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We report on the ferromagnetic resonance studies on ZnMnO films grown by the pulsed-laser deposition technique. ZnMnO films were annealed in different atmospheres. The films grown and annealed in oxygen demonstrate ferromagnetic behavior at room temperature and below. However, annealing in either nitrogen or argon deteriorates the ferromagnetic response of the films. Further annealing the films in oxygen recovers the ferromagnetic response. Our results suggest that oxygen plays a major role for controlling the ferromagnetic properties in ZnMnO films. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2172218]

Following the theoretical prediction[1] that transition metals, especially Mn, doped with GaN and ZnO could show large ferromagnetic Curie temperature, numerous studies have been carried out on (Zn,Mn)O and (Ga,Mn)N systems. The recent discovery of ferromagnetism[2–5] in (Ga,Mn)N at temperatures much higher than the room temperature has initiated research interest that these materials can indeed have profound technological impact. Recently, ferromagnetism in bulk, nanostructures, and Mn ion-implanted ZnO films has been observed.[5–7] The reported ferromagnetic transition temperature varies from 50 to 300 K. On the other hand, ZnMnO films prepared by magnetron sputtering,[8] pulsed-laser deposition,[9] and polycrystalline samples[10] did not show ferromagnetic behavior. Recently, ferromagnetism has been reported[11] in both ZnMnO bulk and thin film with ferromagnetic Curie temperature $T_C > 420$ K. This has aroused intense interest in this wide band gap semiconductor for possible spintronic applications. There are large controversies and differences in the results of this system, which is attributed to the difference in preparation techniques. Apart from this, the metastable behavior of ferromagnetism, which is not related to the carrier-mediated phenomenon,[12] raised the questions on the real origin of ferromagnetism in the ZnMnO system.

In this paper, we demonstrate the observation of room-temperature ferromagnetism in epitaxial ZnMnO films grown by pulsed-laser deposition technique in oxygen ambient. When the films were annealed in nitrogen, the ferromagnetic response weakened. However, upon further annealing in oxygen, the ferromagnetism was completely recovered, illustrating the fact that oxygen plays a major role for controlling the ferromagnetic properties.

ZnMnO/sapphire (0001) epitaxial films were grown by the pulsed-laser deposition (PLD) technique (KrF excimer, $\lambda = 248$ nm, laser repetition rate of 5 Hz) with a pulse energy

density of $1-2$ J/cm^2. High-density $Zn_{0.94}Mn_{0.06}O$ (ZnMnO) target was synthesized by mixing stoichiometric amounts of ZnO and MnO$_2$ (both 99.99% purity) powders, calcinating at 400 °C for 12 h followed by isostatic pressing at 400 MPa, and finally sintered at 500 °C. An arsenic doped ZnMnO target was also synthesized using the same technique in order to fabricate *p*-type ZnMnO. Clean single crystalline sapphire substrates were loaded into the chamber and heated just after the ultimate base pressure $< 4 \times 10^{-8}$ Torr was reached. The films of about 500 nm thickness were deposited at a substrate temperature of $T_s = 550$ °C with an oxygen partial pressure (PO_2) of $1-50$ mTorr. *In situ* annealing was performed in 1 mTorr of PO_2 for 1 h just after the film was deposited. However, in order to make *p*-type ZnO *in situ* annealing was performed at 200 °C in 1 mTorr of nitrogen for 1 h just after the film was deposited. The hole concentration of the films was found to be between 4 and 8×10^{17} cm^{-3} after nitrogen annealing from the Hall effect measurements, revealing the *p*-type nature of the films. The thickness of the films is between 300 and 500 nm. The x-ray diffraction (XRD) patterns of the films were performed in a Rigaku x-ray diffractometer using Cu $K\alpha$ radiation. The magnetization was measured using Quantum Design superconducting quantum interference device (SQUID, MPMS). Finally, the ferromagnetic resonance (FMR) experiments were done on a Bruker EMX spectrometer operating at 9.6 GHz microwave frequency.

Figure 1 shows the XRD patterns of ZnMnO/sapphire (0001) films grown at $T_s = 500$ °C with a $PO_2 = 1$ mTorr. The films were postannealed in different atmospheres as noted in the figure. The XRD patterns for all films reveal only one strong orientation (00*l*) at (002) and (004), illustrating the epitaxial nature of the film. First, it is interesting to note that the (002) peak in a film grown at $T_s = 500$ °C and at $PO_2 = 1$ mTorr exhibits a broad full width at half maximum (FWHM) of 0.4°. The (004) peak is observed for all films and a typical XRD pattern is shown in the inset of Fig. 4 for

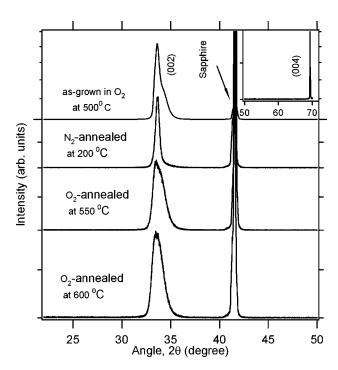[a)]Electronic mail: apradhan@nsu.edu

FIG. 1. X-ray diffraction pattern of ZnMnO films grown on sapphire substrates for different annealing conditions. A typical XRD pattern for the (004) peak is in the inset of Fig. 4 for the film grown at T_s=500 °C. The intensity is plotted in log scale.

FIG. 2. Atomic force microscopic images of (a) as-grown (T_s=500 °C) and (b) *in situ* oxygen-annealed (T=550 °C) films. The scale is 2 μm × 2 μm.

the film grown at T_s=500 °C. On the other hand, the XRD peak for the nitrogen-annealed film shows a narrower FWHM (~0.25°) without any significant shifting of the 2θ value, illustrating better crystalline behavior in the film. However, the (002) peak broadens again upon subsequent annealing in oxygen. Further *ex situ* annealing in O_2 at 550 and 600 °C yields not only a narrower FWHM in (002) peak, but also the peak position slightly shifts to lower angle. This indicates that the higher oxygenation results in better crystalline quality and incorporation of Mn into Zn lattice.

Figures 2(a) and 2(b) show the atomic force microscopic (AFM) images of the as grown (T_s=500 °C) and *in situ* oxygen-annealed (550 °C) films, respectively. It is very clear from the image that the surface roughness of the as-grown film decreases from 1.5 to 0.8 nm after annealing in oxygen, which is consistent with the XRD results.

Figure 3 shows the magnetic field dependence of magnetization (MH) curves at 300 K in as-grown ZnMnO films. Pronounced ferromagnetic MH loop was seen for the film grown at T_s=500 °C with PO_2=1 mTorr. However, a very weak ferromagnetic loop was seen for the *p*-type ZnMnO (doped with As) film grown at T_s=500 °C and PO_2=1 mTorr with *in situ* nitrogen annealing (1 mTorr) at 200 °C. Our estimated magnetic moment from the temperature dependent magnetization curve is ~0.2μ_B/Mn in films showing pronounced magnetic hysteresis. Although this value is very close to the reported value,[11] but much lower than 5μ_B/Mn reported by others[13] in ZnMnO films showing ferromagnetism. It is noted that according to a recent report on ZnMnO single crystal[14] the observed high value of magnetic moment of Mn, 5.4μ_B/Mn atom, indicates that Mn is in the high-spin state (S=5/2) due to the presence of large Mn
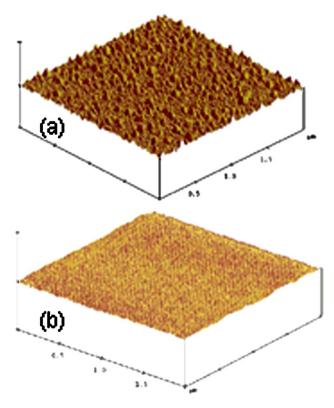
clusters. The detailed magnetization properties for detailed annealing conditions, such as in O_2, N_2, and Ar, are under study.

The ferromagnetic response from the ZnMnO films annealed at different ambient is the central point in this paper. Moreover, ionic state of Mn can be inferred from the ferromagnetic response of the films. Figures 4(a) and 4(b) show FMR spectra recorded at two temperatures, 300 and 77 K, respectively, for *n*-type ZnMnO films annealed in different ambient. The shape of the curve indicates that apart from Mn^{2+} there is a presence of other nonmagnetic ions, which is most likely Mn^{3+}. However, detailed magnetic studies are
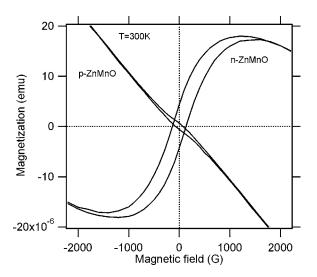

FIG. 3. Ferromagnetic hysteresis loops of as-grown and As doped ZnMnO films are shown for T=300 K.
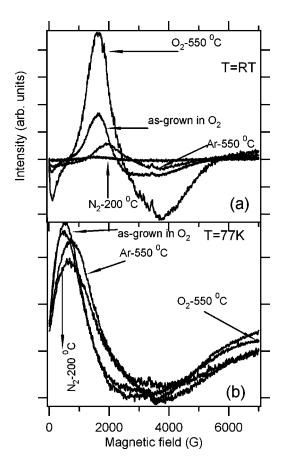
FIG. 4. Ferromagnetic resonance spectra of ZnMnO films at (a) 300 K and (b) 77 K for different annealing conditions.

necessary to resolve this issue. It is noted that FMR studies on the sapphire substrates did not show any ferromagnetic signal. The temperature independent peak observed at about 3300 G is a contribution from the cavity. The resonance peak shifts to lower field values with decreasing temperature. This confirms the true ferromagnetic state. The FMR curves clearly demonstrate that the ferromagnetic response becomes prominent with oxygen annealing. On the other hand, it becomes weaker in the case of nitrogen annealing. It is noted that the ferromagnetic response can be fully recovered in nitrogen-annealed films upon oxygenation. Furthermore, the resonance peak position shifts to higher field values upon annealing the film in either nitrogen or argon. This clearly brings out the fact that the ferromagnetic component in the ZnMnO system is controlled by the oxygen content in the film. It is interesting to note that the *p*-type ZnMnO film (annealed in nitrogen) did not yield any ferromagnetic response from the FMR experiment. This indicates that oxygen is an important factor for the ferromagnetism in ZnMnO.

Mn^{2+} ions can substitute Zn^{2+} sites homogeneously in the dilute limit and Mn atoms have a tendency to form clusters around oxygen in ZnMnO film[9] with higher concentration Mn. However, it is not known whether Mn is forming clusters or magnetic polarons in the dilute limit. However, our results suggest that oxygen is facilitating the formation of a minority phase, most likely in the form of a small cluster, in the ZnMnO system which is responsible for the ferromagnetism. Annealing in nitrogen is supposed to introduce

more carriers which can induce ferromagnetism in this system as predicted.[1] However, either annealing in nitrogen or introducing carriers by doping followed by nitrogen annealing does not help in improving the ferromagnetic properties. On the other hand, the slight change in the oxygen concentration drives the system away from the ferromagnetic state. Hence, the other possible mechanism may be related to the exchange mechanism between two Mn ions via oxygen as occurs in well-known rare-earth-based manganites. In the context of mechanism based on rare-earth manganites, the possible exchange mechanism is the charge transfer between $Mn^{2+}-O-Mn^{3+}$. The ferromagnetic properties in rare-earth-based manganites are specifically determined from two factors; the double exchange of electrons between ferromagnetically coupled Mn^{3+} and Mn^{4+} ions and the Jahn-Teller-type electron-phonon interaction due to lattice distortion. Although, the exact same mechanism may not be valid for ZnMnO system, the experimental results indicate that the ferromagnetism in this system may be coupled to the mechanism related to Mn ions through oxygen, and in which the substitution of Mn into Zn site plays a major role for controlling the exact oxygen concentration. There are alternative explanations, such as both donor and magnetic impurity concentration contributing to the hybridization and charge transfer from a donor-derived impurity band to unoccupied $3d$ states at the Fermi level.[15]

In conclusion, we have demonstrated the ferromagnetic properties in ZnMnO films grown by the pulsed-laser deposition technique. The films show ferromagnetic behavior at room temperature and below when grown and annealed in oxygen. However, either annealing in nitrogen or argon deteriorates the ferromagnetic properties of the films. The results from the ferromagnetic resonance studies suggest that oxygen plays a major role for controlling the ferromagnetic properties in ZnMnO films.

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