Pulsed Laser Deposition and Characterization of $Zn_{1-x}Mn_xO$ Films

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ABSTRACT

Here we present our results of structural, optical, and magnetic measurements of $Zn_{1-x}Mn_xO$ thin films. These films were grown epitaxially on (0001) sapphire substrates by using pulsed laser deposition technique. The maximum Mn content (x=0.36) is found to be much higher than allowed by thermal equilibrium limit (x~0.13) due to the non-equilibrium nature of the pulsed laser deposition. All the films investigated here were found to be single phase with <0001> orientation epitaxial relationship. A linear increase in the c-axis lattice constant was observed with increase in Mn concentration. Optical transmittance measurements showed an increase in the insulating band-gap (E_g) with increase in Mn concentration. DC magnetization measurements showed that there is no long range ferromagnetic ordering down to 10 K.

INTRODUCTION

ZnO is one of the promising members of II-VI semiconductor family with a bandgap of 3.27 eV at 300K. It has a higher binding energy of exciton (60 meV) compared to GaN system, which makes the material a favorable candidate for the potential applications in optical and electrical industries. ZnO based alloys have been reported for bandgap engineering to achieve the desired wavelength for certain applications. ZnO can be alloyed with MgO (8.2 eV) to increase the bandgap or with CdO (2.0 eV) to decrease it [1-2]. Another interesting ZnO-based alloy is $Zn_{1-x}Mn_xO$ which is expected to be applied in the field of spintronics as a dilute magnetic semiconductor (DMS) [3-4]. Spintronics (spin + electronics) is a fastly developing field in physics focussed on spin-dependent phenomena applied to modern electronics devices.

Recently, two groups reported the growth of ZnMnO thin films by using pulsed laser deposition [5-6]. They found that Mn can be incorporated into ZnO thin films with a large concentration (up to 35%), which is far excess the equilibrium limitation (13%). This significant increase in solubility is due to the nonequilibrium nature of the pulsed laser deposition technique, in which the average energy of laser ablated species (100-1000 kT) is 2 to 3 orders of magnitude higher than the equilibrium value.

In this work, we report the epitaxial growth of $Zn_{1-x}Mn_xO$ thin films by pulsed laser deposition. The structures of films were characterized by X-ray diffraction and transmission electron microscopy (TEM). The optical and magnetic properties of the films are also reported.

EXPERIMENTAL DETAILS

Epitaxial $Zn_{1-x}Mn_xO$ (x=0.01-0.36) films were grown on both-side polished (0001) sapphire substrates by pulsed laser deposition technique using a KrF excimer laser. Targets were prepared by standard solid state pressing and sintering method. Stoichiometric amount of ZnO and MnO powders were first mixed and calcined at 450 °C for six hours. The resulting powder

was then pressed into round pallets. These pallets were subjected to sintering at 900 °C for 12 hours in flowing oxygen. Depositions using these targets were carried out at 610~650°C in an ambient oxygen pressure of 5×10^{-5} Torr. The energy density and repetition rate of the laser beam were 2-3 J/cm² and 10 Hz, respectively. The Crystal structures of these films were determined by X-ray diffraction using CuK_α radiation and Ni filter. The exact stoichiometry of the films was determined by Rutherford backscattering technique. Microstructural characterization of these films was performed by cross-sectional high resolution transmission electron microscopy (HRTEM) using JEOL-2010F analytical electron microscope with point to point resolution of 0.18 nm and 0.12 nm in STEM-Z mode. Optical transmittance spectra of these films were recorded at room temperature in the energy range 1-4 eV. Magnetic properties of these films were studied using superconducting quantum interference device (SQUID) magnetometer.

RESULTS AND DISSCUSION

X-ray diffraction pattern (Intensity vs. 2θ) showed the films were single phase and had wurtzite structure with c-axis of the film aligned with that of the sapphire substrate. Fig 1 shows a typical X-ray diffraction pattern of $Zn_{1-x}Mn_xO$ with x=0.01 and 0.20; all other alloys till x=0.36 exhibited similar behavior. It is clear from the figure that there are no other orientations except (000l) reflections of ZnO and sapphire. All the films were in single phase till x=0.36, but for x >0.36 some indication of phase separation was observed in X-ray diffraction. A systematic increase in the lattice parameter 'c' was observed without any change in crystal symmetry. It is to be noted that in this work we have succeeded in doping Mn in ZnO much above the thermal equilibrium limit of x~0.13. This became possible because the
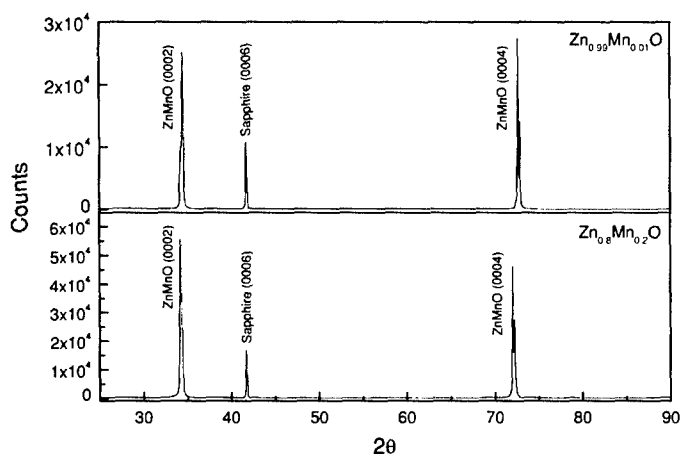

Fig. 1. X-ray diffraction patterns of $Zn_{1-x}Mn_xO$ (x=0.20 and 0.01) films

nonequilibrium processing was involved during the pulsed laser deposition, where the average energy of the laser ablated species is two to three orders of magnitude higher than the equilibrium value.

Fig.2 shows the Rutherford backscattering and channeling data for one of the films. From this figure we estimated the minimum channeling yield to be less than 3.0% near the surface which suggests that Mn atoms are substitutionally confined into the lattice planes rather than between the planes. From a fit to the random backscattering profile, the actual concentration of Mn in these films was determined. Mn contents in the films and the targets were found to be within ±5%.

Fig. 3 shows the selected area diffraction pattern on the $Zn_{1-x}Mn_xO$ (x=0.85)/ sapphire interface area taken at [01 $\overline{1}$0] zone axis of ZnMnO thin film. It shows that the film was epitaxially grown on the substrate. The $Zn_{1-x}Mn_xO$ film has the following epitaxial relationships with the substrate: $Zn_{1-x}Mn_xO(0001) \parallel$ sapphire(0001), $Zn_{1-x}Mn_xO(01 \overline{1}0) \parallel$ sapphire($\overline{1}2 \overline{1}0$), and $Zn_{1-x}Mn_xO$ ($\overline{1}2 \overline{1}0) \parallel$ sapphire (01 $\overline{1}$0). Fig.4 (a) shows the results of HRTEM carried out on the $Zn_{1-x}Mn_xO$/sapphire interface. The interface between the film and the sapphire is sharp and free from any other phase. Due to the large in-plane mismatch (~18%) between the film and the substrate, the epitaxial growth of the film occurs via domain epitaxy where dimensions of the domain become the repeat distance across which matching is maintained [7]. The misfit dislocations were observed at the interface as shown in Fig.4 (b). The dislocation occurs at every 6-th ($\overline{2} \overline{2} \overline{1}$0) plane of sapphire (average). The unit cell of ZnMnO film was found to be rotated by 30° about the c-axis with respect to the sapphire unit cell as reported in pure ZnO on sapphire substrate [9].
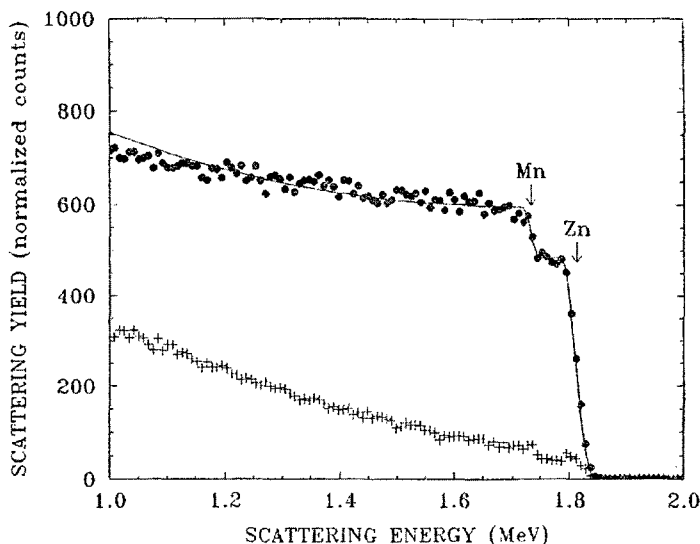

Fig. 2. Rutherford back scattering (•) and channeling (+) data for $Zn_{1-x}Mn_xO$ (x=0.25) film.

Optical absorbance spectra of $Zn_{1-x}Mn_xO$ films were recorded at room temperature, see Fig5. We observed that the absorption edge moves towards the high energy side with the increase in Mn concentration. This indicates the increase in the band-gap (E_g) of the alloy. We
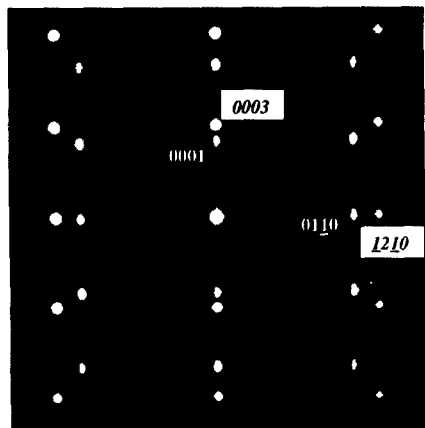

Fig.3 Selected area diffraction pattern (SAD) from 10 μm area for $Zn_{1-x}Mn_xO$ (x=0.15) thin films on sapphire (0001) substrate. The white numbers correspond to ZnMnO and the black numbers in white blocks correspond to sapphire.
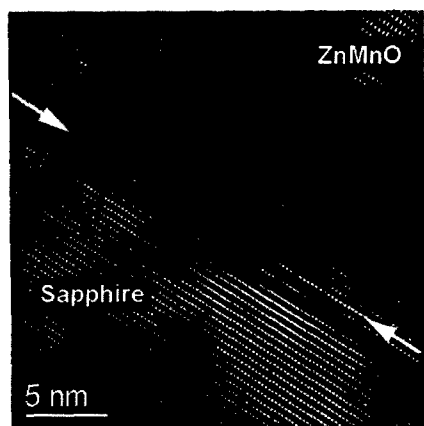

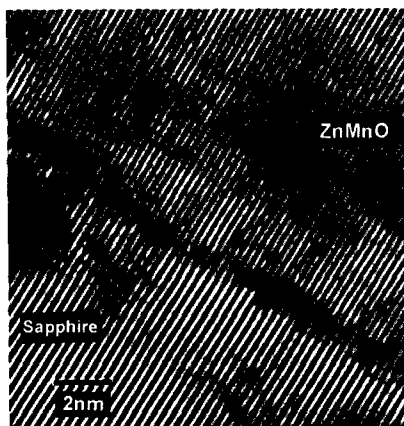Fig. 4(a) High-resolution picture of single crystal $Zn_{1-x}Mn_xO$ (x=15) film grown on sapphire substrate.

Fig. 4(b) IFFT picture from Fig. 4(a). Two reflexes ($\overline{1}2\ \overline{1}0$) and (01 $\overline{1}0$) have been masked in corresponding FFT picture, so only (01 $\overline{1}0$) planes of ZnMnO and ($\overline{1}2\ \overline{1}0$) planes of sapphire are observed. The places corresponding to the misfit dislocations are indicated here.
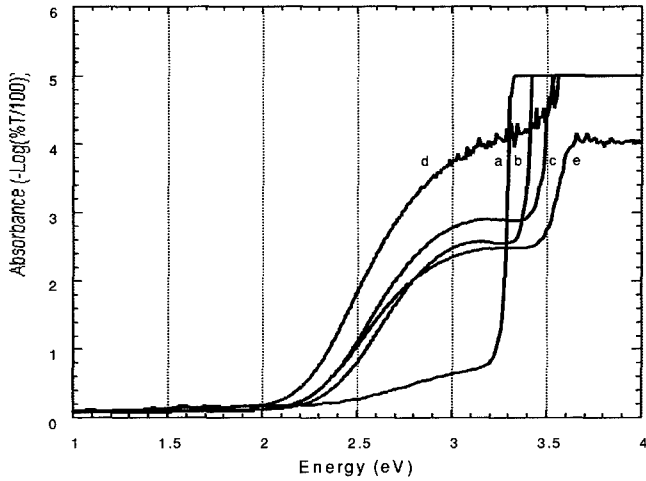
Fig. 5 Optical absorbance spectra of $Zn_{1-x}Mn_xO$ films. Symbols a, b, c, d and e correspond to x=0.01, 0.05, 0.12, 0.18 and 0.25 respectively. Absorbance is related to the percentage transmittance (T) by the relation absorbance=-Log(%T/100).

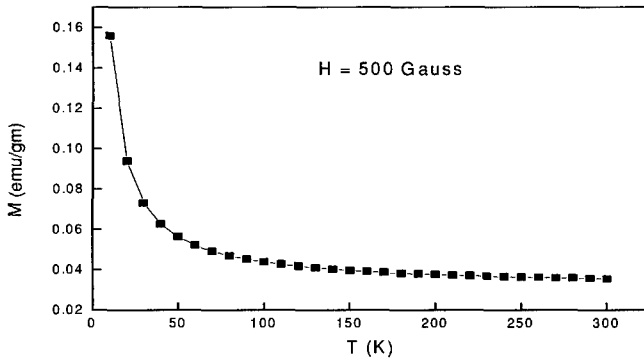Fig.6 DC magnetization vs. Temperature for $Zn_{1-x}Mn_xO$ (x=0.05) film.

also observed significant amount of midgap absorption in these films which is similar to results of other groups [5]. This is believed to be due to the charge-transfer transition between donor and acceptor ionization levels of Mn ions and the band continuum [5].

DC magnetization of these magnetic films was measured using a SQUID. We found these films to be paramagnetic (see Fig6). No evidence of any long range ferromagnetic ordering could be observed in any of these films down to 10 K. This is in contradiction with the theoretical predictions of Dietl [8] et al. Magnetic susceptibility (χ=M/H) data fits well in an expression of the kind $\chi=\chi_0+C/T$. Bohr magnetron number 'p' of Mn was found to be 5.9 by using expression $C=Np^2\mu_B^2/3k_B$ for curie paramagnetism [10], which gives a value of J~5/2 consistent with the doubly ionized ionic state of Mn, substituting Zn sites in the $Zn_{1-x}Mn_xO$ lattice.

CONCLUSION

In conclusion we have prepared high quality epitaxial $Zn_{1-x}Mn_xO$ (x$\leq$0.36) films on sapphire using pulsed laser deposition technique. A systematic study of the microstructural characterization of these high quality epitaxial films showed a 30° rotation of the film with respect to the substrate, similar to III-nitride and pure ZnO growth on (0001) sapphire substrate. Both the c-axis lattice parameter and the band gap E_g are found to be sensitive functions of Mn content. SQUID measurements showed a paramagnetic behavior and no ferromagnetic ordering could be detected in any of these films down to 10 K.

ACKNOWLEDGMENTS

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