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Spray pyrolysis derived ZnMgO:In thin films: Investigation of the structural, optical and electrical properties

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ABSTRACT

$Zn_{1-x}Mg_xO$:In films were deposited on quartz substrates via ultrasonic spray pyrolysis (USP). By tuning the molar ratio of Zn and Mg sources, the tunable band gap in ZnMgO:In films were realized. The obtained films exhibited wurtzite crystal structure with a preferential *c*-axis orientation. Larger grain size was obtained with increasing the Mg introduction. Photoluminescence (PL) indicated that the peaks of near-band-edge (NBE) emission appeared as a blue-shift from 378 nm to 370 nm, labeled as x value increase from 0 to 0.15. Optical band gap (E_g) calculated from the absorption edge further confirmed the blue-shift phenomenon due to the Mg substitution for Zn lattice sites. The average transmittance was about 90% in the visible wavelength region (400–800 nm). The increasing resistivity from $6.70 \times 10^{-3}\ \Omega$ cm to $2.14 \times 10^{-2}\ \Omega$ cm and decreasing mobility from 24.7 cm^2 V^{-1} S^{-1} to 6.46 cm^2 V^{-1} S^{-1} were observed.

1. Introduction

Nowadays, ZnO thin films, including ZnO:Al (AZO), ZnO:Ga (GZO) and ZnO:In (IZO), emerge as the promising materials due to their exceptional properties, such as non-toxicity, environmental-friendliness, cheapness as well as the excellent optical and electrical properties [1–3]. Based on the above

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advantages, ZnO films show potential application in the field of solar cells [4], chemical sensors [5], laser diodes and optoelectronic ultraviolet devices [6,7]. With the direct band gap (3.37 eV) and large exciton binding energy (60 meV), ZnO presents the favorable candidates for the optoelectronic devices [8,9]. However, the achievement of the practical application for ZnO is challenged by the band gap engineering. Many approaches have been adopted to modulate the band gap of ZnO, among which alloying with Mg, Be or Cd elements is the common one [10–13]. For the addition of Mg, Be or Cd elements to substitute for Zn lattice sites in ZnO bulk, band gap modulation of ZnO has been successfully achieved. Recently, $Zn_{1-x}Mg_xO$ films have aroused scientists' great interests for the sake of the close ionic radius of Mg^{2+} (0.57 Å) and Zn^{2+} (0.60 Å) as well as the wide band gap of MgO (7.80 eV) [14,15]. By Mg doping, $Zn_{1-x}Mg_xO$ films with the tunable band gap from 3.37 eV to 7.80 eV were realized [10]. Though the investigation of the large conduction band offset on ZnO/ZnMgO films has been conducted, the transmittance of the films still remains controversial for ultraviolet devices [16,17]. Moreover, band gap modulation with high concentration of Mg doping ($x > 0.3$) for $Zn_{1-x}Mg_xO$ films has been successfully achieved, but the electrical properties decreased ($\rho \sim 1\ \Omega$ cm) greatly [18]. Therefore, it is worthwhile to further investigate the tunable band gap with desirable conductivity by doping.

Current researches on the fabrication of ZnMgO films are reported by pulsed-laser-deposition (PLD) [19], molecular-beam epitaxy (MBE) [20], metal organic chemical vapor deposition (MOCVD) [21], magnetron sputtering (MS) [22] and ultrasonic spray pyrolysis (USP). Among them, USP technique presents the advantage of cost-efficiency; process-simplicity and easy-scalability in the fabrication of ZnO based thin films [23]. Within this study, the USP technology has been employed to deposit $Zn_{1-x}Mg_xO$:In films. To combine the transparent conductive properties with well-tunable band gap, the adjustment of Mg doping content in the starting sources is desirable. In addition, electrical properties correlated to optical and crystal structure properties of the $Zn_{1-x}Mg_xO$:In films are investigated systematically.

2. Experimental details

Indium doped ZnMgO films were deposited by USP technology on the quartz substrates, which were prepared 10 nm ZnO film as the buffer by MS. During the USP deposition, the growth temperature was maintained at 420 °C. The $Zn(Ac)_2{\cdot}2H_2O$, $Mg(Ac)_2{\cdot}4H_2O$ and $In(NO_3)_3$ solutions were used as the precursors of Zn, Mg and In sources, respectively. The optimized In/(Zn + Mg) ratio of 2.25 at.% was employed to control the In doping for obtaining good electrical performance. In addition, different Mg concentration of $Zn_{1-x}Mg_xO$:In films ($x = 0$, 0.05, 0.10 and 0.15) were used in order to achieve the Mg doping. The aerosol of precursor solution was generated by the commercial ultrasonic nebulizer, and transported to the substrates heated at 420 °C according to optimized results. Subsequently, the obtained products were annealed in an oven with mixed $Ar_2 + H_2$ (flux ration = 90:10) atmosphere at 400 °C for 20 min.

Crystal structure were measured by X-ray diffraction (XRD, D8-FOCUS) using Cu Kα radiation ($\lambda = 0.15406$ nm). The morphologies of films were characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-8010) equipped with EDS. The PL spectra were taken by a FluoroMax-4P spectrofluorometer system with Xe light source operating at 325 nm. The optical transmittance was evaluated using UV–VIS-2450 spectrophotometer in the wavelength range from 350 to 1000 nm. The electrical properties were analyzed by Hall-effect measurements (Bio-Rad HL 5500) in the Van der Pauw configuration.

3. Results and discussion

Fig. 1a presents the XRD patterns of In-doped $Zn_{1-x}Mg_xO$ films ($x = 0$, 0.05, 0.10 and 0.15) prepared at 420 °C. As shown in Fig. 1a, polycrystalline and hexagonal wurtzite structure of $Zn_{1-x}Mg_xO$ films are formed with a highly preferential (002) orientation. All diffraction peaks including (002) and (103) planes coincide well with hexagonal-phase (JCPDS 36-1451). No peaks related to Mg or In oxides are detected. It is confirmed that the doping Mg and In elements replace the Zn sites rather than