Materials Science in Semiconductor Processing 75 (2018) 221–233

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Physical properties of solution processable n-type Fe and Al co-doped ZnO nanostructured thin films: Role of Al doping levels and annealing

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ARTICLE INFO

Keywords:
Al and Fe co-doped ZnO thin films
Solution process
Annealing
Refractive index
Oxygen vacancy
Room temperature ferromagnetism
Grain boundary effect

ABSTRACT

The role of annealing temperature and Fe and Al co-doping on structural, optical, electrical and magnetic properties of solution processable ZnO thin films were investigated. ZnO:Fe thin films fixed with 2% of typical ferrous component were obtained to examine the role of 1–10% Al doping. X-ray diffraction analyses clearly indicates that the films to be polycrystalline and preferentially oriented along the c-axis of the hexagonal wurtzite structure. The film thickness, homogeneous distribution and decreasing/increasing of grain size dependence on Al content/annealing temperature (T_A) were assessed by scanning electron microscopy. X-ray photoelectron spectroscopy revealed that Al^{3+} and Fe^{2+} ions to substitute for Zn^{2+} without changing the wurtzite structure. A slight decrease in the optical band gap of ZnO at fixed Fe dopant and a considerable increase of the optical band gap with increased Al doping concentrations and T_A were observed. The refractive index increases with the fixed Fe dopant level and then decreases by Al doping levels, whereas the extinction coefficient clearly increases depended on both of Fe and Al concentrations. The refractive index and extinction coefficient both decrease with T_A. Hall measurements show n-type conductivity and the increase of charge carrier concentration by Al doping levels and T_A. Magnetic studies indicate room temperature ferromagnetism in Al and Fe co-doped ZnO thin films, whereas no room temperature ferromagnetism for the Fe-doped ZnO thin films was observed. An enhanced room temperature ferromagnetism in Al and Fe co-doped ZnO thin films was observed to depend on T_A.

1. Introduction

A great deal of effort has been devoted to transparent conductive oxide (TCO) thin films due to their tunable structural, optical and magnetic properties by inserting transition metal (TM) dopants in the last decade [1–5]. It is known that the TM can tune the physical properties of the TCO thin films because of the exchange interaction between the s and p electrons of host ZnO and d electron of TM ions [6]. Among the various TCO candidates, ZnO is the most important one due to its unique properties such as the wider direct band gap energy (3.3 eV), the larger exciton binding energy (60 meV) and the excellent physical and chemical stability. These properties make it a perfect host candidate for optoelectronic devices like solar cells, flat panel displays, gas sensors and UV semiconductor lasers [7–10].

In addition, ZnO is an attractive and promising diluted magnetic semiconductor (DMS) material since it exhibits ferromagnetism by doping transition metals such as Mn, Fe and Co at room temperature (RT) and is highly transparent to the visible light [1,11–13]. It is reported that the ferromagnetism of polycrystalline pure and doped ZnO can be caused by having enough grain boundaries [37,38]. Moreover, doping additional carriers into ZnO, such as Al, Cu and Ga elements, may also result in RT ferromagnetism [14–18]. For example, Lu et al. [14] reported an enhancement of the magnetization value of ZnCoO thin films by additional Al doping, produced by molecular beam epitaxy (MBE) technique. Similar enhancements in the magnetization values were also observed in Al doped ZnCoO and ZnMnO thin films produced by sol-gel [15] and sol-gel derived auto combustion [16] techniques, respectively. However, limited reports are available on trivalent and Fe

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https://doi.org/10.1016/j.mssp.2017.11.033
Received 2 November 2017; Received in revised form 20 November 2017; Accepted 22 November 2017
1369-8001/

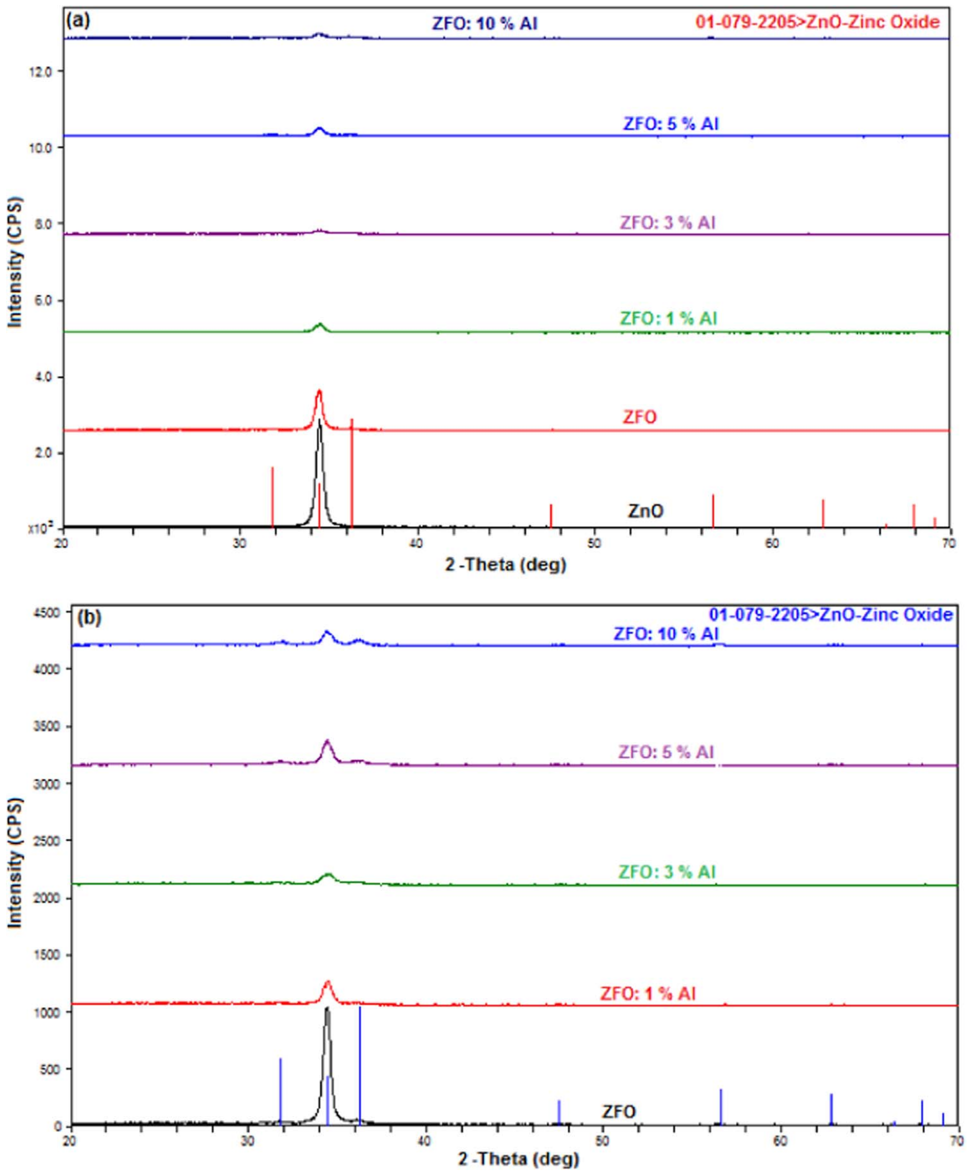

Fig. 1. (a) XRD patterns of ZnO, ZFO and ZFO: Al (1%, 3%, 5% and 10%), (b) ZFO and ZFO: Al (1%, 3%, 5% and 10%), (c) ZFO: Al (1%, 3%, 5% and 10%) thin films, (d-h) research for secondary phases in ZFO: Al (1%, 3%, 5% and 10%) thin films and (i) ZFO: Al (1%) thin films annealed at different T_A.

co-doped ZnO thin films. Recently, an incremental trend in magnetization of Al-doped ZnFeO derived via pulsed laser deposition (PLD) technique [19] and B doped ZFO produced by a modified and chemically derived citrate gel method has also been reported [20].

Inconsistent with the above mentioned studies, the lack of RT ferromagnetism in the $Zn_{1-x}Fe_xO$ and ZnCoO:Al films were observed by Goktas et al. [3] and Kaspar et al. [21], respectively. The results obtained to date suggest a clear discrepancy among findings, probably due to the differences in film growth methods, the annealing conditions and the chemicals used as starting powders type and solvents.

In the present study, the Al and Fe co-doped ZnO thin films were derived by solution and coating process, which is a comparatively simple, low cost and convenient to synthesis nanoparticles and thin films with high purity and homogeneity [1,3,5]. Such a thin film Fe and Al co-doped ZnO, produced by solution technique has not been studied yet in the literature. For this reason, this is the first report revealing the role of annealing temperature, Al and Fe co-doping contents on the structural, electrical, optical and magnetic properties of ZnO thin films synthesized by solution process.

2. Experimental details

ZnO thin films with fixed Fe doping ratio (2%) and different Al doping levels (1–10%) and average film thickness of 900 nm were deposited on glass substrates by sol-gel dip coating technique. To synthesize the films, the sols were formed by using appropriate molar