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Ferromagnetism in doped TiO_2 thin films prepared by PLD

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Abstract. Transition-Metal-doped TiO_2 thin films, with nominal composition $Ti_{0.9}TM_{0.1}O_{2-\delta}$ (TM = Mn, Fe, Co, Ni, Cu), were grown by pulsed laser deposition (PLD), in order to study the role of dopants in the origin and significance of room temperature ferromagnetism in these systems. The crystallographic structures and their magnetic properties were characterized and the experimental results are compared to ab-initio calculations previously reported. The films are ferromagnetic at room temperature in the cases of Fe, Co, Ni and even Cu impurities, but not in the case of Mn doping. Our results support the hypothesis that oxygen vacancies play a key role in the origin of magnetism in doped TiO2 films, and can explain the diversity of magnetic moments observed experimentally for films grown under different conditions.

1. Introduction

Dilute magnetic semiconductors (DMS) consist of nonmagnetic semiconducting materials doped with a few atomic percent of impurity magnetic cations and are envisioned as functional components of many proposed spintronic devices [1]. Considerable success has been achieved in this direction in the domain of III-V and group IV semiconductors [2 and references therein], although these systems have low Curie temperatures that limit its applications.

The prediction of above-room-temperature ferromagnetism (FM) in Mn:ZnO by Dietl et al. [3] and the first report of high temperature FM in anatase $Co:TiO_2$ by Matsumoto et al. [4] have attracted much attention as well as controversy.

Co-doped TiO_2 anatase has been reported as the most magnetically robust DMS, with Curie temperatures above 400K. At first, ferromagnetism in Co-doped TiO_2 was explained in terms of carrier induced mechanism, as in III-V based DMS´s [5]. However, Griffin et al. in a recent work provided experimental evidence of intrinsic ferromagnetism in insulating Co doped anatase TiO_2 films [6]. Other authors, like Shinde et al. [7], claimed that ferromagnetism is due to the formation of Co clusters within TiO_2 structure. So far, the precise mechanism is still controversial and is being actively debated in the literature, but with no doubt the magnetic behavior is strongly sensitive to the synthesis method. Recently, the idea that vacancies and defects are essential to ferromagnetic order is being strongly considered [8]. It seems that the appearance of a magnetic moment may depend on the

vacancy concentration in the oxide and on the structure. An experimental observation of magnetism in an undoped nonmagnetic oxide and in Cu doped TiO_2 films has been recently reported and attributed to vacancies also [9, 10].

We present here the structural and magnetic characterization of a set of pulsed lased deposited thin films with nominal composition $Ti_{0.9}TM_{0.1}O_{2-\delta}$ (TM = Mn, Fe, Co, Ni, Cu). Our results support the hypothesis that oxygen vacancies play a key role in the origin of magnetism in doped TiO_2 films and discard that clustering of magnetic dopants should be a condition for the presence of magnetism in DMS.

2. Experimental details

Thin films of approximately 10 at. % Fe, Co, Ni, Mn or Cu-doped $TiO_{2-\delta}$ were deposited on $LaAlO_3$ (001) substrate (LAO) by Pulsed Laser Deposition (PLD), using a Nd:YAG laser operating at 266 nm. The doped TiO_2 target was prepared from high purity TiO_2 and metallic TM powders in stoichiometric quantities. The powders were mixed for three minutes using a ball-mill, then uniaxially pressed (200 MPa) into a disk, and finally sintered. The substrate temperature, laser energy density, oxygen pressure, and pulse repetition rate were 800 °C, 2 J/cm^2, 20 Pa, and 10 Hz, respectively. The composition was determined by Energy Dispersive X-Ray Analysis (EDX), and no contaminants where found within the accuracy of the method (< 1 wt. %). The crystalline structure was studied by X-Ray Diffraction (XRD). The measurements of magnetization *M* as a function of the applied magnetic field *H* were performed with a commercial Vibrating Sample Magnetometer Lake Shore 7407 at room temperature, with the external field applied parallel and perpendicular to the plane of the film.

3. Results and Discussion

Our films (80-120 nm thickness) were transparent and strongly textured, showing only the (001) reflections of the anatase structure. Furthermore the Ni, Mn, Cu and Fe doped TiO_2 films showed very weak additional lines corresponding to the rutile phase. Only in the cases of Fe and Co doping, (104) ilmenite reflection is also present. The lattice mismatch between anatase TiO_2 (001) and $LaAlO_3$ (001) is only 0.26 %, much less than for rutile, so anatase is favored when deposition is performed on (001) LAO substrate.

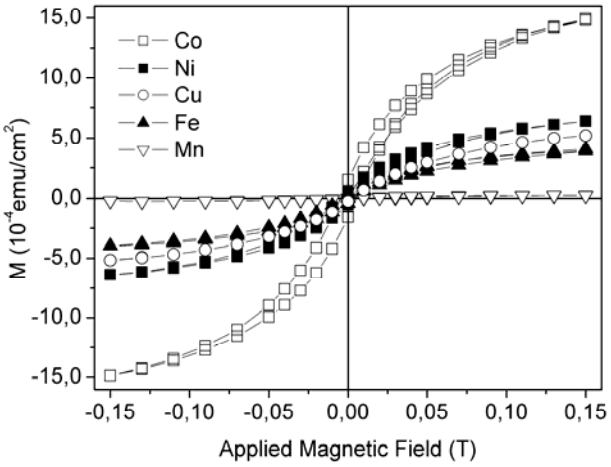

Figure 1: Room temperature magnetization curves of $Ti_{0.9}TM_{0.1}O_{2-\delta}$ films (TM = Mn, Fe, Co, Ni, Cu) with the magnetic field applied parallel to the plane of the film

After subtraction of the diamagnetic contribution of the $LaAlO_3$ substrate we obtained the result depicted in Fig. 1, where significant room temperature magnetization is displayed for Co. For Ni, Cu and Fe doped films a hysteretic behavior is also found, but the amplitude of the spontaneous

magnetization is smaller than that of the Co doped film. Practically no magnetic effect was observed in the Mn doped sample. In order to quantify the magnetic parameters (saturation magnetization M_s, intrinsic coercivity Hc, and remanent magnetization M_r) we use the following fitting function for the demagnetization data:

$$M = M_s \left[\left(\frac{2}{\pi} \right) \left(\arctan\left(\frac{H + H_c}{H_c} \right) \frac{1}{2} \left(\tan \frac{\pi}{S} \right) \right) \right] + \chi H \qquad (1)$$

where $S=M_r/M_s$. The first term is the usual function used to represent a ferromagnetic hysteresis curve [11] and the second one is a linear component representing a possible paramagnetic contribution. The parameters obtained from the fitting are summarized in Table I. The moment per 3d dopant deduced from the saturation magnetization (assuming 10 at.% of dopant and a 100 ± 20 nm film thickness) are those shown in Fig. 2. As can be seen, the experimentally obtained magnetic moment for Co ions is close to the expected one for Co^{+3} in its high spin state (4 μ_B), while Fe and Ni magnetic moments are considerably smaller than the former. For the Cu doped films, significant room temperature magnetic behavior, so strong to give a magnetization equivalent to 1.5 μ_B /Cu was found. This unexpected result supports the idea that neither doping with magnetic atoms nor clustering of them are essential to find room temperature ferromagnetism in TiO_2 films. Nevertheless, the presence of magnetic ions replacing Ti in the anatase or rutile structure will also contribute to the magnetic response depending on the concentration and distribution of them. Particularly, in the case of Mn, no ferromagnetic signal was found in our films.

Table 1: Saturation magnetization (M_s), Coercive Field (H_c) and magnetic susceptibility (χ) obtained from the experimental M vs B curves

3d dopant	Mn	Fe	Co	Ni	Cu
M_s (emu/cm^2)	$0.03_1 \times 10^{-3}$	$0.36_2 \times 10^{-3}$	$1.36_4 \times 10^{-3}$	$0.56_2 \times 10^{-3}$	$0.48_2 \times 10^{-3}$
H_c (Oe)	0_9	42_4	56_2	49_3	35_3
χ (emu/cm^2 Oe)	-	$2.0_1 \times 10^{-8}$	$0.7_2 \times 10^{-8}$	$0.4_1 \times 10^{-8}$	$0.5_1 \times 10^{-8}$

A theoretical study for a system of these physical characteristics: concentration, dopant distribution, surface effect, same TiO_2 phase, etc., has been not performed yet. Therefore only a qualitative comparison with a theoretical work is possible and the following discussion is performed under this consideration. Ab initio calculations on doped TiO_2 rutile reported in [12] predict larger atomic moments for Fe (2.24 μ_B/at.) and Mn (2.54 μ_B/at.) than for Co (0.63 μ_B/at.), while no magnetic moment is found for Ni and Cu. They are originated on the impurity *d*-states, which are hybridized with *p*-oxygen states, and a related feature appears in the host band energy gap. However, the magnetic ordering results antiferromagnetic for Mn and also for Fe in some geometrical distributions but ferromagnetic for Co. Then, the experimental low saturation magnetization values for Fe and Mn doped films, as compared to Co doped one, can be understood.

However, when oxygen vacancies are introduced along with the magnetic impurities in the ab initio calculations, the results show that a strong interaction between oxygen vacancies and impurities increases the local magnetic moment and induces a magnetic behavior in the cases of Ni and Cu [10,13]. It also predicts that doping lowers the formation energy of vacancies, so that doped systems would have more vacancies than the undoped ones. Hence, the experimental observation of magnetism in samples doped with Cu may result from a high concentration of oxygen vacancies.

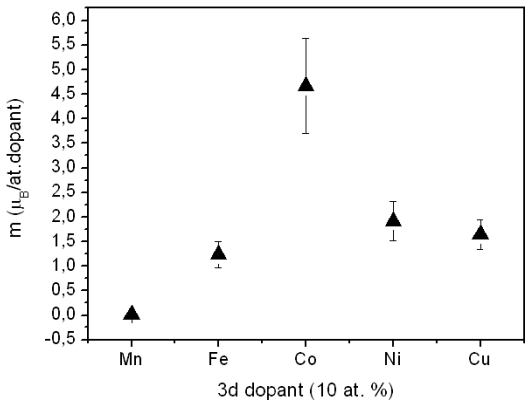

Figure 2: Dopant atomic magnetic moment in $Ti_{0.9}TM_{0.1}O_{2-\delta}$ films (TM = Mn, Fe, Co, Ni, Cu) deduced from the saturation magnetization

4. Conclusions

We have found that doping TiO_2 thin films with magnetic or non-magnetic ions result in a magnetic behaviour that depends on the spatial distribution of the dopant and on the concentration of oxygen vacancies. When doping with Mn, no room temperature ferromagnetic signal is found due to antiferromagnetic ordering, while for Cu doping the TiO_2 films displayed a vacancy mediated magnetism since it has been shown that its presence increases the formation of oxygen vacancies. For Co, Ni and Fe, the ferromagnetic signal can be due to ferromagnetic coupling between magnetic ions enhanced by the presence of anionic vacancies. Finally, the experimental results of Cu doped samples show that clustering of magnetic dopants is not a condition for the presence of magnetism in DMS.

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