Superlattices and Microstructures 55 (2013) 180–190

Contents lists available at SciVerse ScienceDirect

Superlattices and Microstructures

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

Influence of Sn doping level on antibacterial activity and certain physical properties of ZnO films deposited using a simplified spray pyrolysis technique

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ARTICLE INFO

Article history:
Received 10 November 2012
Received in revised form 7 December 2012
Accepted 14 December 2012
Available online 28 December 2012

Keywords:
ZnO thin films
Spray pyrolysis
Electrical properties
Antibacterial activity
Opto-electronic devices
SEM

ABSTRACT

Nanocrystalline tin–doped zinc oxide (ZnO:Sn) films with different Sn doping levels (0, 2, 4, ..., 10 at.%) were fabricated using a simplified spray pyrolysis technique. All the deposited films were characterized in order to explore the influence of Sn doping level on antibacterial and certain physical properties. The XRD studies revealed that all the films exhibited preferential orientation along the (002) plane irrespective of the Sn doping level. The electrical sheet resistance (R_{sh}) sharply decreases with the increase in the Sn doping level and attain a minimum value (3.88×10^2 Ω/□) at 6 at.% and then increases for further doping. The reason for this observed variation in the R_{sh} value is discussed in detail. The optical studies showed that all the films exhibited good transparency (≈85%) in the visible region. The obtained photoluminescence (PL) spectra endorsed the good crystalline quality of the films and enhancement of the optical band gap (E_g) caused by Sn doping. From the SEM images, it is inferred that the incorporation of Sn has the tendency of repairing the porous structure of ZnO films. The antibacterial activity of ZnO:Sn films was found to be enhanced with the increase in Sn incorporation into the ZnO lattice.

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0749-6036/$ - see front matter
http://dx.doi.org/10.1016/j.spmi.2012.12.011

1. Introduction

Transparent conductive oxide (TCO) films such as tin oxide (SnO_2), zinc oxide (ZnO), titanium dioxide (TiO_2) and indium oxide (In_2O_3) have significant and potential role in the fabrication of next generation of optoelectronic devices in the UV region and display devices. Among these TCOs, ZnO based thin films have recently gained much attention owing to its unique advantages over other oxide thin films. It is a direct, wide band gap (E_g) semiconductor ($E_g \approx 3.37$ eV) having hexagonal wurtzite structure with a large exciton binding energy (60 meV) [1]. Due to its high optical transparency, high electrical conductivity and high stability in the presence of hydrogen plasma, it has fascinated for many electronic and optoelectronic applications including sensors [2], piezo field emitters [3], transparent electrodes [4], field emission devices [5], light emitting diodes [6] and electroluminescent devices [7]. Furthermore, doped ZnO films significantly improve the efficiency of the above said devices.

The introduction of novel powerful antimicrobial agents is of great importance for the control of pathogenic bacteria. Currently, the antibacterial agents can be classified into two categories; organic and inorganic reagents. Inorganic antibacterial agents are more stable at high temperatures and pressures compared with the organic materials [8]. ZnO is one of the significant inorganic metal oxides exhibiting excellent antibacterial activities [9]. The efficient antibacterial property of ZnO nanostructure make it a suitable candidate for its possible application in the food preservation and packaging systems, variety of medical and skin coatings, water purification, bio-imaging and drug delivery. Recently, it is well established that the doping process improves the antibacterial efficacy of ZnO. Especially, the dopants like Sn, Mn, Mg, Sb, Co and N play a vital role in enhancing the antimicrobial activities of zinc oxide [10–14].

Therefore, in the present study, tin–doped zinc oxide (ZnO:Sn) thin films with different Sn doping levels (0, 2, 4, ..., 10 at.%) have been fabricated using spray pyrolysis technique and their certain physical properties along with the antibacterial activity have been explored in order to understand the influence of tin doping level. The reason for choosing spray pyrolysis technique is that, it is simple, inexpensive and has flexible process modifications for large area TCO coatings. Moreover, it has many advantages over other preparation techniques such as solvent casting method [15], pulsed laser deposition [16], chemical bath deposition (CBD) [17], sol–gel [18], salvo-thermal process [19] and rf-magnetron sputtering [20].

2. Experimental details

2.1. Preparation of ZnO:Sn films

Sn doped zinc oxide films were deposited onto the glass substrates with different Sn doping levels (0, 2, 4, ..., 10 at.%) by employing spray pyrolysis technique using perfume atomizer. In this perfume atomizer, the atomization was achieved based on hydraulic pressure without using any carrier gas. The starting solution was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) (0.1 M) salt in a mixture of deionized water, methanol and acetic acid taken in the ratio of 6:3:1 respectively. Tin doping was achieved by adding different proportions (2, 4, ..., 10 at.%) of tin (II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$) with the starting solution. Temperature of the substrate was maintained at 340 ± 5 °C using a temperature controller with chromel–alumel thermocouple. The intermittent spray deposition followed in this study involves a spray and 10 s interval. The substrates were cleaned ultrasonically with organic solvents before starting the deposition process in order to improve the adhesive nature of the film.

2.2. Film characterization

The thickness of the samples was measured using stylus technique (Profilometer: Surf Test SJ-301) and the obtained values are presented in Table 1. The crystal structure of the films was analyzed using X-ray powder diffraction (PANalytical-PW 340/60 X′ pert PRO) technique with CuK_α ($\lambda - 1.5406$ Å) as