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The Structural, optical and electrical properties of nanocrystalline ZnO:Al thin films

Boubaker Benhaoua [a], Achour Rahal [a], Said Benramache [b,*]

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

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ABSTRACT

The Al doped ZnO thin films were deposited by ultrasonic spray technique. The influence of Al doping on structural, optical and electrical properties of the ZnO thin films was studied. A set of Al doped ZnO (0–3.5 wt.%) were deposited at 350 °C. Nanocrystalline films with a hexagonal wurtzite structure with a strong (002) preferred orientation were observed after Al doping. The maximum value of grain size (33.28 nm) is attained with Al doped ZnO at 3 wt.%. Texture coefficient $TC(hkl)$ of the four major peaks where evaluated. Optically, in visible region the transmissions spectra $T(\lambda)$ show that the whole doped films exhibit lower values than the non doped one which has as transmittance more than 80%; whereas in the same region the optical transmissions of the doped films are affected by the doping ration. The band gap (E_g) increased after doping from 3.267 to 3.325 eV with increasing concentration of doping from 0 to 2.75 wt.%, respectively, according to the Burstein–Moss effect (blue shift of E_g) then beyond 3 wt.% in doping the band gap exhibit a slight decreasing due to the coexistence of Roth and Burstein–Moss effect. The electrical resistivity of the films decreased from 20 to 5.26 (Ω cm). The best results are achieved with 2.75 wt.% Al doped ZnO film.

1. Introduction

During the past few years, wide band gap II–VI semiconductors have attracted the interest of many research groups due its application in light-emitting diodes (LEDs) and laser diodes. Among

* Corresponding author. Tel.: +213 779276135.
E-mail address: benramache.said@gmail.com (S. Benramache).

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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 gas sensors, surface acoustic wave and transparent contacts [3–5].

ZnO thin films can be produced by several techniques such as reactive evaporation and thermal annealing [6], molecular beam epitaxy (MBE) [7], magnetron sputtered technique [8], pulsed laser deposition (PLD) [9], the low-temperature solution method [10], the sol–gel technique [11], chemical vapor deposition, electrochemical deposition [12] and spray pyrolysis [1], have been reported to prepare thin films of ZnO. Among these, we will focus more particularly in this paper on the spray ultrasonic technique because of its simplicity and suitability for large-scale production, it has several advantages in producing nanocrystalline thin films, such as, relatively homogeneous composition with fine and porous microstructure., a simple deposition on glass substrate because of the low substrate temperatures involved, easy control of film thickness. It is possible to alter the mechanical, electrical, optical and magnetic properties of ZnO nanostructures.

The above discussion has been about ZnO nanostructures, but the same features are seen in the case of ZnO-based microcavities, which are generally used as active layer facilitate in polariton injection [13]. The Al doped ZnO thin films have various applications such as transparent conductive, ferromagnetism, semiconductors, piezoelectric and solar cells, the films have low resistivity and good optical gap energy at low temperature, and transparent in the visible region [14]. There are several reports on ZnO nanostructures doped with different elements, such as (Fe, Ga, Li, N, Cu, P, Al, F, Mn, Ni, In, S, Co) [14–21]. The films (ZnO:Al) are considered to be an outmost important material due to its high conductivity, good transparent conducting oxide (TCO) and cost less.

In this paper, we have prepared Al doped ZnO thin films on microscope glass substrate through ultrasonic spray technique where substrate temperatures are maintained at 350 °C for all experimentation. General study of the Al doping concentration from 0 to 3.5 wt.% started by 1 wt.% was carried out in other article [22], around 3 wt.%. Only the effect of the Al doping concentrations of the ZnO films has been studied. The main goal for this research is to carry out the optimum concentration around 3 wt.% of Al doping which gives highly semiconducting properties of Al doped ZnO thin films such as transparence and conductivity.

2. Experimental procedure

2.1. Preparation of spray solution

ZnO solution were prepared by dissolving 0.1 M ($Zn(CH_3COO)_2$, $2H_2O$) in the solvent containing equal volumes absolute methanol solution (99.995%) purity and bidistilled water, then we have added a few drops of concentrated HCl solution as a stabilizer, the mixture solution was stirred at 50 °C for 120 min to yield a clear and transparent solution.

ZnO:Al solution were prepared by adding to the precedent solution an aluminum chloride, 6-methoxyethanol, such that the ratio of Al/Zn. This Al content can be varied between 0 and 4 wt.% (i.e. 0, 1, 2, 2.25, 2.5, 2.75, 3, 3.25 and 3.5 wt.%). The solution became clear and homogeneous after stirring for 120 min at 70 °C.

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

2.2. Deposition of thin films

The resulting solutions were sprayed on 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 deposition was performed at 350 °C fixed substrate temperature during 2 min as time deposition [23].