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Role of defects in tuning ferromagnetism in diluted magnetic oxide thin films

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In order to answer the question of whether there is another source of magnetism that plays an important role in tuning ferromagnetism in diluted magnetic oxide thin films, investigations on magnetic and structural properties of some types of transition-metal-doped semiconductors had been done. Results on Cr-doped ZnO and Ni-doped SnO_2 films fabricated under various conditions implied that structural defects and/or oxygen vacancy, indeed, very much influence the magnetism in those systems. An elimination of defects, as well as filling up oxygen vacancies, might cause certain degradation to the ferromagnetic ordering of some specific types of compounds.

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Diluted magnetic semiconductors (DMS) have been considered as very promising candidates for spintronics. Recently, many research groups have done profound studies on room-temperature ferromagnetism (FM) in various types of transition-metal (TM)-doped-oxide thin films, such as TM-doped ZnO,[1] TM-doped TiO_2,[2] or TM-doped SnO_2.[3–5] In this field, there are many controversial issues that need to be clarified: for example, why does T_C not depend on the concentration of magnetic element; why can doping by nonmagnetic elements, such as V, result in strongly ferromagnetic samples; why, in some case is the bulk simply not magnetic, but the thin films of the same compositions could be magnetic, etc.[6–9] In those systems, the ferromagnetism cannot simply be attributed just to a secondary phase, even though standard theories of magnetism could hardly explain it. Several assumptions have been addressed at the moment: the role of anisotropy, the connection between defects and magnetism, oxygen vacancy, long-range exchange interaction, etc.[1,8,10,11] In DMS, nonmagnetic host ions are partially substituted by dopant ions, which are randomly localized over the host lattice. Thus, this kind of disorder certainly breaks the translation symmetry of the system. As a consequence, no simple theory can sufficiently explain everything.[12] Bergqvist *et al.* claimed that the magnetic percolation might strongly influence the ordering in DMS, and the agreement between theory and experiment could be achieved only if the magnetic atoms are randomly positioned. Or in other words, the magnetic ordering in the semiconductor lattices critically depends on the preparation conditions of the samples that may result in a wide range of ordering temperatures.[13] Recently, Hong *et al.* reported that applying appropriate growth conditions would be a very crucial factor in order to obtain room-temperature FM.[9] The question arises of whether, in DMS, there is some other source for magnetism rather than simply the ferromagnetism induced by the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction. In order to verify this issue, we have thoroughly investigated the magnetic and structural properties of Cr-doped ZnO and Ni-doped SnO_2 thin films, which were fabricated under different growth conditions as well as different treatments.

Thin films of Cr-doped ZnO and Ni-doped SnO_2 were fabricated by the pulse-laser deposition (PLD) technique (KrF, $\lambda = 248$ nm, 10 Hz, 1.8 J/cm^2) from $Cr_{0.05}Zn_{0.95}O$ and $Ni_{0.05}Sn_{0.95}O_2$ ceramic targets, respectively. The typical thickness of the films is about 200 nm. (001) $LaAlO_3$ and *R*-cut Al_2O_3 substrates were used for $Ni:SnO_2$ and $Cr:SnO_2$ films, respectively. Basically, we used the substrates with the same size of 5×5 mm^2. But as for $Ni:SnO_2$ films, in order to verify the effects of constraints and/or defects, films with different thickness, and also deposited onto substrates of different sizes, were made. Regarding the films of $Ni:SnO_2$, the substrate temperature was 700 or 750 °C; during deposition, the oxygen partial pressure P_{O_2} was kept as 10^{-4} or 10^{-6} Torr; after deposition, films were cooled down to room temperature under the same oxygen pressure as during deposition. As for films of Cr:ZnO, two sets of growth conditions were used: films were fabricated at 650 °C under an oxygen partial pressure P_{O_2} of 10^{-1} Torr, then cooled down under 300 mTorr, or at 400 °C under P_{O_2} of 10^{-6} Torr, then cooled down under 20 mTorr. In order to elucidate the effects of oxygen on magnetism, some samples of Cr:ZnO were also postannealed at 500 °C during 12 h in an oxygen atmosphere with a pressure of 760 Torr. The structural study was done by x-ray diffraction (XRD). The chemical composition was determined by Rutherford backscattering spectroscopy

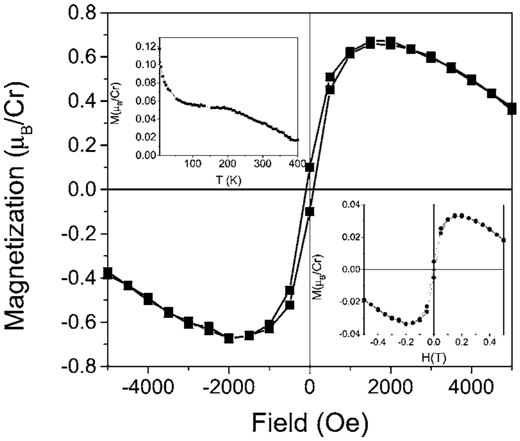

FIG. 1. Magnetization vs magnetic field at 300 K for a Cr:ZnO film fabricate at 650 °C under a P_{O_2} of 10^{-1} Torr. The upper inset shows the *M-T* curve taken at 0.5 T. The bottom insets show the *M-H* curve taken at 300 K for the film that was postannealed in an oxygen atmosphere.

(RBS). The magnetic moment M was measured by using a Quantum Design superconducting quantum interference device (SQUID) system under magnetic fields H from 0 up to 0.5 T for a range of temperatures T from 400 K down to 5 K.

The Cr:ZnO films deposited at 650 °C showed clearly room-temperature FM (see Fig. 1). Apart from the region of high field of the *M-H* curve showing a down slope that must be related to some residual contribution of the substrate that could not be deducted completely,[14] the film is obviously room-temperature ferromagnetic with the Curie temperature T_C higher than 300 K. One can see from Fig. 2(a) that this film has a wurtzite structure with all the peaks of ZnO; however, those peaks are rather broad and have no strong intensity, indicating that this film likely does not have a very good crystallinity. Note that after annealing, the magnetic moment of the film reduced to be one order smaller (see the bottom inset of Fig. 1) while simultaneously, the film crystallization was clearly improved. By comparing the spectra in Figs. 2(a) and 2(b), one can see clearly that after annealing, the film has much sharper peaks with a stronger intensity. The same tendency could be seen for Cr:ZnO films that were fabricated at 400 °C. The as-grown film is clearly ferromagnetic [Fig. 3(a)], but the FM disappears when that film was postannealed in an oxygen atmosphere [Fig. 3(b)]. From Fig. 3(b), one can see that the film lost the ferromagnetic ordering and was formed as diamagnetic instead. The disappearance of the FM goes along with a much better crystallinity [compare XRD spectra in Figs. 4(a) and 4(b)]. One crucial point that needs to be noted is that the film deposited at 400 °C and then postannealed is not ferromagnetic, but then has very good crystallization. In fact, its lattice parameters are closest

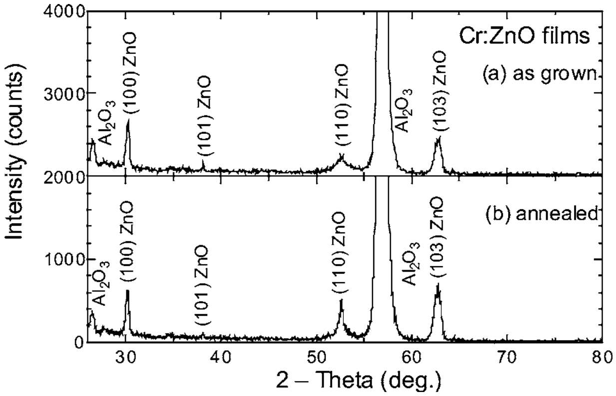

FIG. 2. XRD patterns for Cr:ZnO films fabricate at 650 °C under a P_{O_2} of 10^{-1} Torr: (a) as-grown film and (b) postannealed film.

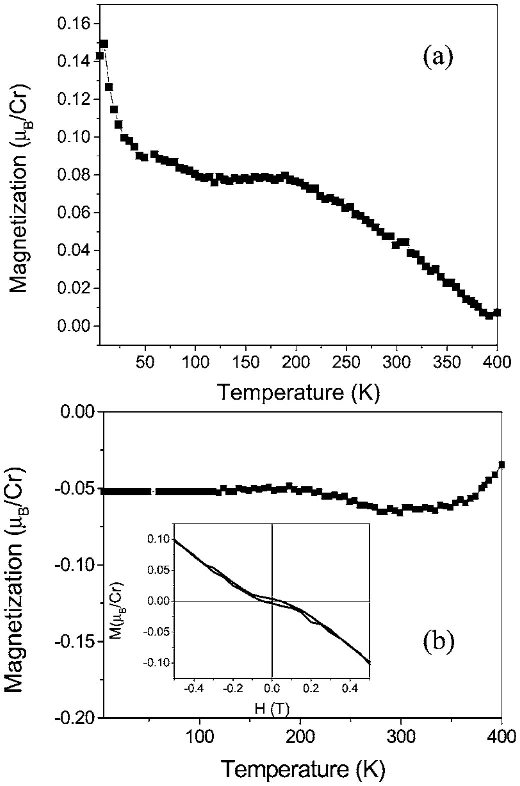

FIG. 3. Magnetization vs temperature at 0.5 T for Cr:ZnO films fabricated at 400 °C under a P_{O_2} of 10^{-6} Torr: (a) as-grown film and (b) postannealed film. The inset shows the *M-H* curve taken at 300 K for the postannealed film.

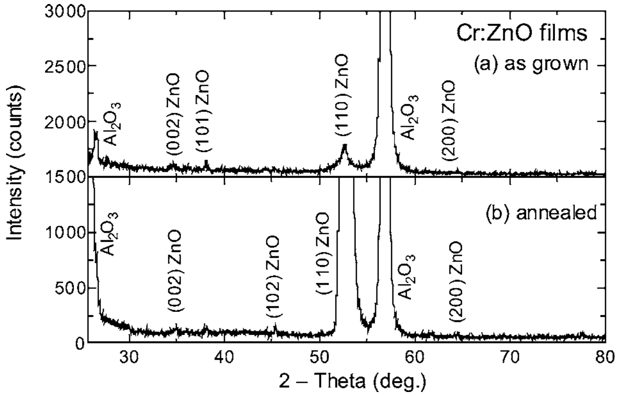

FIG. 4. XRD patterns for Cr:ZnO films fabricated at 400 °C under a P_{O_2} of 10^{-6} Torr: (a) as-grown film and (b) postannealed film.

to those of nondoped ZnO ($a=3.467$ Å, $c=5.129$ Å), whereas the lattice parameters of other ferromagnetic samples of Cr:ZnO are quite different ($a=2.95$ Å, $c=3.91$ Å; $a=2.96$ Å, $c=3.91$ Å, or $a=2.65$ Å, $c=5.14$ Å). We must assume that, in this type of compound, perfect crystallinity does not go along with FM. Moreover, filling up oxygen vacancies does not enhance the FM at all. Our results seem to have something in common with what Manivannan *et al.*[15] reported about a possible switching between the ferromagnetic and the paramagnetic states of Co:TiO_2 if changing the treatment between reheating in air and hydrogenating, as well as Ref. 11 reporting about an enhancement of the FM of the Fe:TiO_2 films if they were annealed in vacuum. We should say that there must be a great delicacy concerning the oxygen treatment. Or, in other words, there must be certain correlations between defects and/or oxygen vacancy and FM in DMS compounds.

The Ni:SnO_2 films fabricated at 700 °C under a P_{O_2} of 10^{-4} Torr are strongly ferromagnetic at room temperature [see Figs. 5(a) and 5(b)]. The films have T_C above 400 K and a very large magnetic moment of almost 2 μ_B/Ni. This value is too large to be attributed to Ni metal or Ni oxide clusters. By changing the thickness of the film to be double, we have obtained exactly the same quantitative values of magnetization. (Note that this was determined precisely by using the exact number of atoms deducted from RBS data. Besides, it was supposed that all the Ni atoms could contribute to the magnetism of the films.) This firmly confirms that the observed magnetic moment is indeed intrinsic and not due to any oxidation at the interface between the film and the substrate or other external factors. Surely, one may question whether there is some anisotropy in those films. Our results showed that the magnetic moment of the films measured when the magnetic field is parallel to the film plane is almost twice as large as that measured when the magnetic field is perpendicular to the film plane.[16] This is similar to the case of Co:ZnO that Venkatesan *et al.* reported, where they suggested that in those types of compounds, there must be some other source, such as defects that contribute to the magnetism of the system.[1] It was also stated that the FM might be destroyed when the carriers and their associated defects were eliminated. Recently, Scharwtz and Gamelin reported that the room temperature ferromagnetic ordering in Co^{2+}:ZnO could be switched between "on" and "off" when introducing or removing defects of ZnO.[17] Similarly, high T_C ferromagnetism could be generated by introducing defects at the interface between nanocrystals of Ni^{2+}:ZnO.[18] This crucial assumption concerning magnetism induced by defects could be supported somewhat by our two tests. First, very surprisingly, as for the Ni:SnO_2 films fabricated at 700 °C under a P_{O_2} of 10^{-4} Torr (which has the large magnetic moment as described earlier), if we deposited on a substrate with a double size (5 mm × 10 mm), the ferromagnetic ordering completely disappeared and the film became paramagnetic [see Fig. 5(c)]. From the structural viewpoint, not much difference could be seen from the difference in lattice parameters, except that in the latter case, the (110) and (211) peaks of SnO_2 also appear besides the (101) and (200) peaks, which are the same as in the earlier case. This case of Ni:SnO_2 is not the same as that of Cr:ZnO, mentioned earlier, because we have not seen any better FM in a more poorly crystallized sample. However, the observed paramagnetism in the film deposited on a double-sized substrate certainly implies that when the constraints on the film were more relaxed, the FM could be enormously reduced. Concerning the oxygen effect, our second test revealed that in Ni:SnO_2 films (deposited on 5 mm × 5 mm substrates), it is shown that having more oxygen could reduce the FM considerably. The *M-H* curves of the Ni:SnO_2 films deposited at

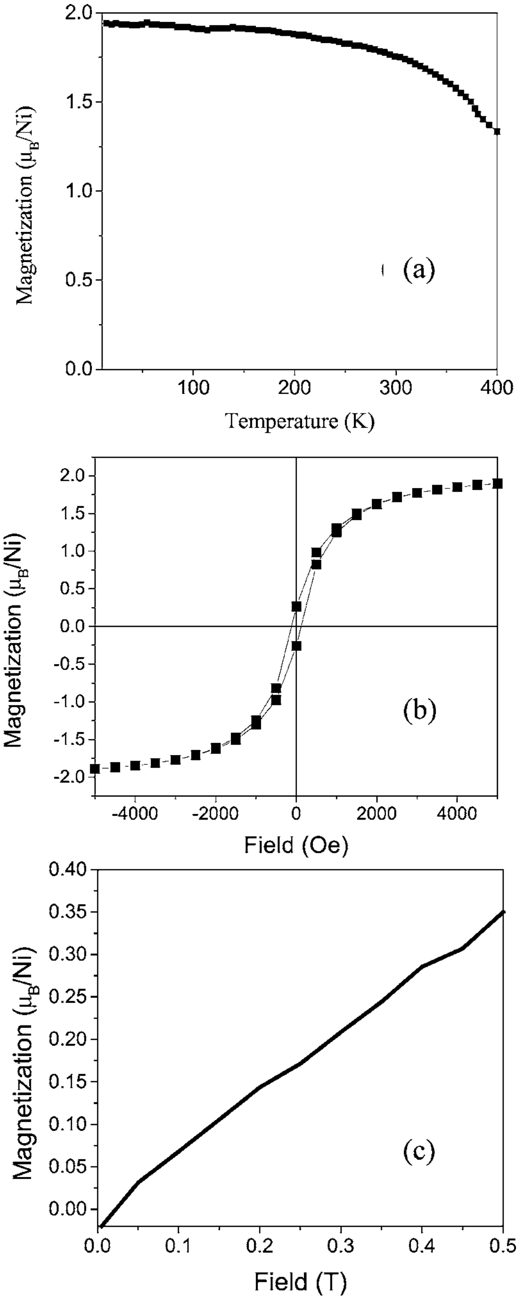

FIG. 5. Magnetization (a) vs temperature under 0.5 T; (b) vs magnetic field at 300 K for a Ni:SnO_2 film fabricated at 700 °C under a P_{O_2} of 10^{-4} Torr on a $LaAlO_3$ substrate of 5 mm × 5 mm, and (c) vs magnetic field at 300 K for a Ni:SnO_2 film fabricated at 700 °C under a P_{O_2} of 10^{-4} Torr on a $LaAlO_3$ substrate of 5 mm × 10 mm.

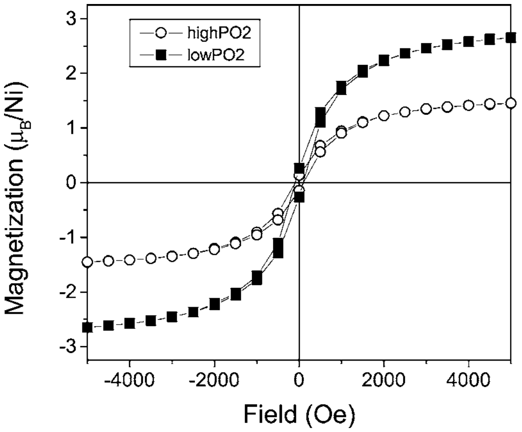

FIG. 6. Magnetization vs magnetic field at 300 K of Ni:SnO_2 films fabricated at 750 °C under P_{O_2} of 10^{-6} Torr (low P_{O_2}) and of 10^{-4} Torr (high P_{O_2}).

750 °C under a high P_{O_2} (10^{-4} Torr) and a low P_{O_2} (10^{-6} Torr) could be seen from Fig. 6. Even though both of those films are room-temperature ferromagnetic, the film with more oxygen has a much smaller magnetic moment. The effect of growing at a high P_{O_2} is just similar to some kind of annealing. With regard to XRD patterns, even if it is not possible to emphasize that the film, which has a weaker FM, should have a better crystallinity, one can see that in this case, the (110) peak of SnO_2 exists [compare the spectra in Figs. 7(c) and 7(d)]. This is similar to what was observed in the film grown on the large-sized substrate. Most probably, it could be one of the reasons for a reduction of the FM in the films. From both cases of Cr:ZnO and NiSnO_2 thin films, there is an open question about the correlations between the structural and magnetic properties. There is no doubt that defects and oxygen vacancy must play important roles in magnetism of these systems.

In conclusion, investigations on some typical cases of DMS thin films strongly imply that structural defects and oxygen vacancies likely very much influence the magnetism of these systems. For some types, an elimination of defects might contribute enormously to a reduction of the ferromagnetic ordering. It is also obvious that filling up oxygen vacancies seems to degrade the magnetic moment of the DMS samples. On the other hand, for some other types, the constraints could also be one of the reasons to support a sample to maintain its ferromagnetic ordering.

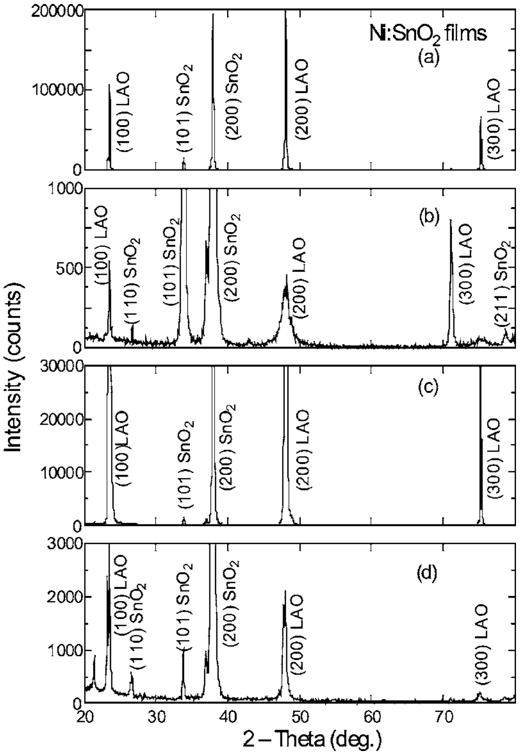

FIG. 7. XRD patterns of Ni:SnO_2 films: (a) fabricated at 700 °C under a P_{O_2} of 10^{-4} Torr on a $LaAlO_3$ substrate of 5 mm × 5 mm; (b) fabricated at 700 °C under a P_{O_2} of 10^{-4} Torr on a $LaAlO_3$ substrate of 5 mm × 10 mm; (c) fabricated at 750 °C under P_{O_2} of 10^{-6} Torr, and (d) fabricated at 750 °C under P_{O_2} of 10^{-4} Torr.

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