Materials Research Bulletin 83 (2016) 442–452

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Effect of fluorine (an anionic dopant) on transparent conducting properties of Sb (a cationic) doped ZnO thin films deposited using a simplified spray technique

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ARTICLE INFO

Article history:
Received 17 March 2016
Received in revised form 3 June 2016
Accepted 23 June 2016
Available online 23 June 2016

Keywords:
A. Thin films
A. Semiconductors
B. Optical properties
C. Photoelectron spectroscopy
D. Electrical properties

ABSTRACT

By adding fluorine, an anionic co-dopant with antimony, a cationic dopant, Sb + F doped ZnO films are prepared using a simplified spray technique and the effect of fluorine concentration (0, 5, 10 and 15 at.%) on electrical, optical, structural and surface morphological properties are studied. The results show that the resistivity of ZnO:Sb:F film decreases gradually with the increase in F doping level, reaches a minimum value of 7.27×10^{-3} Ωcm at 10 at.% and starts increasing thereafter. The possible mechanisms for this variation in resistivity are addressed. The optical transmittance slightly improves due to F doping. The surface morphological studies reveal that the shape and size of the grains are affected remarkably by Sb doping but not affected appreciably by the additional F doping. The XRD, XPS and EDAX analyses confirm the formation of hexagonal wurtzite ZnO structure and the presence of the expected elements in the final product.

1. Introduction

The increasing industrial and commercial requirements for low cost and high performance photovoltaic devices motivate the material scientists to develop more efficient transparent conducting oxide (TCO) thin films as TCO is one of the important components of the photovoltaic cells [1,2]. Low electrical resistivity and high optical transparency of TCO layers in the solar cells are important factors that determine the device efficiency. There are various types of TCOs including indium oxide (In_2O_3), tin oxide (SnO_2), tin doped indium oxide (ITO) and zinc oxide (ZnO). Among these TCOs, indium tin oxide is the most widely used TCO material due to its extreme high conductivity and transparency [3]. But, indium is rare, expensive and toxic material, which shows instability under hydrogen plasma atmosphere. Therefore, development of TCOs which are low in cost, non-toxic and abundant is very vital considering the safety measures as well as the feasibility for commercial applications [4].

Among the various indium free TCO films, zinc oxide (ZnO) film has been extensively studied in recent years due to its unique nature such as low cost, abundance, lower toxicity and high chemical stability [5]. Moreover, ZnO belongs to the group II–VI n-type semiconducting materials with wide direct band gap of 3.37 eV at room temperature and large exciton binding energy of 60 meV. Because of its tunable electrical and optical properties, it is considered as a promising candidate for several electronic devices including thin film transistor (TFT) [6].

However, the electrical resistivity of ZnO thin films is not as low as that of ITO films. Undoped ZnO thin films show high electrical resistivity owing to low carrier concentration. In order to reduce the electrical resistivity of ZnO thin films, many researchers attempted different ways such as

(i) Doping with various cationic and anionic dopants,
(ii) Annealing at different ambiences,
(iii) Aging the starting solution and
(iv) Changing the substrate temperature suitable for other parameters.

Among these ways, doping is the primary route to tune the electrical properties of ZnO. The widely used possible cationic and anionic dopants of ZnO are given in the Table 1.

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http://dx.doi.org/10.1016/j.materresbull.2016.06.033
0025-5408/

Table 1
Widely used cationic and anionic dopants of ZnO.

Cationic dopants	In, Al, Ag, Cu, Ga, Ti, Sn, Zr, B, Sb
nionic dopants	F, N, Cl

It is obvious from Table 1 that for cationic doping, we have several options. But, in the case of anionic doping only a few elements are mostly studied. They are fluorine (F), nitrogen (N) and chlorine (Cl). Off these, F has attracted more attention because of the following reasons.

- Fluorine is a halogen (high electronegative element) and more reactive element, which can substitute the oxygen in the ZnO matrix as it has compatible ionic radius with respect to oxygen. An extra free electron is created by this substitution for conduction due to the single bond with Zn (ie. Zn-F) [7].
- Moreover, fluorine as a dopant can cause an increase in the carrier mobility, because, the substitution perturbs the valence band, thereby leaving the conduction band relatively free from scattering [8].

Several reports reveal that when a cationic dopant is added with ZnO, the resistivity decreases initially up to a certain doping level, depending on the other process parameters [9–11]. However, the resistivity then begins to increase with the increase in doping concentration which is generally attributed to the solubility limit of that particular dopant in the ZnO lattice. Therefore, the researchers go for a second dopant along with the cationic dopant of interest. This simultaneous doping of an anionic dopant along with a cationic dopant is attempted by several research groups [12,13]. For co-doping (simultaneous doping) of cationic and anionic elements researchers have attempted for several combinations. Especially, for a cationic dopant along with F, several researchers have selected various elements like Al, In, Sn, B, Zr, Mg, Ga and Nd. But, Sb + F doping is hardly investigated and reported in the literature. To the best of our knowledge, for the first time, in this work, we have prepared antimony (Sb) and fluorine (F) co-doped ZnO thin films by simplified spray pyrolysis technique. The effects of co-doping on electrical, optical, structural and surface morphological properties are investigated and reported in this article.

Various deposition techniques such as sol-gel spin coating technique [14], RF magnetron sputtering [15], spray pyrolysis [16], pulsed laser deposition [17] and thermal evaporation method [18] are adopted to obtain good quality transparent conducting zinc oxide thin films. Among these methods, spray pyrolysis technique offers several advantages over many of the other techniques. The remarkable advantages of spray pyrolysis technique include simplicity, inexpensiveness, safety, non-vacuum, high growth rate and mass production capability for large surface area deposition and easy doping. Especially, this method is free from any “in situ” activation (eg. plasma, photo, electro, etc.,) which otherwise is essential to induce chemical reaction used in most of the chemical vapour deposition processes. In this technique, it is also possible to modify the mechanical, electrical and optical properties of ZnO nanostructures by appropriately changing the process parameters [19–21].

2. Materials and methods

Undoped, antimony doped (Sb), antimony and fluorine (Sb + F) co-doped thin films were deposited onto glass substrates by a simplified spray pyrolysis technique. Zinc acetate dihydrate (Zn $(CH_3COO)_2 \cdot 2H_2O$) was used as the host precursor due to its low dissociation enthalpy [22]. Appropriate amount of zinc acetate dihydrate was dissolved in a mixture (50 mL) of deionized water, methanol and acetic acid taken in the volume proportion of 7:2:1 to prepare 0.1 M of precursor solution. Antimony tri chloride ($SbCl_3$) and ammonium fluoride (NH_4F) were used as dopant precursors for Sb (2 at.%) and F (5, 10, 15 at.%), respectively. These two dopant precursors of required amount were added with the starting solution and stirred well to obtain the spray solution. Before the start of the deposition process, the glass substrates were cleaned thoroughly using HCl acid, acetone and deionized water in the given order. Then the substrates were ultrasonically cleaned with deionized water to remove the contamination if any on the surface of the glass substrates. The temperature of glass substrates was maintained at 350 ±5 °C using a temperature controller. The solutions were atomized using perfume container nozzle (generally used for cosmetic purpose). When aerosol droplets come close to the substrates, highly adherent thin films were produced due to the pyrolytic process.

The structural properties of the films were studied using X-ray diffractometer (PAN analytical-PW 340/60 X’Pert PRO) with Cu-Kα radiation of wavelength 1.5406 Å. The optical transmittance spectra were recorded using a UV–vis-NIR double beam spectrophotometer (LAMBDA-35). The surface morphology studies were observed using field emission scanning electron microscope (Carl Zeiss Ultra 55 FESEM). The room temperature photoluminescence (PL) spectra of the films were recorded using a spectro-fluorometer (Jobin Yvon_FLUROLOG-FL3-11) with the Xenon lamp of wavelength 325 nm as excitation source. The chemical state of the constituent elements of doubly doped films was investigated by X-ray photoelectron spectroscope (K-Alpha^{TM+}). The electrical parameters of the films were measured using a Hall probe technique.

3. Results and discussion

3.1. Structural studies

The X-ray diffraction analysis was carried out by recording the X-ray diffractometer patterns in the range of 20–80° to investigate the crystal structure and preferred crystal orientation of the deposited films. Fig. 1 shows the X-ray diffractograms of undoped, Sb doped and Sb + F co-doped ZnO thin films which indicate that all the films have polycrystalline nature and exhibit hexagonal

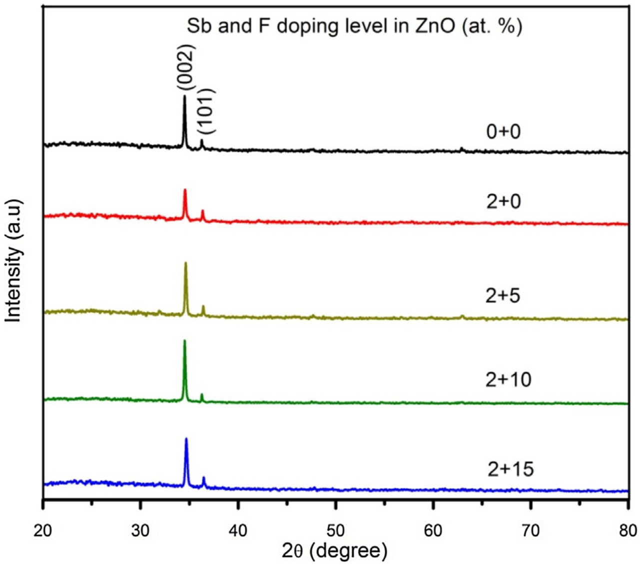

Fig. 1. XRD patterns of undoped, Sb doped and (Sb + F) co-doped ZnO thin films.