Optik 125 (2014) 5864–5868

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

The crystalline structure, conductivity and optical properties of Co-doped ZnO thin films

Said Benramache[a,b,*], Boubaker Benhaoua[b], Okba Belahssen[a,c]

[a] Material Sciences Department, Faculty of Science, University of Biskra, Biskra 07000, Algeria
[b] VTRS Laboratory, Institute of Technology, University of El-Oued, El-Oued 39000, Algeria
[c] Mechanics Department, Faculty of Technology, University of Tébessa, Tébessa 12000, Algeria

ARTICLE INFO

Article history:
Received 23 October 2013
Accepted 31 May 2014

Keywords:
ZnO
Thin film
Semiconductor doping
Ultrasonic spray technique.

ABSTRACT

Transparent conductive Co-doped ZnO thin films were deposited by ultrasonic spray technique. Conditions of preparation have been optimized to get good quality. A set of cobalt (Co)-doped ZnO (between 0 and 3 wt%) thin films were grown on glass substrate at 350 °C. The thin films were annealed at 500 °C for improvement of the physical properties. Nanocrystalline films with hexagonal wurtzite structure and a strong (0 0 2) preferred orientation were obtained. The maximum value of grain size $G = 63.99$ nm is attained with undoped ZnO film. The optical transmissions spectra showed that both the undoped and doped ZnO films have transparency within the visible wavelength region. The band gap energy decreased after doping from 3.367 to 3.319 eV when Co concentration increased from 0 to 2 wt% with slight increase of electrical conductivity of the films from 7.71 to 8.33 $(\Omega\,\mathrm{cm})^{-1}$. The best estimated structure, optical and electrical results are achieved in Co-doped ZnO film with 2 wt%.

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1. Introduction

Wide band gap II–VI semiconductors have attracted the interest of many research groups during the past few years due to the possibility of their applications in light-emitting diodes (LEDs) and laser diodes. Among the II–VI semiconductors, ZnO is an important optoelectronic device material for use in the violet and blue regions because of its wide band gap (3.37 eV) and large exciton binding energy (60 meV) [1,2]. ZnO thin films are promising candidates for applications in short-wavelength light-emitting devices, lasers, field emission devices, solar cells and sensors [3,4].

ZnO thin films can be produced by several techniques such as reactive evaporation, molecular beam epitaxy (MBE), magnetron sputtering technique, pulsed laser deposition (PLD), sol–gel technique, chemical vapour deposition, electrochemical deposition [5–7] and spray pyrolysis [8]. Among those techniques that have been reported to prepare thin films of ZnO, we will focus more particularly in this paper on the spray ultrasonic technique which is a low cost and suitable method for large-scale production. It offers several advantages in producing nanocrystalline thin films, such as, a simple deposition on glass substrate with a large range of temperatures, easy control of the film thickness and fine and porous microstructure with relatively homogeneous composition. Moreover, it is possible to alter the mechanical, electrical, optical and magnetic properties of ZnO nanostructures with doping. There are several reports on ZnO nanostructures doped with different elements, such as Al, Mn, Na, Mg, Ni, Ag [9–13].

The cobalt-doped ZnO thin films (ZnO:Co) have various applications such as transparent conductive; ferromagnetism; semiconductors; piezoelectric and solar cells; the films have low resistivity, good optical gap energy at low temperature and good transparency in the visible region [14]. Due to its high conductivity, good transparency and lower cost, the films are considered to be an utmost important material.

In this paper, we have prepared Co-doped ZnO thin films on microscope glass substrate through ultrasonic spray technique. The solution was sprayed on substrate at 350 °C, and their thin films were annealed at a temperature of 500 °C to improve their physical properties. The effect of the Co concentrations on the ZnO films has been studied, in order to find optimum Co doping concentration which gives highly semiconducting properties of Co-doped ZnO thin films.

2. Experimental procedure

2.1. Preparation of spray solution

ZnO solution was prepared by dissolving 0.1 M $Zn(CH_3COO)_2$, $2H_2O$ in the solvent containing equal volume of absolute ethanol

* Corresponding author at: University of Biskra, Material Sciences Department, Faculty of Science, Biskra, Algeria. Tel.: +213 779276135.
E-mail address: saidzno2006@gmail.com (S. Benramache).

http://dx.doi.org/10.1016/j.ijleo.2014.07.055
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solution of 99.995% purity and bi-distilled water, then we have added drops of HCl solution as a stabilizer, the mixture solution was stirred at 50 °C for 120 min to yield a clear and transparent solution.

ZnO:Co solutions were prepared by adding to the precedent solution a cobalt chloride, 4-methoxyethanol with ratio of Co/Zn lying in the range of 1–3 wt%. The solution became clear and homogeneous after stirring for 120 min at 50–70 °C.

2.2. Deposition of thin films

The resulting solutions were sprayed on the heated glass substrates by ultrasonic nebulizer system (Sonics) which transforms the liquid to a stream formed with uniform and fine droplets of 35 μm average diameter (given by the manufacturer). The depositions were performed at 350 °C as substrate temperature and 2 min as time of deposition; then the thin films were annealed at 500 °C, during 120 min period, for improvement of the physical properties [15].

The substrate was R217102 glass in a size of 1 cm × 1 cm × 0.1 cm, prior to pumping; the substrates (R217102 glass) were cleaned with alcohol in an ultrasonic bath and blow dried with dry nitrogen gas.

2.3. Characterization

Crystallographic and phase structures of the thin films were determined by X-ray diffraction (XRD, Bruker AXS-8D) with CuKα radiation ($\lambda = 0.1541$ nm) at scanning range between $2\theta = 25°$ and 55°. The optical properties of the deposited films were measured in the range of 300–800 nm using an ultraviolet–visible spectrophotometer (UV, Lambda 35); whereas, the electrical conductivity of the films was measured in a coplanar structure obtained after evaporation of four golden stripes on the surface of deposited films. All spectra were measured at room temperature (RT) in air.

3. Results and discussion

3.1. The crystalline structure Co-doped ZnO thin films

The X-ray diffraction patterns of undoped and Co-doped ZnO thin films, deposited on glass substrates at 350 °C are presented in Fig. 1. As can be seen, the diffraction peaks at $2\theta = 31.8°$, 34.5°, 36.4° and 47.5° correspond to the (1 0 0), (0 0 2), (1 0 1) and (1 0 2) planes, respectively. Whereas the Co-doped ZnO thin films with 1 and 3 wt% have only preferential (0 0 2) orientation. The film doped at 2 wt% has higher and sharper diffraction peak indicating an improvement in (0 0 2) peak intensity compared to the undoped ZnO thin film and the films doped at 1 and 3 wt%. The deposited films exhibit nanocrystalline structure with hexagonal wurtzite structure from the spectra [16,17]. This indicates that all films have preferential *c*-axis orientation along the (0 0 2) plane [18]. One can see that the high intensities directions were affected by the different degree of substitution of Zn^{2+} ions by Co^{2+} ions. The result indicates that the doping level of the films improved the structural properties. In order to confirm this remark, one can go for the calculation of the texture coefficient $TC(h\,k\,l)$. The later can be calculated from the X–ray data using the well-known formula of the intensity peaks corresponding to the (1 0 0), (0 0 2), (1 0 1) and (1 0 2) planes [5]:

$$TC(h\,k\,l) = \frac{I(h\,k\,l)/I_0(h\,k\,l)}{N^{-1}\sum_n I(h\,k\,l)/I_0(h\,k\,l)}. \quad (1)$$

where $I(h\,k\,l)$ is the measured relative intensity of $(h\,k\,l)$ plane, $I_0(h\,k\,l)$ is the standard intensity of the plane $(h\,k\,l)$ taken from the JCPDS data, N is the reflection number and n is the number of diffraction peaks. The variations of $TC(h\,k\,l)$ values for four major peaks of the thin films are presented in Fig. 2.

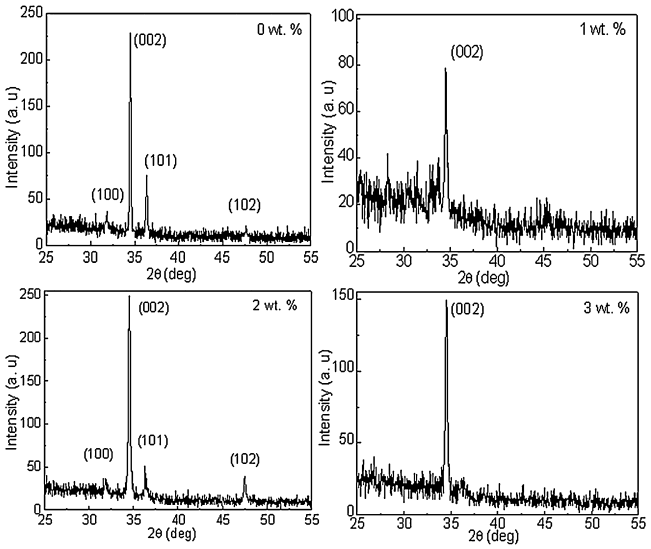

Fig. 1. X-ray diffraction spectra of undoped ZnO film and Co-doped ZnO films at different concentrations.

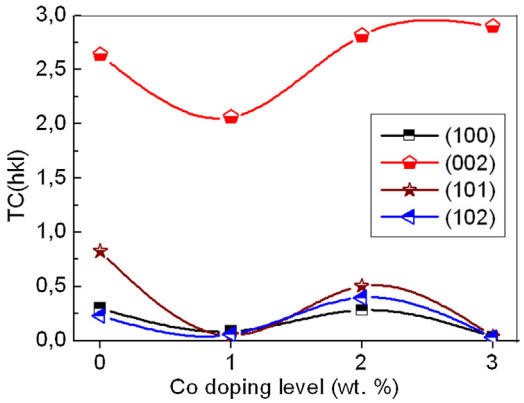

Fig. 2. Variation of TC (1 0 0), TC (0 0 2), TC (1 0 1) and TC (1 0 2) with doping level in ZnO:Co thin films.

We can also observe that the texture coefficient of (0 0 2) peak is the highest one conforming that all films having preferential *c*-axis orientation along the (0 0 2) plane as it was mentioned in the above paragraph. The texture coefficient of (1 0 0), (1 0 1) and (1 0 2) planes of the Co-doped ZnO thin films for 1 and 3 wt% are approached near zero. The enhanced crystalline quality of Co-doped ZnO thin films was obtained with 2 wt%. With the increase of Co concentration, the intensity of (0 0 2) peak was increased, whereas the full width-at-half-maximum (FWHM) is decreased as it was shown in Table 1; this remark is similar to the previously reported one in the litera-

Table 1
Bragg angle 2θ, the interplanar spacing d_{002}, the full width at half-maximum FWHM, the crystallite size G, lattice parameters c and the residual stress σ for ZnO:Co thin films were measured as a function of doping level.

Doping level (wt.%)	2θ (°)	d (Å)	FWHM (°)	G (nm)	c (nm)	σ (GPa)
0	34.54	2.59470	0.13	63.99	5.18939	−1.436
1	34.49	2.59834	0.28	29.61	5.19668	−0.805
2	34.54	2.59470	0.14	59.42	5.18939	−1.436
3	34.55	2.59397	0.26	31.88	5.18793	−1.562

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