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Oxide-based dilute ferromagnetic semiconductors: ZnMnO and Co:TiO₂

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We report on ferromagnetic properties of ZnMnO and Co:TiO₂ films grown by pulsed laser deposition with varying growth conditions. We have demonstrated that ZnMnO films show ferromagnetic properties at room temperature. However, oxygen plays a dominant role in the occurrence of ferromagnetism. Introducing carriers into ZnMnO films did not improve the ferromagnetic properties. Our experimental results indicate that the mechanism for ferromagnetism lies, probably, within the perspective of charge transfer between Mn ions through oxygen. On the other hand, our experimental results suggest that the ferromagnetism in Co:TiO₂ films is controlled by the presence of small metal Co²⁺ clusters in the rutile TiO₂ matrix, which are mainly present at the interface and on the surface of the films. © 2006 American Institute of Physics.

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Recently, there has been much attention paid to dilute magnetic semiconductors (DMSs) due to their potential for the development of magneto-optic electronics in the rapidly developing area of spintronics.^{1–4} While III-V and II-VI semiconductors show convincingly carrier-mediated interaction (intrinsic),⁵ the search for magnetism in oxide semiconductors, such as ZnMnO, raises several controversies regarding the nature of the magnetism.^{6–10}

Following the theoretical prediction of ferromagnetism¹¹ in II-VI semiconductors, the recent report on the intrinsic carrier-mediated ferromagnetism observed in ZnMnO bulk and films¹² renewed the interest in this wide-band-gap semiconductor. However, the experimental evidence by other report¹³ suggests that the observed ferromagnetism is due to the oxygen-vacancy-stabilized metastable state. On the other hand, although Co-doped TiO₂ (Co:TiO₂ or CTO) has received interest,^{14,15} the origin of the ferromagnetic properties, particularly a possibility arising either from both Co clusters and Co incorporation into the TiO₂ matrix in the anatase phase¹⁴ or intrinsic phenomenon¹⁶ of Co substitution into Ti lattice, and the ionic state of Co remain ambiguous.

In this paper, we demonstrate that the thin films fabricated by the pulsed laser deposition (PLD) by varying annealing conditions clearly bring out the fact that oxygen plays a major role in controlling the ferromagnetism in ZnMnO system. On the other hand, ferromagnetism in rutile-phase-stabilized Co:TiO₂ films is controlled either by the interstitial Co²⁺ ions or small metal clusters.

Both ZnMnO and CTO epitaxial films were grown on sapphire (0001) substrates by the PLD technique and synthesis conditions for both systems are described elsewhere.^{17,18} As-doped ZnO the films were *in situ* annealed in nitrogen for

5 min at 200 °C. The resistivity of the *p*-type ZnMnO films is in the range of 1–2 Ω cm with hole concentrations between $(4–8) \times 10^{17} \text{ cm}^{-3}$.

Figure 1(a) shows the XRD curves for (0002) peak of ZnMnO/sapphire (0001) films grown at $T_s=500$ °C and $PO_2=1$ mTorr, followed by immediate *in situ* postannealing at different temperatures. It is noted that the XRD patterns for all films reveal only one strong orientation (002), illustrating the epitaxial nature of the film. However, it is interesting to note that the XRD peak position in a film grown at $T_s=500$ °C and at $PO_2=1$ mTorr exhibit a peak with a broad full width at half maximum (FWHM). The *in situ* postannealing at 600 °C exhibits the similar XRD peak pattern, indicating that Mn is substituted into Zn sublattice. In *p*-type ZnMnO film grown at $T_s=520$ °C and at $PO_2=1$ mTorr, the (002) peak shifts to higher angle as shown in Fig. 1(a). The XRD results of high oxygen pressure growth are similar to our previous report in which a narrow FWHM was seen with increasing substrate temperature.¹⁷ Apparently, the (002) peaks for the as-grown and annealed films at 600 °C turn out to be a superposition of two peaks, one from ZnO and the other from Mn-doped ZnO. We argue that a small amount of Mn is incorporated into the Zn site and forms a minority phase. The Mn doping introduces a minority phase into the pure ZnO phase, resulting in poor crystallinity that broadens the (002) peak linewidth.

Figure 1(b) shows the XRD pattern of CTO films grown on sapphire (0001) which reveals one dominating plane (002) of the rutile-phase, illustrating the epitaxial nature of the film and rutile-phase stabilization. However, a small but discernable peak at about 44.5° was observed. This is certainly due to Co (002) reflection preferably oriented in the plane (*c* axis) in a small metal cluster form. In order to study the variation of Co density as a function of film thickness, time-of-flight secondary-ion-mass spectroscopy (TOF-SIMS)

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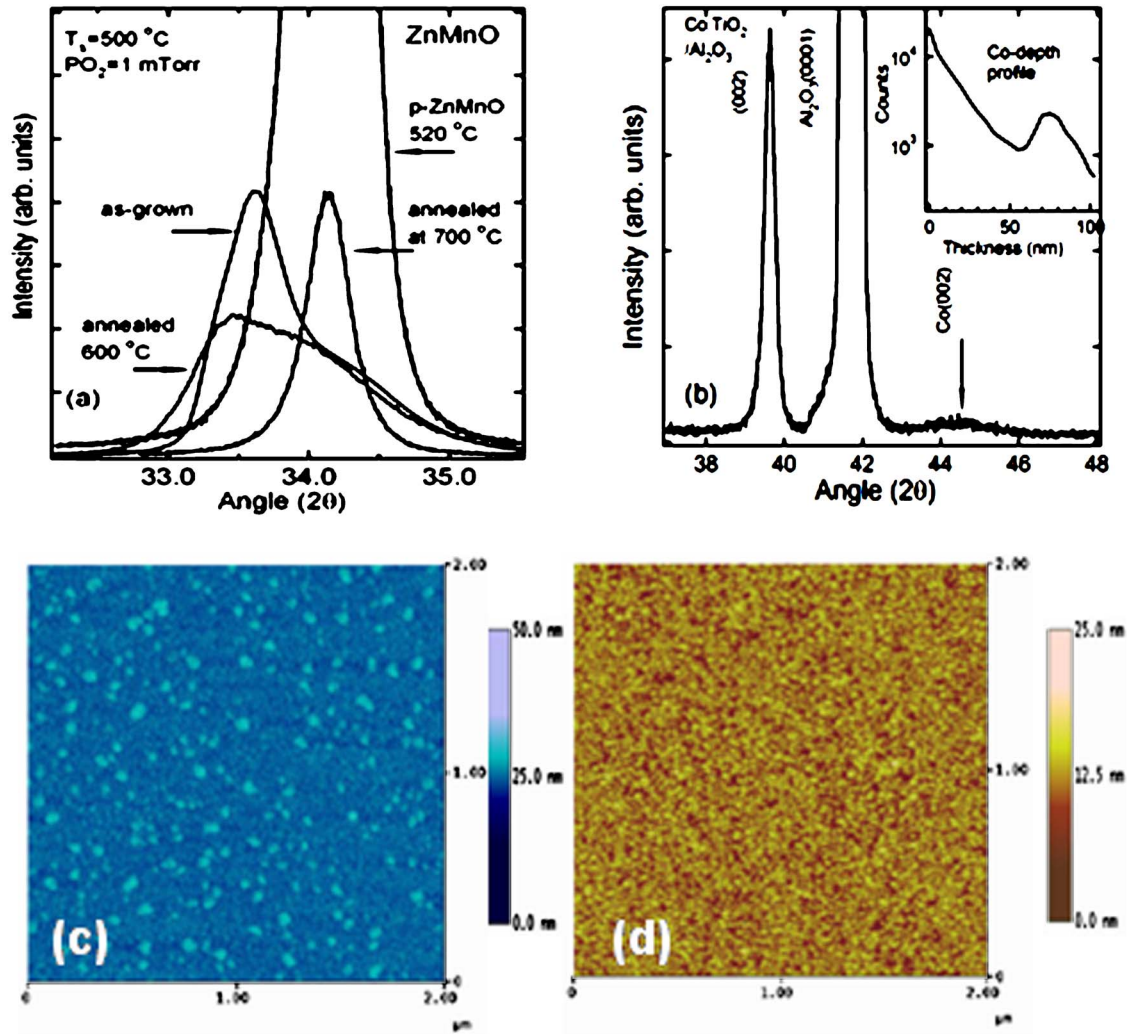


FIG. 1. (a) XRD patterns of (a) ZnMnO films (only rocking curves) grown for different conditions and (b) Co:TiO₂ film on sapphire substrates. The inset in (b) is the TOF-SIMS of Co-depth profile. AFM images of (c) ZnMnO film grown at $T_s=500$ °C and $PO_2=1$ mTorr with *in situ* oxygen annealing at 600 °C and (d) *p*-type ZnMnO film.

result is presented in the inset of Fig. 1(b). It is clear that the density of Co is much higher at the surface and decreases as the film thickness decreases. However, surprisingly, the Co density suddenly increases at the interface (~ 57 nm which is the thickness of the film) where a sharp jump emerges in Al-depth profile, illustrating that Co diffuses into the substrates and probably acts as a nucleation center for the formation Co clusters.

Figures 1(c) and 1(d) show the atomic force microscopic images of ZnMnO films with *in situ* annealed in O₂ at 600 °C and with As doping followed by N₂ annealing (*p*-type ZnMnO), respectively. Although, both films show nanocrystalline behavior with crystallite size of about 10 nm, the ZnMnO films with *in situ* annealing in O₂ at 600 °C show some clusters which are dispersed in the matrix. These clusters may be the prime suspect for the presence of the minority phase as discussed above. The surface roughnesses of the films are about 1.7 and 0.9 nm for ZnMnO and *p*-type ZnMnO films, respectively. The Co:TiO₂ film is consisted of self-assembled nanoparticles.

Figures 2(a) and 2(b) show the magnetic-field dependence of magnetization (*MH*) curves at 300 K in ZnMnO

and Co:TiO₂ films, respectively. The film grown at $T_s=500$ °C with $PO_2=1$ mTorr with *in situ* oxygen annealing (1 mTorr) at 600 °C exhibits pronounced ferromagnetic hysteresis loop. The field at which the maximum in magnetization, H_m , (low field to high field) is achieved is about 1000 G. No T_c was noticed for this film within the measured temperature range of 10–350 K (not shown here). Further increase in annealing temperature shrinks the hysteresis loops drastically as shown in Fig. 2(a). However, very weak ferromagnetic loop was observed for the *p*-type ZnMnO films as shown for the two films in Fig. 2(a). On the other hand, CTO film displays ferromagnetic hysteresis at room temperature.

Figure 3 shows the FMR spectra at 300 K in the films grown at $T_s=500$ °C and $PO_2=1$ mTorr with various *ex situ* annealing in either oxygen or nitrogen. The FMR curves clearly indicate that the ferromagnetic response becomes stronger on oxygenation, where as it weakens on nitrogen annealing. However, subsequent annealing in oxygen recovers the ferromagnetic response. On the other hand, the *p*-type ZnMnO films did not exhibit any ferromagnetic response. The peak at about 3.4 kG is the electron paramagnetic re-

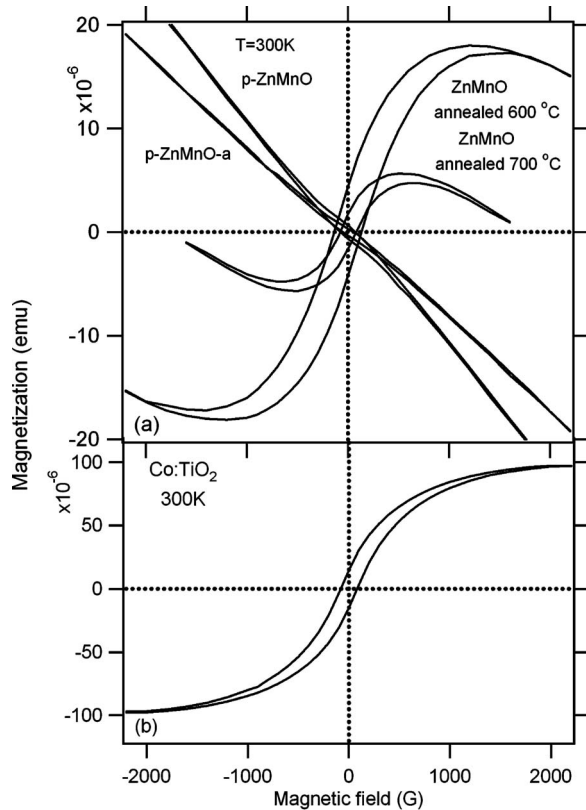


FIG. 2. (a) Ferromagnetic hysteresis loops of ZnMnO and *p*-type ZnMnO films grown at various conditions are shown for $T=300$ K and (b) Co:TiO₂ film at room temperature.

sponse from the cavity. However, the *p*-type ZnMnO did not show any change in the FMR response at lower temperatures.

This raises a concern about the actual mechanism of ferromagnetism in ZnMnO system. Our results suggest that although carriers did not help in ferromagnetism in ZnMnO system, oxygen plays a dominant role in the occurrence of ferromagnetism in ZnMnO. It is suggested that the ferromagnetism in this system may be coupled to the mechanism related to Mn ions through oxygen, and in which the alloying of Mn into Zn site plays a major role for controlling the exact oxygen concentration. The slight change in the oxygen concentration drives the system away from the ferromagnetic state.

In Co:TiO₂ film, the FMR spectra exhibit pronounced hump at around 2500 G at 100 K and the hump feature weakens as temperature is raised to 200 K, as shown in Fig. 3(b). This is a clear signature of ferromagnetic Co²⁺ as Co³⁺ does not show up in FMR spectra. The decrease of the FMR signal with increasing temperature may be related to the presence of Co³⁺ ions at higher temperature. This provides strong experimental evidence in favor of the presence of Co²⁺ ionic state which is responsible for the ferromagnetism in rutile-stabilized CTO films in contrast to the intrinsic ferromagnetism observed in anatase phase of Co:TiO₂.^{19,20}

In conclusion, we have demonstrated that ZnMnO films show ferromagnetic properties at room temperature. However, oxygen plays a dominant role in the occurrence of ferromagnetism. The carriers do not play any role for ferromag-

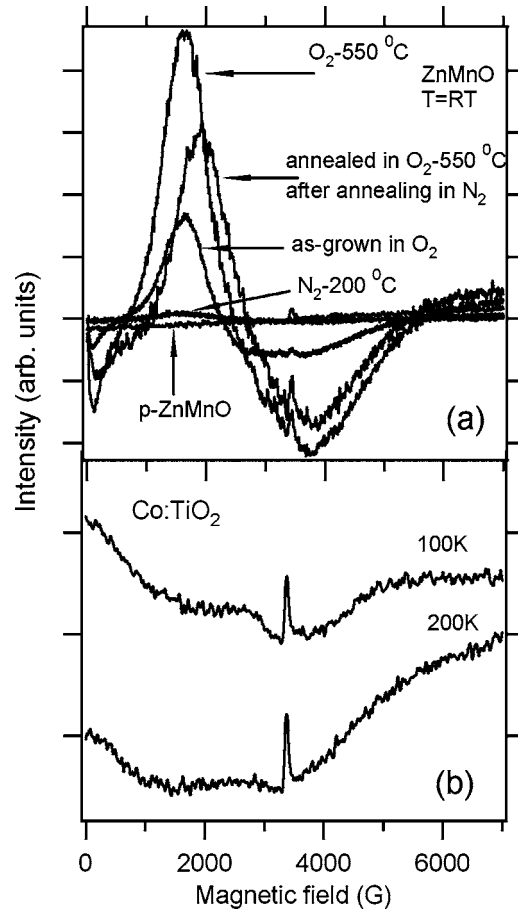


FIG. 3. Ferromagnetic resonance spectra of (a) ZnMnO and *p*-type ZnMnO films grown at various conditions at $T=300$ K and (b) Co:TiO₂ film at $T=100$ and 200 K.

netism in ZnMnO films. Our experimental results indicate that the mechanism for ferromagnetism lies, probably, within the perspective of charge transfer between Mn ions through oxygen. On the other hand, the ferromagnetism observed in rutile-phase-stabilized Co:TiO₂ film is due to the Co²⁺ ions.

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