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Correlation between defect and magnetism of low energy Ar^{+9} implanted and un-implanted $Zn_{0.95}Mn_{0.05}O$ thin films suitable for electronic application

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ABSTRACT

The structural, morphological, optical and magnetic properties of Ar^{+9} implanted 5 at% Mn doped ZnO films have been investigated to detect the correlation between ferromagnetism (FM) and defect. Sol–gel derived films were implanted with fluences 0 (un-implanted), 5×10^{14} (low), 10^{15} (intermediate) and 10^{16} (high) ions/cm^2. Rutherford back scattering (RBS), X-ray diffraction (XRD), atomic force microscope (AFM) and magnetic force microscope (MFM), UV–visible, photoluminescence and X-ray absorption spectroscopy (XAS) and superconducting quantum interference device vibrating sample magnetometer (SQUID VSM) were employed for investigation. XRD indicated single phase nature of the films. Absence of impurity phase has been confirmed from several other measurements also. Ion implantation induces a large concentration of point defects into the films as identified from optical study. All films exhibit intrinsic FM at room temperature (RT). The magnetization attains the maximum for the film implanted with fluence 10^{16} ions/cm^2 with saturation magnetization (M_S) value 0.69 emu/gm at RT. Magnetic properties of the films were interpreted using bound magnetic polaron (BMP). BMP generated from the intrinsic exchange interaction of Mn^{2+} ions and V_{Zn} related defects actually controls the FM. The practical utility of these films in transparent spin electronic device has also been exhibited.

1. Introduction

Dilute magnetic semiconductors (DMS) have attracted much research interest because of their potential applications in the field of spintronics. The euphoria started following the prediction of RT FM in Mn doped ZnO by Dietl et al. [1]. The ferromagnetic interaction between localized moments of the Mn ions is mediated by free holes in the material [1]. In ZnO, the exchange interaction for Mn is fundamentally different from the other transition metal ions. Mn *d*-states lie in the valence band while the other transition metals *d*-state introduces states within the gap [2]. Experimental realization of *p*-type ZnO with high concentration of acceptor type defects is really a difficult thing. An alternative model shows that FM in Mn doped ZnO system arises due to the exchange interactions between the localized Mn spins with carriers (hole) that are present in the material, but localized at Mn^{2+} ions [2]. This model named bound magnetic polaron (BMP) model assumes exchange interaction between Mn^{2+} ion and localized holes that are near to the Mn ion [2]. The BMPs so formed overlap with neighboring BMPs and induce ferromagnetic interaction among Mn spins. But a lot of contradictory experimental results in ZnO based DMS system particularly for Mn doped ZnO are present hence no strong physical understanding has been developed. Recently the clouds of confusion and contradiction hovering over Mn doped ZnO based DMS seems to be dissolved substantially. This is because of emergence of a general consensus that defects play a crucial role in controlling the magnetic properties of such systems [2–5].

Importance of defects induced ferromagnetism in transition metal doped ZnO, especially nanocrystalline samples, has been put forward very strongly. These defects are predominantly zinc/oxygen vacancy or interstitial types. Theoretical calculation by Liu et al. [3] demonstrated that different defects species like oxygen

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vacancy (V_O), zinc vacancy V_{Zn} and interstitial zinc (Zn_i) have carried magnetic moment of 0.98μ_B, 1.998μ_B, and 2.00μ_B, respectively. Among all these defect species the role of V_{Zn} seems to be most favorable for mediating ferromagnetic interaction in $Zn_{1-x}Mn_xO$ system [4–8]. Theoretical calculation on electronic structure and magnetic interaction between Mn ions in the model structure of $Mn_{Zn}+V_{Zn}$ shows stability of ferromagnetic states against antiferromagnetic states [5]. Experimentally it has been demonstrated that cation vacancies (V_{Zn}) play the determining role in mediating FM for Mn doped ZnO [6]. Also Xu et al. [8] experimentally demonstrated that FM in $Zn_{1-x}Mn_xO$ compounds originates due to alignment of magnetic moments mediated by some acceptor defects such as (V_{Zn}). Actually a delicate balance of different defect species and attainment of optimum defect concentration along with substitutional incorporation of Mn at the Zn site is responsible for ferromagnetism.

In one of our work, we have seen that Mn doped ZnO bulk sample synthesized by solid state reaction method is ferromagnetic; and the observed FM is found to be correlated with defects present in the samples [6]. We had also studied the effect of Li^{3+} ion irradiation on different physical properties of Mn doped ZnO powder samples previously [9,10]. Defect induced modification of physical (obviously including magnetic) properties were occurred there [10]. However for the same Mn doped ZnO bulk sample derived from sol–gel route any ferromagnetic ordering has not been found [11]. So far as sol–gel derived Mn doped ZnO thin films are concerned there are very few reports of achievement of FM [12]. Recently Rajamanickam et al. gives a brief review on magnetic properties of Mn doped ZnO system prepared through various different techniques and finally came to the conclusion that magnetism in diluted doped system is very much sensitive to preparation routes, doping concentration, effect of co-doping as well as preparation conditions [13]. In this present work ferromagnetism in sol–gel derived $Zn_{0.95}Mn_{0.05}O$ films above 300 K has been reported. Observation of FM above room temperature seems to be quite interesting so far as practical application of these films. Further observation of FM at and above RT also assures the unhindered and flawless operation of this particular DMS system at least up to RT. Another point which is noteworthy is that moderately high temperature (500 °C) annealing during growth of these films. It has been observed that 500 °C annealed $Zn_{0.95}Mn_{0.05}O$ films possess good ferromagnetic interaction at 300 K [12]. During the growth of the films annealing temperature has been maintained at 500 °C because it provide better crystallinity of the films as well as removes the organic residue from the film samples efficiently [12].

In this article, the structural, optical and magnetic properties of polycrystalline $Zn_{0.95}Mn_{0.05}O$ films have been analyzed. The presence of vacancies and relative defect concentrations is found to regulate the occurrence/destruction of ferromagnetism in the films. Characterization of the un-implanted $Zn_{0.95}Mn_{0.05}O$ film was performed in great detail. Low energy (81 keV) Ar^{9+} ion implantation has been performed to generate defects in Mn doped ZnO films in a controlled fashion. A decrease in saturation magnetization has been observed for the low fluence implanted films in comparison with un-implanted film. However magnetic property of the $Zn_{0.95}Mn_{0.05}O$ film improves when it is implanted with fluence 10^{16} ions/cm^2. Ferromagnetic property of the samples has been explained by assuming formation of BMP inside samples. A particular point defect mostly (Zn vacancy types) establishes magnetic exchange with Mn^{2+} ions. Overall the idea of defect mediated FM in ZnO based DMS system seems to be strengthened from this work. The utility of these films in future electronic devices has also been exhibited.

2. Experimental details

$Zn_{0.95}Mn_{0.05}O$ films were synthesized by sol–gel spin coating technique. Stoichiometric amount of zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and manganese acetate dihydrate [$Mn(CH_3COO)_2 \cdot 2H_2O$] was added to a solution containing 2-propanol and di-ethanolamine (DEA). DEA was used as the sol stabilizer. The precursor solution thus obtained was used for spin coating on glass substrates to prepare the films. The spinning rate and period were optimized to 1500–1700 rpm and 30 s, respectively. After coating, the films were dried at 300 °C for 15 min in a furnace to evaporate the solvent. It was followed by heat treatment at moderately high temperature 500 °C for 30 minutes to get good quality films. The process of coating and subsequent annealing were repeated for five times to obtain the desired film thickness.

The films were implanted with 81 keV Ar^{9+} ions with fluence viz. 5×10^{14}, 10^{15} and 10^{16} ions/cm^2 at RT. The area of all the films was maintained at (1 cm^2). Beam dimension was also maintained at (1 cm^2). Rutherford Back Scattering (RBS) measurement has been performed for estimation of the thickness of the film. Structural, morphological, optical and magnetic properties of un-implanted and implanted 5 at% Mn doped ZnO films were examined. Structural properties were investigated by using powder X-ray diffraction (XRD) technique. XRD patterns of the synthesized films were recorded with Cu-K_α radiation using an automatic powder diffractometer (Philips, Model: PW1830), equipped with (θ–2θ) geometry. Surface morphology of the films was investigated through atomic force microscope (AFM) and magnetic force microscope (MFM). Optical properties of the films were studied by UV–visible and photoluminescence (PL) spectroscopy. UV–visible spectra were recorded using a spectrophotometer (Perkin Elmer; Model: Lambda 35) in the wavelength range 200–1000 nm. The Spectra were recorded by taking a similar glass as the reference so that only transmission due to the film was obtained. PL spectra of the films at room temperature were recorded by using an excitation source of 325 nm line of He–Cd laser with an output power ($\sim$10 mW). Additionally we have performed energy dispersive X-ray analysis (EDX) of un-implanted and implanted (fluence 10^{16} ions/cm^2) films to estimate the relative proportion of Zn, Mn and O in the samples. For a potential DMS the question of segregated ferromagnetic clusters is of utmost importance. X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) measurements of 5 at% Mn doped ZnO film were carried out using INDUS 2 Synchrotron Source (2.0 GeV, 100 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore. The XANES measurements at the K edge of Zn and Mn have been recorded at room temperature in the fluorescence mode. Magnetic measurements were performed using superconducting quantum interference device vibrating sample magnetometer (SQUID VSM, Quantum Design). The field dependent magnetization (M–H) measurement was performed at 300 K, 250 K and 200 K for all of the films. Further M–H measurement has been done at 325 K for un-implanted and implanted (fluence 10^{16} ions/cm^2) film.

3. Result and discussions

The thickness of the films has been estimated by using RBS measurement and it was found to be $\sim 500 \pm 10$ nm. Low energy ion implantation (81 keV Ar^{9+} ion beam) with various fluence was performed on $Zn_{0.95}Mn_{0.05}O$ films. When energetic ions penetrate inside the material, it loses energy by two nearly independent processes: (i) nuclear energy loss represented as (S_n) (elastic process), which dominates at an energy of about 1 keV/amu; and (ii) electronic energy loss represented as (S_e) (inelastic process), which