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Growth of ZnO:Mn/ZnO:V Heterostructures and Ferroelectric-ferromagnetic Characterization

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ABSTRACT

The wide band gap semiconductor ZnO is well known for its multifunctionality in the form of ferromagnetism (FM), piezoelectricity, and magneto optics. ZnO has been found to grow with intrinsic oxygen deficiencies which in turn are believed to give ferromagnetism and high conductivity in this material. Doping Zn^{2+} sites by V^{5+} ions creates a mixed valency as well as strain in the original ZnO hexagonal structure because of the reduced ionic size of vanadium. The mixed valency creates charge polarity between Zn-O and V-O bonds. This charge polarity and the rotation of the nonlinear V-O bonds with respect to Zn-O bonds under electric field have been shown to produce ferroelectricity. Furthermore, Mn doping of ZnO has also shown enhancement in ferromagnetic properties in ZnO. For this material to be a viable ferromagnetic material the magnetic properties should not be from segregated phases. In the present study we have grown undoped, Mn, and V doped ZnO thin films using pulsed laser deposition (PLD). ZnO target with 2% atomic Mn doping and a target with 0.5% atomic V doping were prepared by solid state reactions and sintering. Films were grown both epitaxially on sapphire substrates and in polycrystalline form on silicon substrates. Magnetization measurements by the PPMS showed M vs. H hysteresis loops with saturation for all ZnO: Mn films. V doped films showed high saturation polarization for film deposited at high pressures. We have also fabricated epitaxial bilayers of ZnO:V/ZnO:Mn on sapphire substrates. Ferroelectric and ferromagnetic properties of these heterostructures are presented.

INTRODUCTION

Room temperature ferromagnetism seen in ZnO is attributed to the intrinsic oxygen deficiency. Recently, some studies have also revealed the introduction of a strong magnetic moment to ZnO by doping with Mn [1]. $Zn_{1-x}Mn_xO$ has attracted more attentions because of the wide band gap of ZnO and the high thermal solubility of Mn in ZnO. Theoretically Mn doped ZnO is predicted to have the critical temperature (Tc) well above room temperature [2]. Mn when doped nominally in ZnO is found to be in Mn^{2+} oxidation state and the ferromagnetism is carrier induced for Mn concentrations below 5 at.% [3]. In contrast to the ref. 3, Kundaliya et al. [4] have claimed that the ferromagnetism in Mn:ZnO system is due to the metastable phase (Mn_2O_3) rather than by the carrier induced interaction among substituted Mn ions in ZnO. Our analysis shows that the ferromagnetism shown at epitaxial Mn doped ZnO induced from carrier induced interaction and can be explained by using RKKY interaction. Vanadium (V) doped ZnO has been shown to be ferroelectric [5]. Our goal was to find the growth conditions to maximize the magnetic moment in Mn doped ZnO and investigate the multiferroic behavior in Mn:ZnO and V:ZnO heterostructures.

EXPERIMENTAL DETAILS

ZnO:Mn and ZnO:V thin films were deposited on both c-cut sapphire (0001) substrates and Si (100) substrates using pulsed laser deposition (PLD). A pulsed KrF excimer laser (248nm) operating at 10Hz was focused on ZnO:Mn and ZnO:V targets inside a vacuum chamber equipped with a multi target changer sequentially exposing different targets to the laser beam and enabling the in situ growth of hetero-structures with relatively clean interfaces. The laser beam energy was set at 154mJ/pulse. The energy density at the target surface was $2J/cm^2$. The target to substrate distance was kept constant at 6cm. The ZnO:Mn and ZnO:V targets were fabricated by conventional solid state reaction by mixing stoichiometric amounts of high purity ZnO,MnO_2 powders in case of ZnO:Mn target and ZnO, V_2O_5 powders in case of ZnO:V target, cold pressing and followed by sintering for 12h at 1000 ˚C in air. The deposition chamber was pumped to a base pressure of under 10^{-6} T before preparing the thin films and back filling the chamber with high purity oxygen gas. All the films were deposited for 30 mins. The thicknesses of the films were determined using a profilometer. The prepared thin films were measured by X-ray diffraction for crystal structure. All XRD measurements were carried out with Cu Kα radiation. EDS measurements were carried out on the target. The concentration of Mn was found to be 2.2at.% in the ZnO:Mn target and that for V was found to be 0.5 at.% in the ZnO:V target.

RESULTS AND DISCUSSION

Prior to growing the heterostructures, thin films of ZnO:Mn and ZnO:V were grown separately. The growth pressures for ZnO:Mn thin films were varied from 0 mT to 300 mT while growth temperature was chosen to be 600^oC. At this growth temperature we observed the best crystallinity in our films. In these ferroelectric/ferromagnetic structures the multiferroic coupling is mediated by the interfacial stress. For this reason films were deposited on c-cut sapphire substrates in order to maintain an epitaxial relation. Films were also grown in polycrystalline form on Si (100) substrates for comparison.

ZnO:Mn thin films

The crystal structure and film orientation of the as-grown films were determined from □-2□ scans of XRD. All XRD patterns indicate that the films are single phase and c-axis preferred oriented. The intensity has been plotted in log scale to emphasize the absence or presence of impurity phases. Figure 1(left) and 1(right) shows the x-ray diffraction scans for the films deposited on Al_2O_3 substrate and Si (100) substrate at 600˚C varying the background oxygen pressure during deposition from 0mT to 300mT respectively. Note that in figure 1 (a) for all the films there was no segregation of the Mn_3O_4 phase in the diffraction data. The Mn_3O_4 phase is ferromagnetic with a Curie temperature of less than 50K. However the epitaxial relationship between sapphire substrate and films broke down at higher deposition pressures and other ZnO planes are observed besides the (0002) plane. For the films deposited on Si (100) substrates there was Mn_3O_4 phase segregation at higher pressures which gave a significant difference in magnetization of these films at 10K.

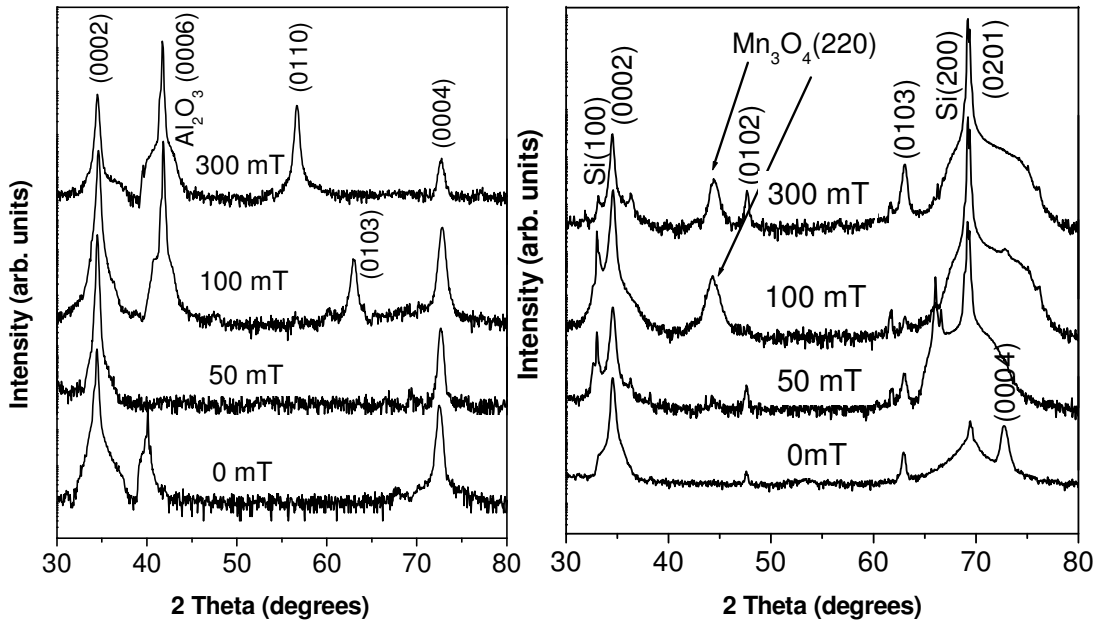

Figure 1. XRD data for Mn doped ZnO thin films deposited at 600˚C with varying oxygen background pressure on c-cut sapphire substrates (left) and Si(100) (right) substrates

The magnetization measurements of the thin films were done using Quantum Design Physical Property Measurement System (PPMS) in the ranges of magnetic field (H) from -5T to 5T at temperatures of 10K and 300K. The magnetic field was applied parallel to the film plane. The main hysteresis loops that are reported were obtained after removal of the diamagnetic contribution from the substrates. Figure 2 shows the M vs H loops of ZnO:Mn thin films grown on Al_2O_3 substrates at varying pressures. We observed a drop in the saturation magnetization at 300 K with increasing pressure from 1.47 emu/cm^3 for film deposited at no oxygen background pressure to 0.32 emu/cm^3 for film deposited at 300mT of oxygen pressure. This behavior could be explained on the basis of spin glass behavior as reported by Fukumura et al. [6]. It has been reported that ZnO films deposited at low oxygen pressure have large carrier concentration, with carriers originating from intrinsic defects as Zn interstitials and oxygen vacancies [7]. The less availability of conduction electrons for films deposited at higher O_2 pressures suppresses the magnetic interaction between the Mn^{2+} ions that is mediated by the carriers. This results in a lowering of saturation. Also in order to confirm that Mn doping did play a role in enhancing the ferromagnetic properties of ZnO films hysteresis loops were measured for undoped and Mn doped ZnO films both grown under the same conditions. There has been report of observed room temperature ferromagnetism in undoped ZnO thin films [8]. The saturation magnetization in the Mn doped film was found to be four times higher than undoped ZnO film, both showing room temperature ferromagnetism. (data not presented here)

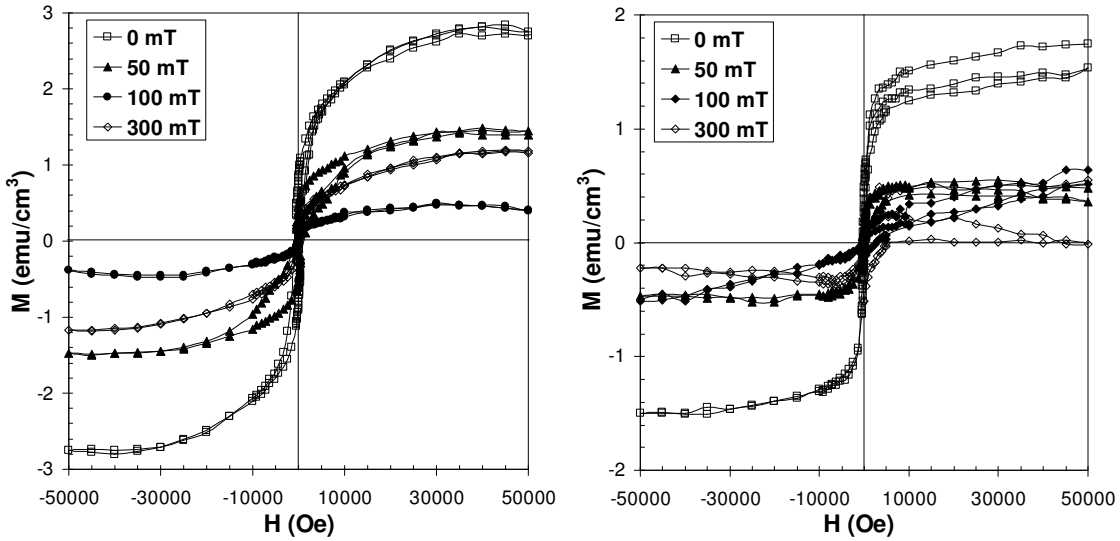

Figure 2. Magnetization loops at 10 K (left) and 300 K (right) for field applied parallel to the film plane for Mn doped ZnO (2 at.% Mn) films deposited at 600˚C on sapphire substrates by varying the background oxygen pressure during deposition from 0 mT to 300 mT.

Figure 3 shows the M vs H loops for films deposited on Si (100) substrates at the given conditions. There is a huge change in the sat. mag. at 10 K for the film deposited at 300 mT O_2 pressure. The saturation magnetization for the film deposited at 300 mT is 3.07 emu/cm^3 as compared to 1.83 emu/cm^3 for the 0 mT deposited film. This could be due to cluster formation of Mn_3O_4 phase which is observed in XRD data in figure 1. Apart from the 300 mT film all other films had lower saturation magnetization than those grown epitaxially on sapphire.

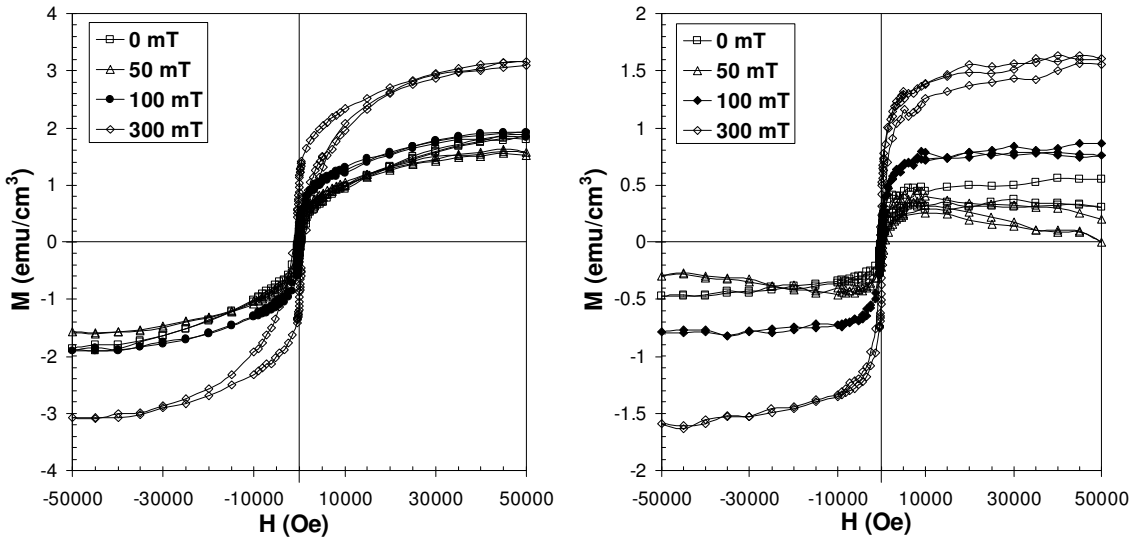

Figure 3. Magnetization loops at 10 K (left) and 300 K (right) for field applied parallel to the film plane for Mn doped ZnO (2 at.% Mn) films deposited at 600˚C on Si (100) substrates by varying the background oxygen pressure during deposition from 0 mT to 300 mT.

ZnO:V thin films

V-doped ZnO films were grown epitaxially on sapphire substrates at 600˚C under different oxygen pressure from 100 mT to 500 mT. XRD data showed good epitaxial relationship with no impurity phases. The films with higher oxygen pressure were more insulating due to less intrinsic oxygen deficiency. Higher O_2 pressure facilitated formation of strong polarity V-O non collinear bonds in V^{5+} substituted Zn^{2+} sites [5]. The saturation polarization was higher for the film grown at higher pressure as shown in figure 4 below. The saturation and remnant polarization are comparable to the values obtained previously [9].

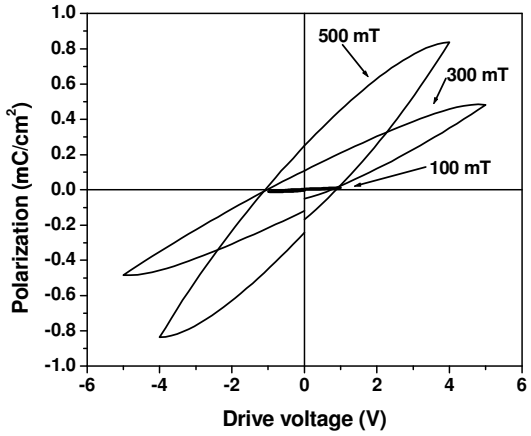

Figure 4. Polarization loops for ZnO:V films deposited on sapphire substrates.

ZnO:Mn / ZnO:V heterostructure

The ZnO:Mn/ZnO:V epitaxial heterostructure was grown as shown in figure 5. The ZnO:V layer was poled by applying 4 V of d.c. bias voltage across coplanar sputter coated Pt electrodes as shown in figure 5.

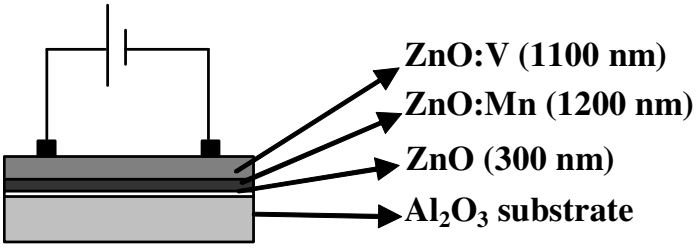

Figure 5. ZnO:Mn/ZnO:V epitaxial heterostructure grown on c-cut sapphire substrate

Figure 6 (left) shows the rocking curve about the (0002) ZnO plane. The FWHM of the rocking curve shows high degree of in plane orientation in the structure. Figure 6 (right) shows the M vs H loops at 300K of the heterostructure before and after poling. Large drop in the sat. mag. by an order of magnitude indicates an interaction between the magnetic moment and the polarization.

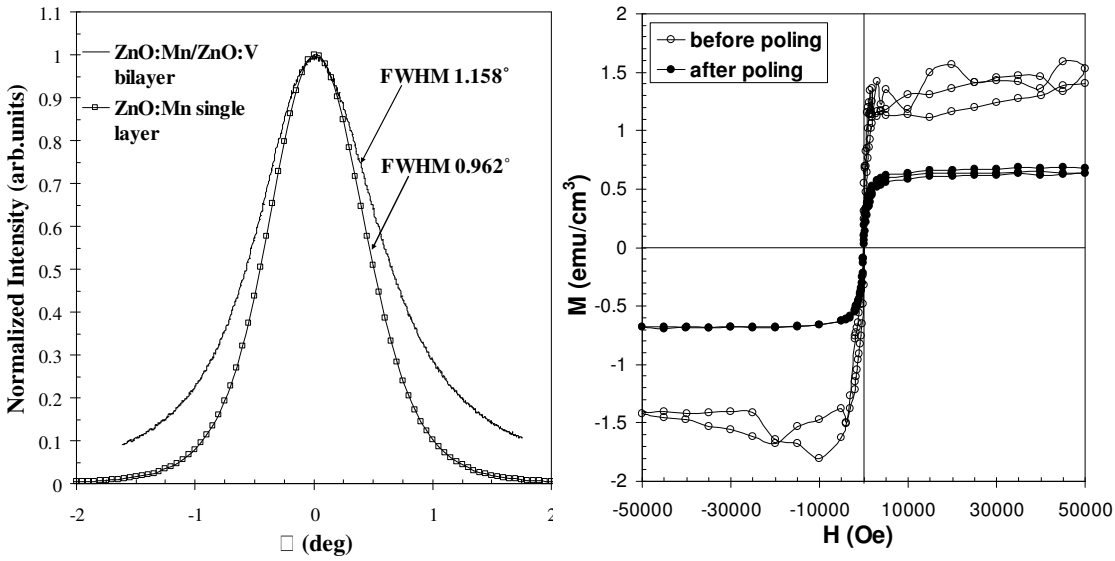

Figure 6. (left) Rocking curves about the (0002) plane of ZnO. (right) Magnetization loops at 300K before and after poling the ZnO:Mn/ZnO:V epitaxial heterostructure.

CONCLUSIONS

In conclusion, room temperature ferromagnetism has been observed in Mn doped ZnO thin films. Magnetization from Mn doped ZnO films grown under various growth conditions suggested that high temperature and low oxygen pressure enhanced the FM behavior. Epitaxial films of V doped ZnO were successfully grown and the ferroelectricity was investigated. The ZnO:Mn/ ZnO:V heterostructure showed possible magnetoelectric coupling at room temperature.

ACKNOWLEDGMENTS

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