Effect of Doping Concentration on $Zn_{1-x}Mn_xO$ Thin Films Grown by RF Magnetron Sputtering

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Z. Naturforsch. **63a,** 585 – 590 (2008); received September 28, 2007

We have investigated the effect of doping concentration on structural, optical and magnetic properties of Mn-doped ZnO thin films deposited on Si (100) substrate by RF magnetron sputtering. The films have been characterized by X-ray diffraction (XRD), photoluminescence (PL) and superconducting quantum interference device (SQUID) magnetometry. It is observed from XRD, that the increase of Mn content increases the FWHM which indicates the degradation of crystalline quality. The photoluminescence spectrum reveals that the incorporation of Mn ions suppresses the deep level emissions considerably in comparison to those observed in pure ZnO. The near band edge (NBE) emission of Mn-doped films is shifted to the lower energy side (red shift) in comparison to pure ZnO film. The room temperature SQUID magnetometer results reveal that all the films show paramagnetic behaviour due to the lack of interactions among Mn moments.

Key words: Sputtering; Mn-Doped ZnO Thin Films; Diluted Magnetic Semiconductor.

1. Introduction

Recently much attention has been paid to diluted magnetic semiconductors (DMSs) because of their potential application in "spintronic" devices, which utilize both the electron spin in magnetic materials and the charge of electrons in semiconductors [1]. The main challenge for practical application of DMS materials is the realization of a Curie temperature preferably above room temperature in order to be compatible with junction temperatures.

Among the transition-metal (TM)-doped conventional III-V and II-VI semiconductors, TM-doped ZnO DMS have received great attention because ZnO has a very large electron mass and hence is expected to have large interactions between the charge of the conduction electrons and the electron spin of the magnetic ions [2]. Based on mean field theory it has been predicted that ZnO is a promising candidate for DMS materials to realize a Curie temperature above room temperature [3, 4].

In this communication, we report on Mn-doped ZnO films grown by RF magnetron sputtering. Some groups have claimed ferromagnetism in (Zn,Mn)O systems [5, 6], while others have observed only the spin-glass [7] and paramagnetic behaviour [8]. Based on local density approximation, Sato and Yashida [9] reported about the possibility of ferromagnetism in p-$Zn_{1-x}Mn_xO$. In contrast, ferromagnetism in n-$Zn_{1-x}Mn_xO$ has also been reported in [6, 10]. The mechanism responsible for ferromagnetism is complicated and the reproducibility of ferromagnetic behaviour is still a challenging problem. Hence, there are lots of reports on the growth of Mn-doped ZnO thin films by different techniques such as molecular beam epitaxy (MBE) [11], pulsed laser deposition (PLD) [12] and sol gel [13, 14] to observe ferromagnetism. The purpose of this communication is to investigate the ferromagnetic behaviour in Mn-doped ZnO films grown by RF magnetron sputtering. The grown films will be characterized with respect to their structural, optical and magnetic properties.

2. Experimental

Mn-doped ZnO films have been deposited on Si (100) substrate by RF magnetron sputtering technique. All the targets have been prepared by standard solid-

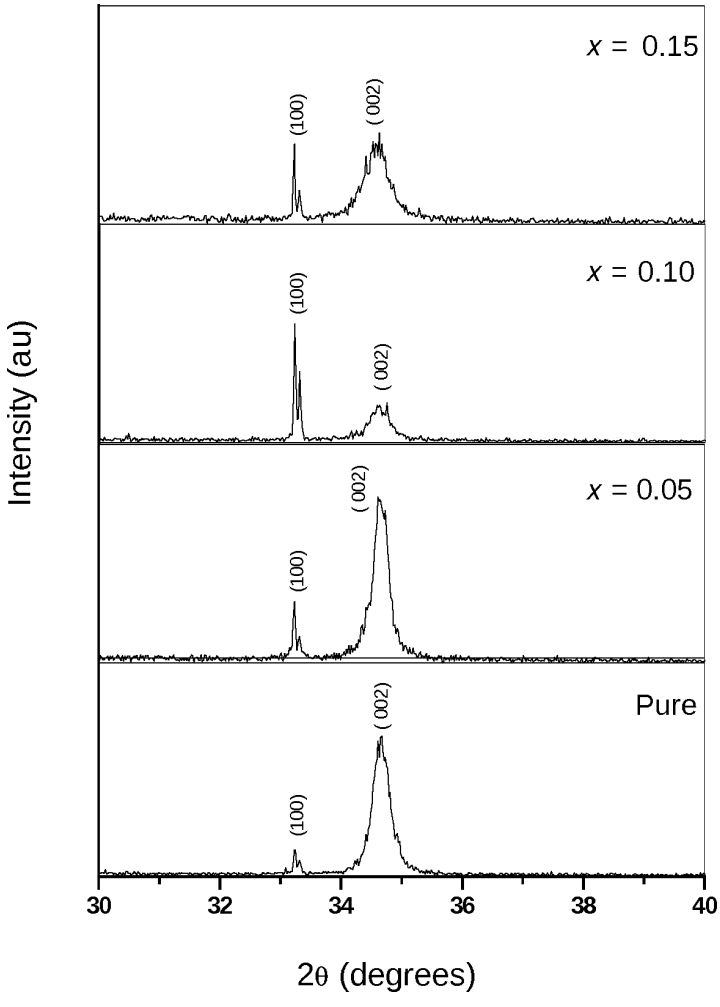

Fig. 1. XRD patterns of pure and Mn-doped ZnO films grown on Si (100) substrate.

state reaction routes. Prescribed amounts of ZnO (purity 99.99%) and MnO (purity 99.99%) powders have been thoroughly mixed for 10 h by ball milling and pressed in a form of cylindrical pellets. All pellets have been sintered at 950 °C for 6 h at slow ramping and cooling rates. Pellets thus prepared have been used as targets (50 mm, i. d., 2 mm thick) for sputtering. The distance between the target and substrate was fixed as 5 cm. The chamber has been evacuated to a basic pressure of $8 \cdot 10^{-6}$ mbar before the sputtering gas (Ar) was allowed to inflate. The sputtering process was then carried out in an $(Ar + O_2)$ atmosphere of 0.2 mbar with RF power of 100 W and substrate temperature of 450 °C for 30 min. The thickness of the films has been measured by filmetrics (F20) and was found around 120 nm. X-Ray diffraction (XRD) studies have been performed with the grown films using CuK_α radiation ($\lambda = 1.540562$ Å). Photoluminescence (PL) spectra of the Mn-doped ZnO films have been acquired in a FluoroMax-2 fluorescence spectrometer (JOBIN YVON-SPEX) with a 325-nm (Xe lamp) excitation source. The magnetic properties of the films were analyzed using a SQUID (superconducting quantum interference device) magnetometer in the range -5 T to 5 T.

3. Results and Discussion

3.1. Structural Properties

The crystal qualities of pure and Mn-doped ZnO thin films grown on Si (100) substrate have been characterized using X-ray diffraction. Figure 1 shows the XRD patterns of $Zn_{1-x}Mn_xO$ films together with those

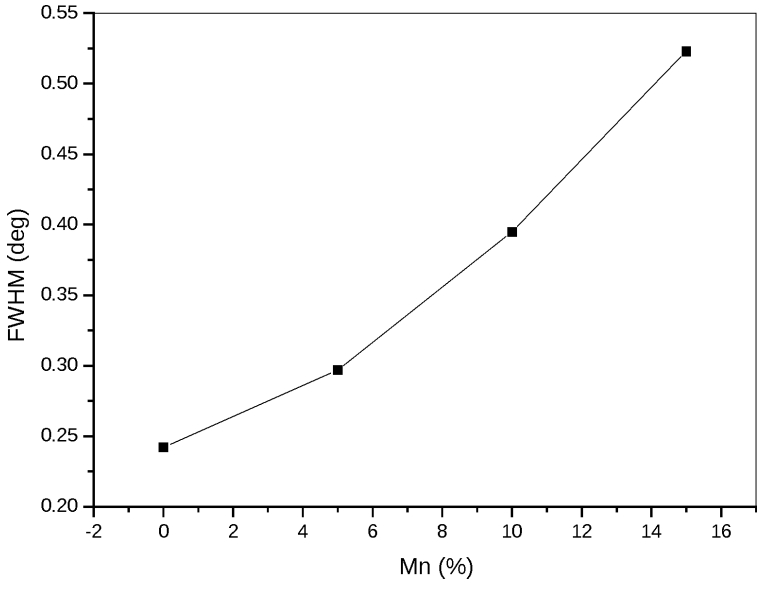

Fig. 2. Dependence of the FWHM of (002) on Mn content.

of a pure ZnO film. The Bragg reflections corresponding to the {002} and {100} planes of ZnO have been observed in all films, which indicates that the samples are of wurtzite structure. Further, the absence of secondary phases due to Mn suggests that, even after doping of Mn up to $x = 0.15$, which is beyond the thermal equilibrium limit of $x \approx 0.13$, the wurtzite structure of ZnO is maintained. One observes that the pure ZnO and the 5 mol% Mn ($x = 0.05$)-doped ZnO films have {002} preferential orientation while in other films ($x = 0.10, 0.15$) no such characteristics have been observed. This implies that the quality of the film declines as the dopant content increases. In order to confirm this, the FWHM of {002} diffraction peak of pure and Mn-doped ZnO have been plotted as functions of the dopant content as shown in Figure 2. It is seen that the FWHM increases as the dopant content increases, which is mainly attributed to the incorporation of a larger number of Mn ions. Such broadening of the FWHM because of the incorporation of more Mn ions has also been reported by Mofor et al. [15]. The diffraction angle, 2θ, has been found to vary only insignificantly from 34.67° to 34.62°, which is slightly larger than that of the unstressed powder value (34.42°) [16]; this specifies that the films are under compressive strain. Moreover, the slight shifts of the diffractive peaks to smaller angles by adding Mn shows a slight increase in the lattice constant c, since the ionic radius of Mn^{2+} (0.67 Å) is larger than that of Zn^{2+} (0.60 Å) [17].

3.2. Optical Properties

The photoluminescence (PL) spectra of pure and Mn-doped ZnO films grown on Si (100) substrate have been recorded and are depicted in Figure 3. The PL spectrum of pure ZnO has a strong near band edge (NBE) emission at 3.39 eV. Deep level emissions are observed in the same spectrum around 2.25 eV (yellow band, Y), 2.65 eV (green band, G) and 2.92 eV (violet band, V). It is believed that these yellow and green bands are essentially due to transitions from an oxygen vacancy to a zinc vacancy/oxygen interstitial [18, 19] and an oxygen vacancy to a zinc vacancy/valence band [15, 20 – 22], respectively, while the violet bands are due to transitions from an oxygen vacancy to a valence band [23]. It is worth noting that the addition of Mn into ZnO films reduces the intensity of the deep level emission which proves the incorporation of Mn into the Zn lattice. This agrees well with the results of XRD. It is observed that the NBE position is shifted towards the lower energy side (red shift), as the content of Mn increases. The band gap (NBE position) and the grain size of the $Zn_{1-x}Mn_xO$ films as a function of the dopant content are shown in Figure 4. It is emphasized that the band gaps of all the films are higher than the band gap of bulk ZnO (3.27 eV), which indicates that all the films are under compressive strain as found already in the XRD analysis. At higher grain size a higher band gap is observed. According to Scherrer's formula [24, 25], the FWHM and the grain size are in-

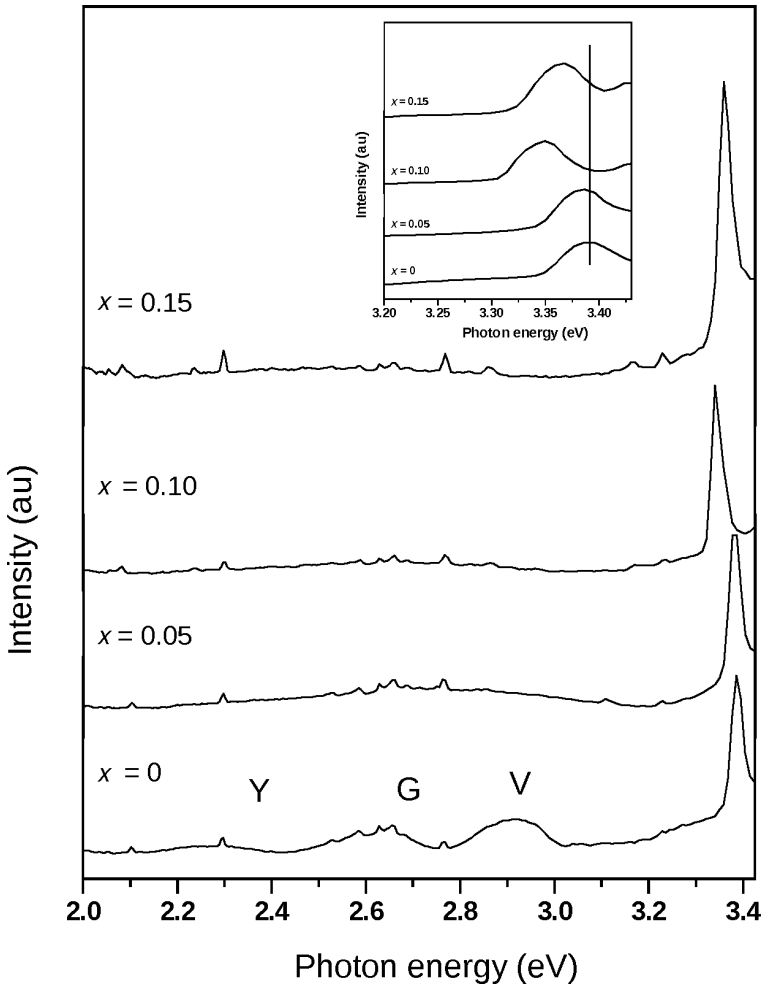

Fig. 3. Room temperature PL spectra of pure and $Zn_{1-x}Mn_xO$ thin films deposited on Si (100) substrate. Inset: PL spectra drawn in the range of 3.32 to 3.43 eV photon energy.

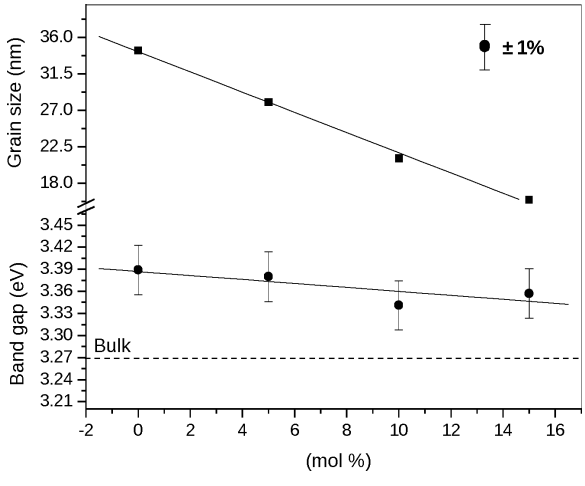

Fig. 4. Influence of Mn content on band gap and grain size of the $Zn_{1-x}Mn_xO$ films.

versely related and hence the incorporation of Mn reduces the grain size. If the grain size is smaller, there is a larger number of grain boundaries, which causes the shrinkage of the band gap. A similar change of the band gap with variation of Mn content was observed by He et al. [26].

3.3. Magnetic Properties

In order to observe the presence of ferromagnetic behaviour, the magnetic characteristics (M vs. H) of all the three samples have been studied at room temperature (300 K) using a SQUID magnetometer. The applied magnetic field varied from +5 T to −5 T. The actual magnetization of the film has been determined by subtracting the diamagnetic contribution of the silicon substrate from the raw data using the equation

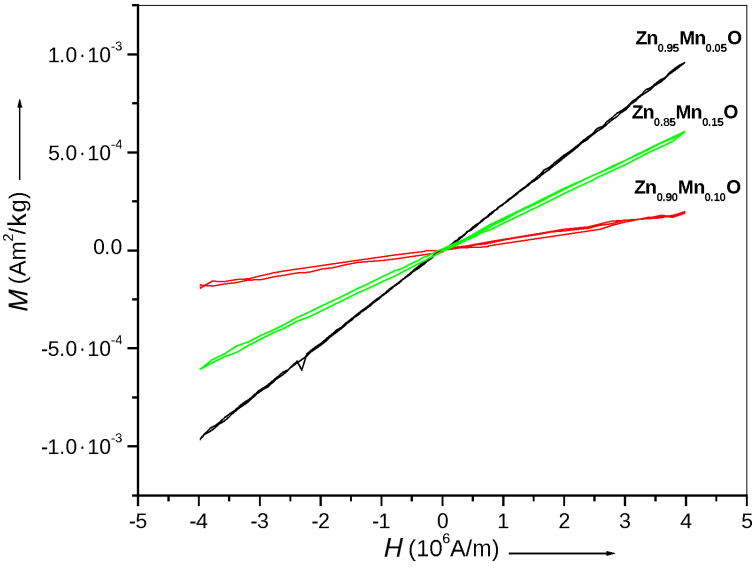

Fig. 5. *M-H* curves of $Zn_{1-x}Mn_xO$ ($x = 0.05, 0.10, 0.15$) films at 300 K.

$M_{\text{Film}}(H) = M_{\text{Total}}(H) - \chi_{\text{substrate}} H$, where $\chi_{\text{substrate}}$ is the susceptibility of the substrate [14]. Figure 5 shows the *M-H* curves of the $Zn_{1-x}Mn_xO$ ($x = 0.05, 0.10, 0.15$) thin films. It is seen that all the films exhibit typical paramagnetic behaviour and vary nonlinearly with the composition. This indicates that there is no interaction between the Mn moments which actually causes ferromagnetic ordering at room temperature. A similar behaviour has also been observed by Cheng and Chien for $Zn_{1-x}Mn_xO$ thin films [8]. This result is in contradiction with the theoretical prediction by Sato and Yashida [9].

4. Conclusion

$Zn_{1-x}Mn_xO$ films with varying doping content ($x = 0.05, 0.10, 0.15$) have been successfully grown on Si (100) substrate by RF magnetron sputtering. The grown films have been subjected to structural, optical and magnetic studies. The XRD results reveal the broadening of the FWHM for the (002) peak due to the incorporation of Mn ions into the Zn lattice leading to the degradation of the crystal quality. The PL analysis shows that pure ZnO has intense deep levels which could be considerably suppressed by the addition of Mn ions. It is also inferred that the incorporation of Mn causes a red shift. Structural and optical measurements have demonstrated that Mn^{2+} ions are present on Zn^{2+} sites in the lattices. In SQUID measurements, no indication of ferromagnetism is evidenced, neither in low doped ($x = 0.05$) nor in highly doped ($x = 0.10$, $x = 0.15$) samples, which is very likely due to lack of free carriers. Further systematic studies are under progress to achieve ferromagnetism at room temperature.

Acknowledgement

N. G. is grateful to the Council of Scientific and Industrial Research (CSIR), Government of India, for providing the financial support.

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