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Morphology controllable flower like nanostructures of Ag doped ZnO thin films and its application as photovoltaic material

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ABSTRACT

Pure and silver doped ZnO thin films were successfully grown on glass substrates by spray pyrolysis technique. The effect of Ag doping different concentration (2, 4, 6 and 8 at.%) on the structural, surface morphological, electrical and optical properties of Ag:ZnO thin films were investigated by X-Ray diffraction (XRD), Scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDS), photoluminescence (PL) and Hall effect measurement respectively. The X-ray pattern results confirmed that the Ag:ZnO thin films were polycrystalline nature with the preferential orientation along (002) plane in wurtzite structure. The SEM image revealed that the surface morphology of the films nano flower shaped grains with Ag doping. The compositional analysis by EDS confirms the presence of Zn, O and Ag. The surface roughness of the films decreases with increase of silver doping concentration was investigated by Atomic force microscopy (AFM). Optical transmittance 85% and a minimum resistivity of $1.23 \times 10^{-3}\ \Omega$ cm, are achieved for films when Ag doped ZnO with 6 at.% and confirm that these films are suitable for transparent conductive oxide (TCO) applications.

1. Introduction

Transparent conducting oxides (TCOs), are important basic material for applications in solar cells and optoelectronic devices because of their wide band gap (3.2 eV), low resistivity, high transparency in the visible region. Among these, zinc oxide is one of the most promising materials as transparent conducting oxide and that has been widely used in thin film solar cells, varistors, sensors etc. [1–3]. The large free exciton binding energy (60 meV), which ensures efficient excitionic emissions ZnO in persist room temperature and higher [4]. The pristine zinc oxide is unstable and is attributed to variation in the surface conductance under oxygen chemisorptions and adsorptions [5]. Its electrical and optical properties can be enhanced by adding Group III and VII dopants, such as Al, B, In, Ga and F [6]. In addition of Group III elements (metal dopants- Al, B, In Ga) into ZnO thin films, it make them as highly conducting materials which could be the alternative as inexpensive transparent conducting layers in several applications such as transparent display devices, and solar cells. In addition of elements (metal dopants- Ag, Al, B, In Ga) into ZnO thin films, it make them as highly conducting materials which could be the alternative as inexpensive transparent conducting layers in several applications such as transparent display [7]. When Ag doped ZnO is used as the transparent conducting oxide (TCO) film, it has several advantages structural, optical and electrical properties of ZnO fims doped metals such as Al, Ga, Y, Mn, Cu, Ag etc. [8].

In the past more than a few years, various methods have been employed to synthesized and prepare ZnO films such as rf magnetron sputtering [9], Spin coating [10], Sol-gel process [11], Pulsed laser deposition [12], Spray pyrolysis technique [13]. Among these technique the preparation of metal oxide thin films become simple and cost effective for the rapid production of metal oxides thin films for various application such as solar cells, LED's laser systems transparent conducting electrodes and soon.

Spray pyrolysis technique has become an extensively used deposition technique for thin film growth. These technique has present many advantages: it is easy, inexpensive, and suitable for mass fabrication with respect to other deposition techniques.

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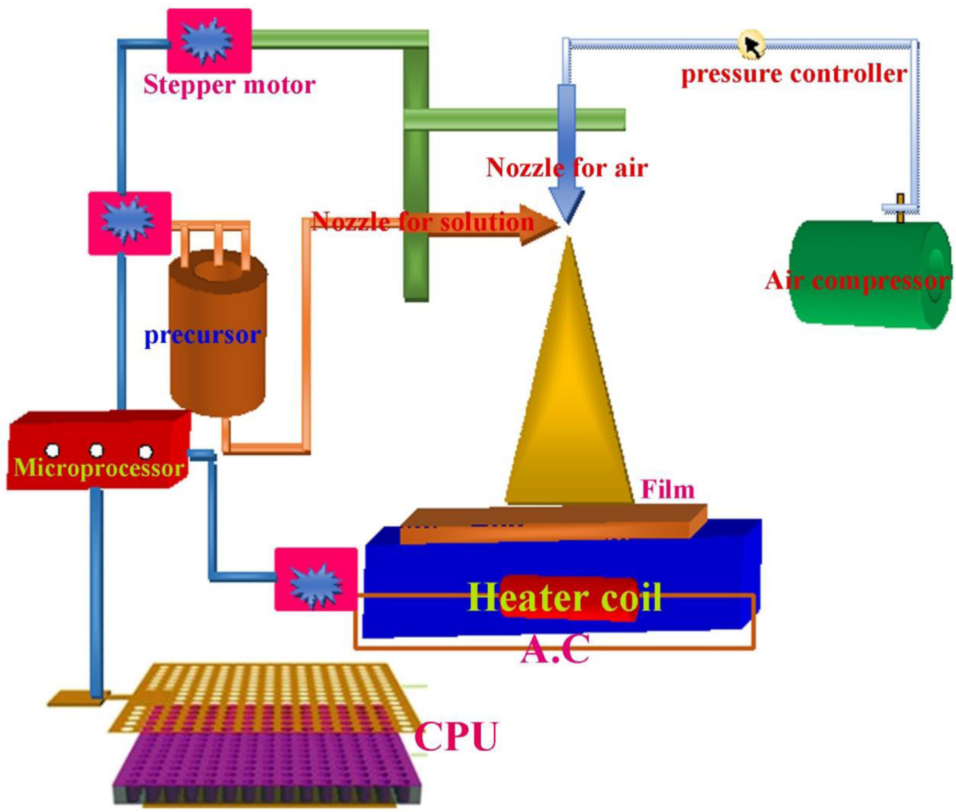

Scheme 1. Spray Pyrolysis setup unit.

2. Experimental procedure

Ag doped ZnO thin films were deposited onto a well cleaned microscopic glass substrate by spray pyrolysis technique. As a starting material, Zinc acetylacetonate (ZnAcAc) was used as a Zn precursor. With the optimized concentration of 0.1 M of ZnAcAc and silver nitrate ($AgNO_3$ Aldrich) as precursor for Ag (atomic ratios of 2 at.%, 4 at.%, 6 at.% and 8 at.%) was dissolved in deionized water. These prepared solution sprayed onto microscope glass substrates with dimensions of 75 × 25 mm^2 at the substrate temperature of (T_s = 400 °C). Before films prepared, glass substrates were well cleaned with HCl solution followed by water bath, acetone and finally rinsed with distilled water and allowed to dry in oven at 110 °C. The experimental setup used in this work consisted of substrate holder, on which the well-cleaned substrates were placed and heated using a heater which was controlled by a feedback circuit (temperature was fixed at 400 ± 5 °C). The prepared precursor solution was injected separately by using an atomizer. The spray rate of the precursor solution was maintained at 3 ml/min throughout the experiment by using microcontroller piston that was attached to the dispenser containing the precursor solution. To achieve a uniform coating, the spray head was allowed to move in X-Y plane using a microcontroller stepper motor. With simultaneous X- and Y-movements at a speed of 20 and 5 mm/s respectively, the spray head was able to scan an area of 200 × 200 mm^2. In this experiment, compressed air was used as a carrier gas with a pressure of 1 Torr with the flow rate of the solution, 3 ml/min. The diameter of the spray nozzle is 0.45 mm and the distance between nozzle and substrate is 20 cm. The substrate temperature was achieved with the help of heater which was controlled by an automatic temperature controller with an accuracy of ±5 °C. With the help of serial port, the entire unit was connected to a computer and the spray parameters were stored Scheme 1. This substrate temperature was already optimized by depositing films at various temperatures and the experimental set-up used for the spraying process is detailed in Arunachalam et al., 2016. The substrates were pre-heated for sufficient time before deposition. In order to dope Ag with ZnO, Silver was added to the starting solution. The solution was sprayed using different atomic percentage of dopant concentrations from 2, 4, 6 and 8 at.%. As the precursor aerosol droplets come close to the heated substrate, a pyrolytic decomposition process occurs and high quality Ag doped ZnO films were formed. After deposition, the films were left for allowed to natural cooling slowly to room temperature and washed with distilled water and then dried and annealed at 500 °C in air. The films deposited with various doping concentrations were characterized by different techniques such as XRD, SEM-EDS, AFM, UV–vis, PL measurement and Electrical measurements.

The chemicals such as zincacetylacetonate (($C_{10}H_{14}O_4$) Zn) and ethanol with the purity of 99% AR grade was obtained from MERCK (Germany), silver nitrate ($AgNO_3$) with the 99% of purity grade, were obtained from Sigma Aldrich. All these chemicals were purchased from A to Z lab needs, Chennai.

2.1. Characterizations techniques

The structural characterization of the deposited films was carried out by X-ray diffraction technique using SHIMADZU-6000 equipped with a monochromatic Cu-Kα radiation (λ = 1.5406 Å). The surface morphology was studied by using JEOL-JES-1600 scanning electron microscope (SEM). Optical absorption spectra were recorded in the range of 300–1200 nm using JASCO V-670 spectrophotometer. The photoluminescence (PL) spectra were recorded at room temperature using prolog 3-HORIBAJOBINYVON with an excitation source wavelength of 375 nm. The surface topological study was carried out by atomic force microscopy (AFM) using Nano