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Structural and optical properties of Mn-doped ZnO nanocrystalline thin films with the different dopant concentrations

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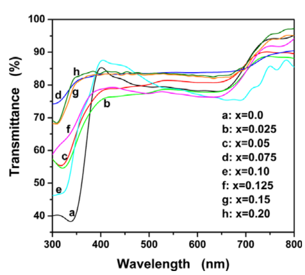
HIGHLIGHTS

- The transparent nanocrystalline ZnO thin films with different Mn doping contents were prepared by a sol–gel technique.
- The surface roughness and average crystallite size of thin films are sensitive to Mn doping contents.
- A board UV peak ascribed to the free exciton emission is observed in the undoped or doped ZnO thin film.

GRAPHICAL ABSTRACT



The transparent nanocrystalline thin films of undoped zinc oxide and Mn-doped ($Zn_{1-x}Mn_xO$) and their optical properties are reported.

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ABSTRACT

The transparent nanocrystalline thin films of undoped zinc oxide and Mn-doped ($Zn_{1-x}Mn_xO$) have been deposited on glass substrates via the sol–gel technique using zinc acetate dehydrate and manganese chloride as precursor. The as-deposited films with the different manganese compositions in the range of 2.5–20 at% were pre-heated at 100 °C for 1 h and 200 °C for 2 h, respectively, and then crystallized in air at 560 °C for 2 h. The structural properties and morphologies of the undoped and doped ZnO thin films have been investigated. X-ray diffraction (XRD) spectra, scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) were used to examine the morphology and microstructure of the thin films. Optical properties of the thin films were determined by photoluminescence (PL) and UV/Vis spectroscopy. The analyzed results indicates that the obtained films are of good crystal quality and have smooth surfaces, which have a pure hexagonal wurtzite ZnO structure without any Mn related phases. Room temperature photoluminescence is observed for the ZnO and Mn-doped ZnO thin films.

1. Introduction

As a wide direct band gap semiconductor and promising luminescent material, ZnO has been widely studied and used for various applications such as vacuum fluorescent displays, transparent conductive contacts, solar cells, laser diodes, ultraviolet

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lasers, thin film transistors, optoelectronic, and piezoelectric applications to surface acoustic wave devices and magnetic semiconductor [1–6] due to its wide band gap (3.37 eV, at room temperature), large exciton binding energy (60 meV), non-linear optical property and room temperature ultraviolet emission. As one of the transparent conducting oxide thin films, ZnO thin film shows a versatile combination of interesting optical, electrical and magnetic properties and plays a role in various technological domains such as solar cells [7], thin film gas sensors [8], varistors [9], spintronic devices [10], photodetectors [11], surface acoustic wave devices [12], light emitting diodes [13], and nanolasers [14].

Badeker reported that CdO thin films possess optically transparent and electrically conducting characteristics [15]. Later, many people began to be interested in the transparent conductive films, including ZnO, SnO_2, In_2O_3 and their alloys [16]. Doping these oxides resulted in improved electrical conductivity without degrading their optical transmission. Al doped ZnO (AZO), tin doped In_2O_3, (ITO) and antimony or fluorine doped SnO_2 (ATO and FTO), are among the most utilized TCO thin films in modern technology. In recent years, transparent conductive film with a range of high visible light transmittance, high electrical conductivity (close to metal) and semiconductor properties, are extensively studied and used for solar cells, displays, gas sensors, antistatic coatings, and modern military industry, aerospace industry.

As one of the versatile and important transparent conductive oxide thin films, ZnO thin film crystallizes in a wurtzite structure, exhibits n-type conductivity and shows a versatile combination of interesting optical, electrical and magnetic properties such as abundance in nature, absence of toxicity, transparency in the visible range, resistivity control over the range, high electrochemical stability, direct band gap (3.37 eV) [17], etc. According to a theoretical prediction by Dietl [18], $Zn_{1-x}Mn_xO$ is expected to be ferromagnetic material with a high Curie temperature. As a matter of fact, although several groups have confirmed the ferromagnetic properties of $Zn_{1-x}Mn_xO$ samples, some experiments have not found any ferromagnetic ordering in $Zn_{1-x}Mn_xO$ thin films. These controversial results seem to come from the defect concentration, the growth condition and the grain size of the textured $Zn_{1-x}Mn_xO$ films. On the other hand, it is believed that the Mn concentration in $Zn_{1-x}Mn_xO$ thin films relates to their microstructures and properties [19].

To date, undoped and doped ZnO thin films have been prepared by various deposition techniques, including chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD), magnetron sputtering, molecular beam epitaxy (MBE), pulsed laser deposition (PLD), spray pyrolysis, the sol–gel method, etc. [20]. Because of its advantages, such as simplicity, safety and low cost, controllability of compositions, good uniformity of thickness, and large area substrate coating, the role of the sol–gel process has been rapidly growing and is popularly used for polycrystalline oxide thin-film deposition [21].

Some studies have been carried out to realize Mn doped ZnO as a DMS, however, studies to understand the other properties of Mn doped ZnO are also necessary, the optical properties of the Mn-doped ZnO thin films have few been reported. Thus, in this paper, we try to investigate $Zn_{1-x}Mn_xO$ (x=0.025, 0.05, 0.075, 0.10, 0.125, 0.15 and 0.20) thin films with different Mn concentrations by an economic and popular technique, the sol–gel process, and the optical properties of the thin films were measured and compared.

2. Experimental

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification. The purity of CTAB was 99% and of the inorganic precursors were not less than 99.9% respectively.

Undoped and manganese doped ZnO films with different Mn atomic fractions were deposited on ordinary glass substrates by the sol–gel process. Zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2\,H_2O$) and manganese chloride tetrahydrate ($MnCl_2 \cdot 4\,H_2O$) were dissolved in a solution of methyl alcohol, respectively. The concentrations were 0.4 mol/L for zinc acetate, and the molar ratio of Mn as a dopant was of 2.5, 5.0, 7.5, 10, 12.5, 15, and 20 at% with respect to Zn, respectively. The resultant solutions were stirred at room temperature for 1 h to yield a clear and homogeneous solution. The CTAB was mixed with methyl alcohol with stirring until a homogenous solution (6.25 mmol/L) was obtained. The manganese chloride solution was then added into the CTAB solution with stirring. When the mixing solution became homogenous, the solution of zinc acetate was added under vigorous stirring. After stirring 1 h, the solution was finally aged at room temperature for 2 h. The ZnO sol prepared without doping was prepared in the same experimental conditions. The glass substrates (Corning Inc. 7059) were ultrasonically cleaned in acetone, alcohol for 15 min, rinsed in deionized water and then dried in hot air before the

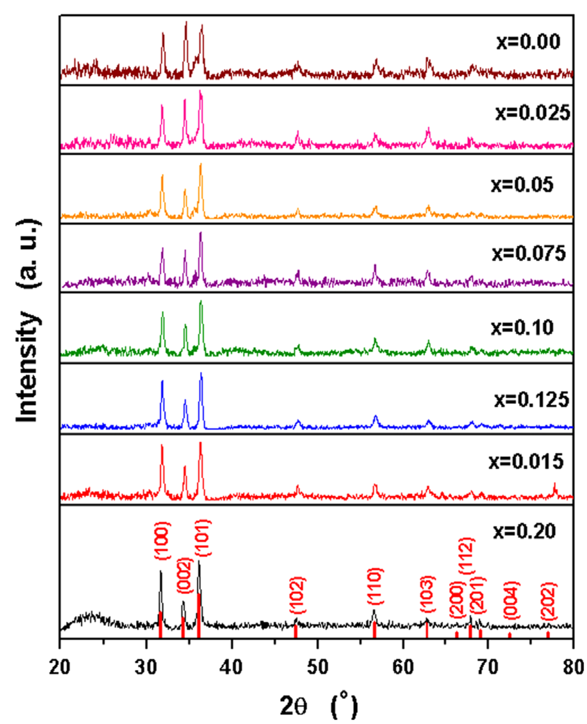

Fig. 1. XRD patterns of ZnO and $Zn_{1-x}Mn_xO$ thin films.

Table 1
The lattice constants and crystalline sizes of un-doped and Mn doped ZnO thin films.

Average lattice constant[a]	Un-doped and Mn doped ZnO thin films							
	ZnO	2.5% Mn	5.0% Mn	7.5% Mn	10% Mn	12.5% Mn	15% Mn	20% Mn
a (Å)	3.231	3.243	3.239	3.237	3.238	3.241	3.245	3.256
b (Å)	3.231	3.243	3.239	3.237	3.238	3.241	3.245	3.256
c (Å)	5.197	5.202	5.203	5.210	5.198	5.191	5.193	5.219
D (nm)[b]	22.70	22.10	21.56	21.50	20.95	20.40	22.57	23.08

[a] Average lattice constant was calculated from (100), (002) and (101) reflections.
[b] Crystallite size D is deduced from the (100) peak width.