Superlattices and Microstructures 72 (2014) 164–171

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Effect of thickness on structural, optical and mechanical properties of Mn doped ZnO nanocrystalline thin films RF sputtered in nitrogen gas environment

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ARTICLE INFO

Article history:
Received 25 March 2014
Received in revised form 1 April 2014
Accepted 2 April 2014
Available online 18 April 2014

Keywords:
RF sputtering
Thin films
Nanostructure
Optical properties
Mechanical properties

ABSTRACT

Thin films of $Zn_{0.95}Mn_{0.05}O$ were synthesized by RF- sputtering in nitrogen gas environment. Structural, optical and mechanical properties of the films with thickness ranging from 398 to 1650 nm are studied. The X-ray diffraction (XRD) results show that the as-deposited films are oriented along the (002) direction with hexagonal wurtzite structure. The field emission scanning electron microscopy (FESEM) studies show an increase in grain size with increase in thickness. Optical transmission studies show band gap values in the range 3.03–3.37 eV. The values of hardness and Young's modulus are found to be in the range 14–18 GPa and 122–167 GPa at an indentation depth of 100 nm respectively. The role of nitrogen doping on the microstructure and properties of films is discussed.

1. Introduction

The zinc oxide (ZnO) has been extensively studied in the recent years due to its lower cost and unique properties such as wide band gap (3.34 eV) at room temperature (RT), large excitonic binding energy (~60 meV) and availability in bulk single crystalline form suitable in optoelectronic

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http://dx.doi.org/10.1016/j.spmi.2014.04.001
0749-6036/

applications [1]. Zamfirescu et al. [2] have shown that a polariton laser, a new generation opto-electronic device, can be realized by using p-doped microcavities based on ZnO. The model polariton laser considered by them have extremely low threshold power of 2 mW at room temperature. It is pointed out that the unique properties of ZnO namely; it emits blue light, can be doped p-type, its excitons are stable at room temperature, have an extremely large oscillator strength, makes it excellently suitable for observing polariton lasing in the visible spectrum. Medard et al. [3] reported studies of excitonic properties of bulk ZnO and strong coupling observation in hybrid ZnO based macrocavities. There are reports of effect of nitrogen doping on un-doped and doped ZnO thin films [4–6]. The objective of these studies has been to obtain p-type conduction and ferromagnetism at room temperature in doped ZnO. Cho [7] reported high temperature ferromagnetism (FM) in amine treated Mn^{2+}:ZnO spin coated thin films and attributed it to the presence of p-type nitrogen defects in the ZnO lattice sites. Igamberdiev et al. [8] prepared $Zn_{0.95}Mn_{0.05}O$ thin films by spray pyrolysis and doped them with nitrogen to obtain p-type conduction. Lasley–Hunter et al. [9] synthesized ZnMnO thin films and found that annealing the films in O_2 enhanced the ferromagnetic moment whereas annealing in N_2 or Ar decreased it. Gu et al. [10] showed from the X-ray photon spectra that the Mn ions exist in the divalent state and O–Zn and N–Zn bonds coexist in N_2 doped $Zn_{0.97}Mn_{0.03}O$ thin films deposited by RF magnetron sputtering. The N_2 gas incorporation in ZnO thin films deposited by reactive sputtering also showed the p-type conductivity [11].

The study of structural, optical and mechanical properties of undoped and doped ZnO is essential for the application of these materials in devices. There is no report on the properties of undoped or doped ZnO thin films deposited only in nitrogen gas environment. In this work we report crystal structure, optical and mechanical properties of RF sputtered $Zn_{0.95}Mn_{0.05}O$ thin films of various thickness deposited in only N_2 gas environment.

2. Experiments

Thin films of Mn doped ZnO were deposited by the RF magnetron sputtering. The sputtering system used in the present work is described in our earlier work [12]. The $Zn_{0.95}Mn_{0.05}O$ target was prepared using standard solid-state reaction method. The substrate to sputter target distance was ~60 mm. The films were deposited on fused quartz substrates in N_2 gas environment under a working pressure of 12 m Torr for 30–120 min using 100 W of RF power. The thickness of the film was measured by stylus surface profilometer (Ambios tech model-1). The as – deposited films were characterized for crystal structure by X-ray diffractometer (PHILIPS) having Cu Kα (λ = 1.5405 Å) target, structural topography by FESEM (Carl Zeiss Ultra 55), optical transmission by JASCO V570 spectrophotometer in the wavelength range of 190–2500 nm and mechanical properties by nanoindentation (Hysitron Triboscan, USA) using a berkovich diamond indenter. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows the XRD plots for films deposited in N_2 – environment for different durations. The peak at (002) confirms the hexagonal wurtzite structure of the films. The as deposited films are oriented along the *c*-axis, normal to the substrate base plane. Since the wurtzite crystal structure is isotropic in the basal plane, the textured thin films on fused quartz can be considered as a *c*-axis oriented single crystal. The peak 2θ values are close to 34.4° that of unstressed bulk ZnO [13]. The peak gradually shifts to lower angle with increase in thickness of the film.

Fig. 1(A) shows that as the film thickness increases the diffraction peak becomes shaper, its intensity is enhanced and its location changes. This behavior shows that the crystallinity of the film increases with increase in thickness and the residual stress is generated during the deposition process. The strain in the $Zn_{0.95}Mn_{0.05}O$ films along *c*-axis perpendicular to substrate are given by the following equation [14]