Effects of Al–Mn co-doping on magnetic properties of semiconducting oxide thin films

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We conducted an experimental investigation of the structural and magnetic properties of Al–Mn-doped ZrO2 and ZnO thin films. It was found that, even though additional Al doping does not substantially enhance ferromagnetism (FM), it influences surface magnetism by enhancing it. Increase of the Al concentration slightly improves the overall magnetization of the Al–Mn-doped ZrO2 sample, however, this effect is also accompanied by a deterioration of the crystallinity of the sample. On the other hand, we found that by co-doping the Mn-doped ZnO samples with Al, the result is a significant increase of the magnetic moment. Apart from the surface effects, the data clearly indicate that the observed FM originates from defects. Our results confirm that co-doping with Al can be an efficient way to enhance magnetism and control the distribution of defects for certain transition-metal-doped semiconducting oxides.

1 Introduction Doped dilute magnetic oxides such as ZrO2, ZnO, and similar semiconducting oxides have attracted a lot of attention during the last decade because of their attractive magnetic properties such as high Curie temperature and possible applications in spintronics and other spin-related devices [1]. Typically, this family of semiconducting materials has been doped with transition-metals such as Co, Mn, etc., in order to improve their magnetic properties. The resulting magnetic properties of the system depend crucially on what dopants are used, the oxygen environment and the nature of the distribution of the dopants in the host lattice (whether such distribution is homogeneous or not). Even though the general belief is that the dopant substitution at the Zr sites in the ZrO2 host is more or less random, there is evidence (for instance, as observed in ZnO samples) that magnetic ions have a tendency to couple via oxygen (O), thus, giving rise to clustering/aggregation processes [2, 3].

This type of mechanism, namely, coupling of magnetic moments via oxygen appears to be very common if not universal [4]. In this framework, one may intuitively expect the formation of a variety of aggregated structures (for instance, cluster-like, chain-like, or lamellar-like structures) due to the mediated magnetic interaction between Mn ions. Interestingly, such a tendency even bears some resemblance to similar processes that happen in systems of magnetic ferro-fluids [5–7]. It is also known that in most of the cases, the tendency towards aggregation results in antiferromagnetic (AF) coupling and this is not at all desirable in the context of various magnetic applications.

Calculations indicate that co-doping with a metallic material (like Al, Cu, etc.) can reduce the tendency of magnetic ions towards forming aggregates, thus, enhancing the homogeneous distribution of magnetic impurities [8]. The basic idea of various theoretical frameworks is that co-doping may effectively introduce FM coupling between magnetic ions. The logic is that, if each magnetic ion of a pair is AF-coupled to an Al (or Cu) dopant, then they become effectively FM-coupled to each other [8, 9]. Based on this argument, it is expected that additional co-doping with...
metallic ions may enhance ferromagnetism in diluted semiconductors at room temperature. In addition, this would also provide a route to suppress the tendency towards aggregation and, thus, achieve a more homogeneous distribution of magnetic dopants.

Room temperature ferromagnetism (FM) was clearly observed in undoped ZnO thin films [10]. It has been found that FM in this compound does not originate from oxygen vacancies, but from defects on Zn sites. Since the magnetization of very thin films is much larger than that of thicker ones, the indication is that defects are located mostly on the surface and/or at the interface between the film and the substrate. We must remark that Mn-doped ZnO films are considered as a rather delicate case in the realm of magnetic materials. Some earlier theoretical work has suggested that doping of ZnO only with Mn would not result in FM behavior since the ground state of Mn-doped ZnO films is expected to be an AF one [11, 12]. This implies that, in order to obtain FM, one should co-dope Mn with another metallic material (like Cu) so as to create additional carriers [8]. However, experiments have shown that doping of ZnO films with 10% of Mn alone could result in FM. This behavior was attributed to oxygen vacancies created during the film growth [13]. The Mn-doped ZnO film of this type is FM at room temperature with a saturated magnetic magnetization of about 7 emu/cm\(^3\). This value is three times larger than that of the undoped ZnO films [10]. Since the undoped ZnO films are themselves FM, it was demonstrated that Mn doping is not directly responsible for the observed magnetism in ZnO films. However, Mn doping contributes some additional FM coupling via the double exchange interaction. Therefore, it is expected that there might be two possible sources of magnetism in Mn-doped ZnO films: (i) defects that may take place on the Zn sites in the ZnO base; and (ii) Mn doping effects.

Recently, we have obtained data for Mn-doped ZrO\(_2\) films. Nanometer-sized Mn-doped ZrO\(_2\) thin films can be FM with a \(T_C\) above 400 K. It is believed that this occurs because of confinement effects and the special oxygen atmosphere that exists only in low-dimensional materials. The maximum saturated magnetic moment (\(M_s\)) is large for a 5% Mn-doped ZrO\(_2\) film and it decreases as the Mn content increases [14]. The intrinsic FM behavior of this material is strongly associated with the cubic structure of Mn-doped ZrO\(_2\) thin films as well as Mn–Mn interactions via oxygen intermediates.

In this work, we investigate the magnetic properties of ZrO\(_2\) and ZnO thin films that have been co-doped with Al–Mn. A key objective of our work is to inquire whether co-doping leads to an enhancement of magnetic moments in diluted semiconducting thin film compounds with possible application in the field of spintronics.

2 Experiments Al\(_{1-x}\)Mn\(_x\)Zr\(_{1-y}\)O\(_2\) (where \(x = 0.01, y = 0; x = 0.01, y = 0.04; \) and \(x = 0.04, y = 0.01\) and Al\(_{0.01}\)Mn\(_{0.01}\)Zn\(_{0.98}\)O targets were prepared by a sol–gel method. 10 nm- and 200 nm-thick Al/Mn-doped ZrO\(_2\) films were deposited by the pulsed laser deposition (PLD) technique (248 nm KrF excimer laser, repetition rate of 10 Hz, energy density was 2.1/cm\(^2\)) on (001) LaAlO\(_3\) (LAO) substrates, while the 10 nm- and 50 nm-thick Al/Mn-doped ZnO were deposited by the same technique (repetition rate of 5 Hz) on \(R\)-cut Al\(_2\)O\(_3\) substrates. The partial oxygen pressure (\(P_{O_2}\)) was 10\(^{-5}\) Torr for Al/Mn-doped ZrO\(_2\) and 10\(^{-6}\) Torr for Al/Mn-doped ZnO films. The substrate temperature was kept at 650°C. After deposition, all films were annealed at 450°C with the same \(P_{O_2}\) as during the growth for 30 min, and then cooled down slowly to room temperature under a \(P_{O_2}\) of 20 mTorr. Some films of Al/Mn-doped ZnO were post-annealed in the tube furnace at 600°C for 10 h in an oxygen atmosphere with a \(P_{O_2}\) of 760 Torr. Note that all films were deposited on substrates with the same size as of 5 mm × 5 mm. The structural analysis was done by X-ray diffraction (XRD) with Cu K\(_\alpha\) radiation. Magnetic measurements were performed by applying the Vibrating Sample Magnetometry (VSM) technique on a Quantum Design, Inc. PPMS-9 T platform in a magnetic field applied parallel to the film plane with values ranging from 0 to 2 T, at room temperature. For the VSM measurements, magnetic moment of films and bare substrates of exactly the same dimensions were measured in the same conditions, in order to eliminate systematic errors.

3 Results and discussion The XRD data for Al–Mn-doped ZrO\(_2\) thin films grown on LaAlO\(_3\) substrates show that the samples are cubic phase with no alien peaks of other phases (see Fig. 1). When we compared the Mn-doped ZrO\(_2\) films (XRD data shown in Fig. 1(a)) to those co-doped with Al (Fig. 1(b) and (c)), we found that Al–Mn co-doping seems to degrade the ZrO\(_2\) crystallinity. The situation is quite different for Al–Mn-doped ZnO films grown on sapphire substrates [15]. In such a case, co-doping of Al and Mn does not result in any significant deterioration of the wurtzite structure of ZnO films: from Fig. 2 one can see that all films of Al/Mn-doped ZnO show a very good ZnO structure.

In Fig. 3 we show the curves of magnetization versus magnetic field taken at room temperature of ZrO\(_2\) films doped with Al alone (1%) and then co-doped with Mn (Al = 1%; Mn = 4%). We compare such results to the ZrO\(_2\) films with the same thickness, but doped with 5% of Mn (no Al). The comparison between magnetic moments shown in Fig. 3(a) and (b) with the data shown in Fig. 3(c) indicates that doping with Al results in a much weaker ferromagnetism (almost two orders of magnitude) [4, 14]. On the other hand, in the co-doped Al/Mn–ZrO\(_2\) films, one can see that a much larger magnetization could be observed in thinner films in comparison to what observed in a thicker film showing that Al doping seems to enhance the surface effects. Although surface effects already exist in Mn-doped ZrO\(_2\) films (see Ref. [4]), one can see from Fig. 3(b) that such effect becomes more pronounced in Al–Mn-doped ZrO\(_2\) films. While Fig. 3(a) shows that thinner films of Al-doped ZrO\(_2\) are paramagnetic while the thicker film is a weak ferromagnetic; Fig. 3(b) shows that with co-doping of 1% Al and 4% Mn for
ZrO₂, the thinner film can have a larger magnetic moment in comparison to the thicker films. We conclude that it is not likely that Al can stabilize defects in ZrO₂ films, a behavior that is somehow different from what was reported for the Al-doped MgO case [9]. In our experiments, defects seem to lie somewhere near the surface of the films with the main effect of disturbing the film’s structure (this is consistent with what was seen from XRD measurements that show a degradation of crystallinity in Fig. 1(b) and (c)). We must also recall that FM in Mn-doped ZrO₂ thin films was shown not to originate from defects (see reproduced figure for undoped ZrO₂ and 5% of Mn-doped ZrO₂ films shown in Fig. 3(c)) [15]. This might explain why co-doping with Al does not seem to be a feasible choice for this case.

This observation was re-enforced when we considered the effect of increasing the Al concentration on the co-doped Al–Mn–ZrO₂ samples. The M–H curves taken at room temperature for Al₀.₀₁Mn₀.₀₄Zr₀.₉₅O₂ and Al₀.₀₄Mn₀.₀₁⁻Zr₀.ₙ₅O₂ films are shown in Fig. 4. One can see that the magnetic moment is only slightly enhanced by increasing the Al concentration. However, in this case, the crystallinity of co-doped ZrO₂ films is degraded. As can be seen from Fig. 1(c), the intensity peaks of the film almost disappear and the film becomes amorphous.

Before discussing about the effects of Al co-doping in Mn-doped ZnO films, we would like to summarize here some of the main properties of ZnO and Mn-doped ZnO films. Un-doped ZnO films can be ferromagnetic (due to defects), however, doping with Mn could enhance the magnetic moment of ZnO films (saturated magnetization was found to be about 7 emu/cm³) [10]. The experiments seem to suggest that, for the case of Mn-doped ZnO films, the sources for ferromagnetism are defects that may occur on the Zn sites in the ZnO host lattice.

Fig. 5 illustrates the effects of Al co-doping on the magnetism of Mn-doped ZnO films (Al = 1%; Mn = 1%). We found that co-doping with Al of Mn-doped ZnO samples results in a significant enhancement of the magnetism (ferromagnetism is a little bit weak for the 50 nm thick-film, however, it reaches about 27 emu/cm³ for the 10 nm-thick film, indicating a strong surface effect). Apart from the observation of an enhanced surface magnetism, our experimental data indicate clearly that the observed FM in

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**Figure 1** XRD patterns for (a) Mn₀.₀₅Zr₀.₉₅O₂, (b) Al₀.₀₁Mn₀.₀₂Zr₀.₉₅O₂, and (c) Al₀.₀₂Mn₀.₀₁Zr₀.₉₅O₂ thin films.

**Figure 2** XRD patterns for Al₀.₀₁Mn₀.₀₁ Zn₀.₉₈O₂ films on R-cut sapphire substrates.
Al–Mn-doped ZnO films is due to defects given that annealing in oxygen atmosphere radically changes the magnetic moments of the films (see the two insets showing two cases for films of 10 nm- and 50 nm-thick Al/Mn-doped ZnO films). Some group has discussed on poly-crystals about effects of grain boundaries and interfaced boundaries on the magnetic properties of ZnO (Ref. [15]), but in our case of very thin films, it would be more correct to attribute the observed enhancement of FM to the confinement effects (i.e., low dimension systems) since the properties of bulk and films should not be seen from the same angle.

When the results for Al/Mn-doped thin films are seen together with the Al/Mn-doped ZrO2 ones discussed earlier, we would conclude that Al doping alone does not provide a...
significant enhancement of ferromagnetism in these types of semiconducting oxide films. However, co-doping of Al with Mn can improve ferromagnetism under the condition that the un-doped host oxide itself is ferromagnetic due to defects (this would be the case of the pristine ZnO film). In other words, our experiments suggest that Al doping can help to stabilize defects in a way that leads to enhancement of the magnetic moments that are already present there.

The case of un-doped ZrO$_2$ films appears to be different from that of ZnO case since ZrO$_2$ films are not ferromagnetic in the first place (as noted in Ref. [14], there is no magnetism due to defects in Mn-doped ZrO$_2$ films). Since co-doping with Al influences the ferromagnetism that arises from defects, it is logical to expect that co-doping with Al would not cause any significant change in Mn-doped ZrO$_2$ films. The only measurable effect observed for the case of Al/Mn-doped ZrO$_2$ thin films should be a more pronounced surface magnetism occurring simultaneously with a deterioration of crystallinity.

4 Conclusion We investigated the effects of co-doping Al with Mn in ZrO$_2$ and ZnO thin films. The results indicate that, for Mn-doped ZrO$_2$ films, Al does not enhance the overall ferromagnetism, but only makes the surface magnetism more pronounced. An increase of the Al concentration causes a slight improvement of the magnetic moment, but simultaneously degrades the crystallinity of the original ZrO$_2$ films.

On the other hand, for Mn-doped ZnO films, we found that co-doping with Al could significantly enhance the magnetic moments. In addition to surface effects, our data show that the observed FM in Al/Mn-doped ZnO films is due to defects. The indication is that co-doping with Al can be an efficient method to enhance magnetism in Mn-doped ZnO films and control the distribution of defects in such a material. Within the larger family of transition-metal-doped semiconducting oxides, we would be tempted to suggest that co-doping with Al will enhance ferromagnetism as long as magnetism originates from defects (like the case of ZnO films). However, we would not expect sizeable effects for the case of intrinsic ferromagnetic materials (like the case Mn–ZrO$_2$ films). Obviously, in order to conclude whether the behavior is universal or not, more studies are needed in the future to see if other oxides (such as TiO$_2$, SnO$_2$, HfO, CeO$_2$, etc.) manifest similar features.

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