetic. One cannot blame that FM in Mn-doped ZrO_2 is due to oxygen vacancies/defects, since it shows clearly that the FM can be obtained only after doping Mn to the ZrO_2 host. The ZrO_2 is known to be wide band gap semiconductor ($E_g \sim 5$–7 eV). Our films of Mn-doped ZrO_2 are very electrically resistive, with almost no free carriers at room temperature. If we try to attribute the observed FM to Mn doping, so that express magnetization per Mn atom, it will lead to the value of Ms as 13.8 μ_B/Mn. To have the magnetization of the sample in unit of Bohr magnetons per Mn, one must normalize based on the number of Mn cations thought to be in the sample. Note that this value of magnetization in Bohr magnetons per Mn is useful only for reference because it may mislead when the oxides are not dilute magnetic