Structure, optical, and magnetic properties of sputtered manganese and nitrogen-codoped ZnO films

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To realize the hole-mediated ferromagnetism, manganese and nitrogen-codoped ZnO ($Zn_{1-x}Mn_xO$:N) films were prepared on sapphire (0001) by reactive radio-frequency (rf) magnetron sputtering from $Zn_{0.97}Mn_{0.03}O$ ceramic targets using N_2 gas. X-ray photon spectra reveal that the doped Mn ions are mainly in divalent states and the coexistence of O–Zn and N–Zn bonds in the films. According to the absorption spectra, the band gap of $Zn_{0.97}Mn_{0.03}O$:N films is about 3.15 eV, which is slightly lower than that of ZnO films (3.20 eV). Compared with $Zn_{0.97}Mn_{0.03}O$ films, ferromagnetic behavior of $Zn_{0.97}Mn_{0.03}O$:N films were significantly changed with a coercivity of about 70 Oe, a saturation magnetization of 0.92 μ_B/Mn^{2+} and a remanance over 0.15 μ_B/Mn^{2+} at 300 K, while at 10 K, they increased to be about 110 Oe, 1.05 μ_B/Mn^{2+} and 0.23 μ_B/Mn^{2+}, respectively. However, rapid thermal annealing treatment in pure oxygen results in a significant decrease on the magnetic properties of the films. © *2006 American Institute of Physics.*
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Oxide diluted magnetic semiconductors (DMS) have recently been of intense focus due to their potential as the active components of spintronic devices designed to process information by manipulating the spins of electrical currents.[1] Recently the theoretical prediction[2] of Curie temperature (T_C) above room temperature in *p*-type (Ga,Mn)N and (Zn,Mn)O has extensively intrigued theoretical and experimental researchers. Transition metal (TM)-doped II-VI and III-V semiconductors have been studied extensively.[3–6] Room-temperature ferromagnetism has been reported by several groups in TM-doped ZnO films prepared by a variety of deposition techniques,[7–9] however, spin-glass[10] and paramagnetic[11] behaviors have also been observed in TM-doped ZnO films. More recently, Mofor *et al.*[12] observed that sapphire substrates caused a ferromagnetic super conducting quantum interference device (SQUID) signal. Therefore, the origin of ferromagnetism in ZnO-based films has not yet been clearly elucidated, so far.

Although holes are considered to be essential for robust ferromagnetism according to the current wisdom, *P*-type ZnO is notoriously difficult to realize experimentally. Nitrogen is considered to be a promising acceptor impurity for *p*-type ZnO. Recently, Tsukazaki *et al.*[13] has succeeded in obtaining *p*-type ZnO using a pure nitrogen source, In this letter $Zn_{0.97}Mn_{0.03}O$:N films were deposited by reactive rf magnetron sputtering using pure nitrogen as a dopant source. The influences of N doping on the optical and magnetic properties were investigated. Results indicated that the doping of nitrogen might have induced holes which significantly enhance the coercivity, remanance, and saturation magnetization of ZnMnO films.

The $Zn_{0.97}Mn_{0.03}O$ target for sputtering was prepared using the standard solid-state reaction process. Fine powders of high-purity MnO_2 and ZnO with prescribed molar ratio were mixed thoroughly and sintered at 1000 °C for 5 h in air. The $Zn_{0.97}Mn_{0.03}O$:N thin films were deposited on (0001) sapphire (α–Al_2O_3) substrates. The sputtering chamber was evacuated by a turbomolecular pump to a base pressure below 4.5×10^{-5} Pa. Mixed argon and nitrogen with a flux ratio of 7:3 was introduced into the chamber as working gas through two mass flow controllers. The total flow rate was regulated at 25 sccm and the chamber pressure was fixed at 1.6 Pa during deposition. The substrate was mounted to a stage at 550 °C and kept a distance of 60 mm from the target. Rapid thermal annealing (RTA) treatment of the as-grown films was carried out in pure oxygen at 550 °C for 3 min in a rapid thermal process furnace.

The thickness of the films was about 300 nm measured by a profilermeter. The crystal structure of the $Zn_{0.97}Mn_{0.03}O$:N film was characterized by x-ray diffraction (XRD) (Cu K_α radiation source). Chemical bonding states and chemical compositions of the films were analyzed by x-ray photoelectron spectroscopy (XPS) (ESCALAB MK-II) with Mg K_α x-ray source ($h\nu = 1253.6$ eV). Inductively coupled plasma-mass ICP spectrometer was applied to determine the Zn and Mn concentrations in the films, which confirmed that the Mn content in the films was approximately the same as that in the target. The absorption spectra of the films were measured using an ultraviolet-visible (UV-VIS) spectrometer at room temperature. Magnetic measurements were performed using a Quantum Design SQUID (MPMS XL-7) magnetometer. The magnetic field was applied parallel to the film plane. Resistivity (ρ) was determined by four-probe measurement and the Hall coefficient was measured using a van der Pauw four-point configuration using a
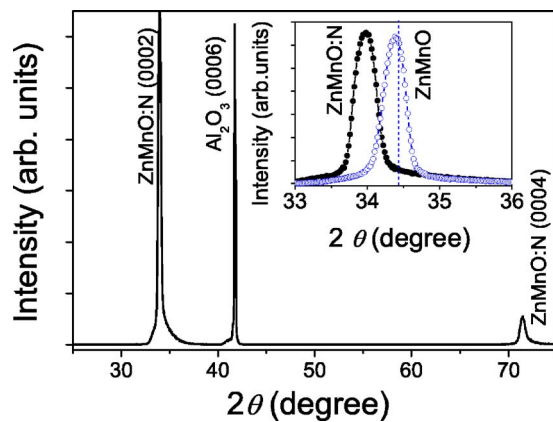
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FIG. 1. $\theta-2\theta$ XRD pattern of $Zn_{0.97}Mn_{0.03}O:N$ film. The inset shows the shift of (0002) peaks of $Zn_{0.97}Mn_{0.03}O:N$ from that of $Zn_{0.97}Mn_{0.03}O$ films. The dashed line indicates (002) diffraction peak of pure ZnO as reference. The d-spacing values of ZnO, $Zn_{0.97}Mn_{0.03}O$, and $Zn_{0.97}Mn_{0.03}O:N$ are 2.603, 2.606, and 2.638 Å, respectively.

physical property measurement system (PPMS) (Quantum Design).

Figure 1 shows a typical XRD pattern of $Zn_{0.97}Mn_{0.03}O:N$ film. Only diffraction peaks from wurtzite ZnO (0002) planes were observed, which indicates a preferential (0001)- oriented growth of the film. No manganese oxide or nitride phases were detected, suggesting that the Mn and N ions might be substituted into Zn and O sites, respectively. A shift of (0002) peak positions related to the change of lattice spacing was clearly observed, as shown in the inset of Fig. 1. It is understandable since both the ionic radii of Mn^{2+} (80 pm) and N^{3-} (146 pm) are relatively larger than that of Zn^{2+} (74 pm) and O^{2-} (138 pm).

Chemical bonding states in the $Zn_{0.97}Mn_{0.03}O:N$ films were characterized by XPS measurement, as shown in Fig. 2. The XPS spectra have been charge corrected to the adventitious C 1s peak at 284.2 eV and the core states of Zn 2p, Mn 2p, O 1s, and N 1s peaks were observed. The binding energy of the Zn $2p_{3/2}$ and Mn $2p_{3/2}$ states are located at 1021.8 and 640.0 eV, respectively, as illustrated in Figs. 2(a) and 2(b). The Mn 2p main peaks have the satellite structure on the higher binding-energy side, and they are in good
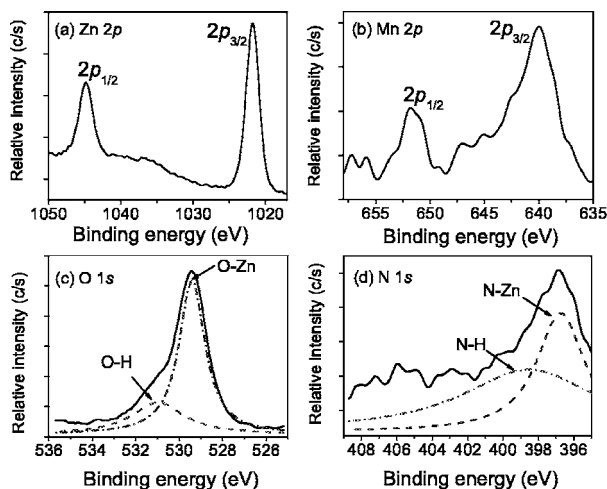

FIG. 2. XPS spectra for $Zn_{0.97}Mn_{0.03}O:N$ film: (a) Zn $2p_{3/2}$ XPS spectrum, (b) Mn $2p_{3/2}$ XPS spectrum, (c) O 1s XPS spectrum, and (d) N 1s XPS spectrum.
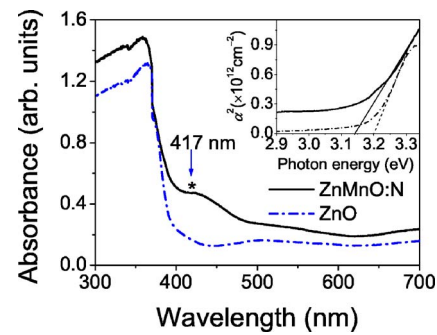

FIG. 3. Absorption spectrum of $Zn_{0.97}Mn_{0.03}O:N$ film compared with that of pure ZnO film. The inset shows the α^2 vs $h\nu$ plots of $Zn_{0.97}Mn_{0.03}O:N$ and ZnO films.

agreement with other reports,[14] which indicates a divalent state of Mn ions in ZnMnO:N films. The O 1s state splits into two peaks as shown in Fig. 2(c). The peak at 529.4 eV can be attributed to the O–Zn bond formation, while the peak at 531.0 eV can be due to the O–H bond formation. The N 1s peak also consists of two components, as shown in Fig. 2(d). At 396.4 eV, a chemical shift in comparison with the N 1s peak for free amine (398.8 eV) was observed, which indicates the formation of N–Zn bonds. An oxygen-to-nitrogen ratio of 2.5:1 estimated by XPS indicates a high doping concentration of nitrogen in $Zn_{0.97}Mn_{0.03}O:N$ films.

Optical absorption spectrum of $Zn_{0.97}Mn_{0.03}O:N$ films is shown in Fig. 3. The absorption spectrum of ZnO was also measured as a reference. All of these films show a sharp absorption edge at about 395 nm (3.14 eV). For $Zn_{0.97}Mn_{0.03}O:N$ films, an absorption edge at about 417 nm (2.97 eV)—indicated by an asterisk—was observed below the direct band-gap absorption. This absorption band is attributed to the d-d transitions between the crystal-field-split $3d^5$ multiplet levels of the tetrahedral Mn^{2+} ion.[15,16] They are assigned as $^6A_1(S) \rightarrow {}^4E(G)$ (2.97 eV) and/or $^6A_1(S) \rightarrow {}^4A_1(G)$ (2.99 eV), which are very close to each other according to the results of configuration interaction calculations.[14] The observation of such multiplet transitions indicates that the Mn^{2+} ions have substituted for Zn^{2+} ions.[17]

The absorption of ZnO film is attributed to direct transition and the absorption coefficient (α) obeys the following relation $\alpha^2 = A(h\nu - E_g)$ for high photon energies ($h\nu$), where E_g is the band gap and A is a constant. The variations of α^2 versus $h\nu$ in the fundamental absorption region are plotted in the inset of Fig. 3. The band gaps E_g are estimated to be 3.20 and 3.15 eV for pure ZnO and $Zn_{0.97}Mn_{0.03}O:N$ films by extrapolation of the linear part, respectively. Compared with ZnO film, a redshift of 50 meV was observed for ZnMnO:N films. The decrease in E_g of ZnMnO:N films is probably related to the increase of lattice constant and the difference in ionicity between Zn–O (3.5) and Zn–N (3.0) bonds.[18] Moreover, the upshift of valence band due to the doping of impurities is also a reason for the decreasing of E_g.

Figure 4 shows the field dependence of magnetization of $Zn_{0.97}Mn_{0.03}O:N$ films measured at 10 and 300 K, both of which showed a hysteresis shape with the coercive field (H_c) of 110 and 70 Oe, respectively. To eliminate the influence of substrates, M-H curves of sapphire substrates were also measured under an identical procedure after treatment. A similar magnetic hysteresis was also observed in sapphire substrates as Mofor et al.[12] reported. Then, the diamagnetic and ferro-
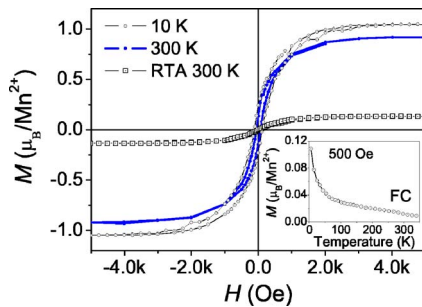
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FIG. 4. Hysteresis loops for $Zn_{0.97}Mn_{0.03}O:N$ measured at 10 and 300 K. The *M-H* curves of $Zn_{0.97}Mn_{0.03}O:N$ after a RTA treatment was also measured at 300 K. The inset shows the field-cooled magnetization as a function of temperature (*M-T*), measured in a magnetic field of 500 Oe.

magnetic contribution from the sapphire was subtracted from the raw data. The saturation magnetizations (M_s) are about 1.05 and $0.92\mu_B/Mn^{2+}$ at 10 and 300 K, respectively, and the remanances (M_r) are around 0.23 and $0.15\mu_B/Mn^{2+}$, respectively. By comparison, we also measured the magnetization of the $Zn_{0.97}Mn_{0.03}O$ film and $Zn_{0.97}Mn_{0.03}O:N$ RTA film which is $Zn_{0.97}Mn_{0.03}O:N$ film experienced a RTA treatment in an oxygen ambient at 550 °C. The maximum spontaneous magnetization of $Zn_{0.97}Mn_{0.03}O$ is close to that of sapphire substrate, indicating there is no obvious evidence of a ferromagnetic behavior for $Zn_{0.97}Mn_{0.03}O$ films without N doping. The maximum spontaneous magnetization of $Zn_{0.97}Mn_{0.03}O:N$ is reduced to $0.13\mu_B/Mn^{2+}$ after the RTA treatment. The M_r of $Zn_{0.97}Mn_{0.03}O:N$ RTA films are lower than $0.02\mu_B/Mn^{2+}$. The inset of Fig. 4 shows the temperature dependence magnetization (*M-T*) measured under a magnetic field of 500 Oe. The curve indicates a typical diluted magnetic behavior which has also been observed in other DMS materials.[19–21] According to Curie–Weiss law, a negative Curie temperature ($\theta = -47$ K) was obtained by extrapolating, suggesting an antiferromagnetic ground state for the system.[19,20] Ferromagnetic hysteresis shrinks with increasing temperature and the negative Curie temperature illustrate a dominant competition between ferromagnetic and antiferromagnetic states, which leads to a complex temperature dependence of field-cooled magnetization as reported by Wang *et al.*[20]

ZnO is generally in *n* type due to shallow donors associated with low-energy native point defects, such as oxygen vacancies (V_O) and Zn interstitials (Zn_i). Even if an active N_2 plasma is used, it is still difficult to achieve high hole densities due to the compensation by O vacancies, N_O-Zn_O or $N_O-(N_2)_O$ complexes.[22] We did try, but in vain, to conduct Hall measurement due to the large resistivity (more than $10^5 \Omega$ cm) of $Zn_{0.97}Mn_{0.03}O:N$ films. However, the $Zn_{0.97}Mn_{0.03}O:N$ RTA films show a relatively low resistivity ($5.0 \times 10^2 \Omega$ cm) because a large amount of nitrogen atoms was driven out of the films during RTA treatment due to the low solubility and less stable of N_O defects under O-rich condition.[23] Similar result was observed in N-doped ZnO films, in which annealing treatment leads to a transformation from ZnO:N alloy to ZnO.[24] The Hall coefficient of $Zn_{0.97}Mn_{0.03}O:N$ RTA film was measured by PPMS at 300 K which shows a *n*-type conduction with carrier density of about 2.166×10^{16} cm^{-3}. We suggest that large amount of holes were introduced by N doping, so consequently the

magnetic properties of $Zn_{0.97}Mn_{0.03}O:N$ films were greatly improved compared with those of $Zn_{0.97}Mn_{0.03}O$ films, due to hole mediated ferromagnetic interactions among magnetic impurities. RTA treatment eliminates most of the nitrogen atoms in the films, hence a dramatic decreasing of hole density, which leads to the weakening of ferromagnetic interactions in $Zn_{0.97}Mn_{0.03}O:N$ RTA films. In our opinion, this result is consistent with the theoretical prediction that hole might be necessary in order to mediate ferromagnetism for high T_C DMS.[2]

In summary, high-quality $Zn_{0.97}Mn_{0.03}O:N$ thin films were deposited by reactive rf magnetron sputtering. XPS and optical absorption spectra indicate the formation N–Zn bonds and the band gap of ZnMnO:N films is lower than that of ZnO films. Compared with the $Zn_{0.97}Mn_{0.03}O$ films, the magnetic properties of $Zn_{0.97}Mn_{0.03}O:N$ films were greatly enhanced, which is attributable to the N doping. The hysteresis behavior indicates that $Zn_{0.97}Mn_{0.03}O:N$ films were ferromagnetic above room temperature.

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