Characterization of ZnO doped SnO_2 thin films deposited by RF magnetron sputtering

S. R. Cynthia

Alagappa Chettiar Government College of Engineering and Technology, Karaikudi.

Email : srcynthiasam@gmail.com

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Abstract

High crystalline quality ZnO doped SnO_2 metal oxide thin films are prepared on Fluorine doped Tin oxide (FTO) glass plates by Radio Frequency (RF) magnetron sputtering method with various sputtering power of 50 W, 100 W and 150 W. The structural, morphological, elemental and optical properties of the as-deposited films were carried out with X-ray diffraction (XRD), field emission–scanning electron microscope (FE-SEM), energy dispersive X-ray analysis (EDX) and UV-Visible-NIR spectrophotometer respectively. The XRD analysis depicted the tetragonal rutile crystalline structure of the prepared films. FE-SEM images show the variation in the surface morphology with RF sputtering power. EDX analysis confirms the purity of the films. The transmittance spectra show a decrease in transmittance of the films with increase in RF sputtering power.

Keywords: metal oxide, RF sputtering , optical properties, morphology, crystalline structure

1. Introduction

The deposition of metal oxides in the thin film forms has been engrossed the researchers for the past few decades due to their application in various fields such as antireflection coatings, optical filters, surface acoustic wave devices, electronic components (both discrete and integrated), fabrication of large area photodiode arrays, solar selective coatings, solar cells, photoconductors, sensors, etc[1]. Among which Tin dioxide (SnO_2) shows an outstanding interest is a typical wide band gap (3.6 eV) n-type semiconductor with high excitation binding energy (130 meV) [2]. SnO_2 is a hopeful material for optoelectronic, catalytic and sensing applications and is highly sensitive to the small amount of impurities that can change its properties drastically [3]. It has been reported that in presence of antimony (Sb) or zinc (Zn) dopants tinoxide SnO_2 displays low resistivity and remains transparent in wavelength that includes the visible region [4]. Zhu *et al* reported that the formation of heterojunction between WO_3-SnO_2 shows an excellent sensing property [5]. Zheng *et al* reported that 10% ZnO–SnO_2 nano-heterostructure showed better response to Cl_2 than pure

SnO_2 [6]. ZnO is a high abundance, non toxic, high transparent and wide band gap (3.3 eV) metal oxide semiconductor [7].

Thin films are deposited by various deposition techniques such as thermal evaporation, electron beam evaporation, spray pyrolysis, chemical deposition, sol-gel, reactive pulsed laser ablation technique and sputtering, among which RF sputtering is the major industrial process due to its high deposition rate, high volume and large area uniformity [8]. In this work ZnO doped SnO_2 thin films were prepared by RF magnetron sputtering method with various sputtering power of 50 W, 100 W and 150 W and their structural, morphological, elemental and optical properties were analyzed.

2. Experimental Procedure

SnO_2 thin films doped with ZnO were deposited on FTO glass plates using RF magnetron sputtering method. For this powder mixture of SnO_2 with 99.999% purity and dopant ZnO (10 wt%) with 99.999% purity were mixed well and grained well using the ball miller by adding polyvinyl alcohol (PVA) as a binder for 20 hours and pelletized with a dimension of 50 mm diameter and 5 mm thickness using hydraulic pelletizer at a pressure of 400 KN. The pelletized target was sintered at 1000 °C for 4 hours. Thin films of ZnO doped SnO_2 were deposited with various RF sputtering powers of 50 W, 100 W and 150 W on quartz glass plates by radio frequency (RF) magnetron sputtering technique (HINDHIVAC; Planar magnetron RF/DC sputtering unit; Model-12'' MSPT). The well cleaned FTO glass substrates were placed 6 cm apart from the target inside the vacuum chamber. The vacuum chamber was evacuated to a base pressure of 1×10^{-6} mbar using rotary and turbo molecular pumps. Now, the high purity (99.999%) argon (Ar) gas was purged into the vacuum chamber with a flow rate of 25 sccm, which maintains the working pressure of the chamber to 1×10^{-3} mbar. Since Ar is an inert gas, it does not react with sputtering target or substrate. The Ar gas acts as a source for Ar^+ ions. In order to avoid overheating inside the vacuum chamber, cooling water was continuously circulated through the target and the chamber. Now, the pre-sputtering process was done for 10 minutes to remove any contaminants on the surface of the target and during this process the substrate was closed with shutter. The RF power of 50 W was applied to the target, the atoms and molecules from the target was sputtered out and condensed as thin film on the substrate surface. The deposition time was fixed as 10 minutes and the substrates were kept at room temperature. Similarly, the sputtering experiments were done for the RF powers of 100 W and 150 W.

The structural property of the sputtering targets and films was studied by X-ray diffraction (XRD) (X'Pert Pro PANalytical, The Netherlands) using CuKα radiation source with λ = 1.5418 Å operating at 40 kV and 30 mA. The compositions of the targets and films were examined with the help of energy dispersive X-ray analysis (EDX) (OXFORD XMX N). The field emission scanning electron microscope (FE-SEM) (Quanta FEG 250) was used to view the surface morphology of the films and the sputtering targets. The optical transmittance and absorbance spectra were recorded by UV-Visible-NIR spectrophotometer (LAB INDIA, UV3000$^+$).

3. Result and discussion

3.1 X-Ray Diffraction Analysis (XRD)

X-ray powder diffraction (XRD) is a prevailing technique used exclusively to identify the crystalline phases present in materials and to measure the structural properties of those phases. The X-ray diffraction pattern of the films deposited at 50 W, 100 W and 150 W are shown in figure 1. All the characteristic peaks are assigned to the tetragonal rutile crystalline structure consistent with the characteristics of the SnO_2 structure in JCPDS card 41–1445 [9]. The films shows preferred orientation along (2 0 0) orientation of the FTO thin film [10]. No phase corresponding to zinc or other zinc compound has been observed in the XRD patterns, indicating that ZnO gets incorporated into the SnO_2 lattice.

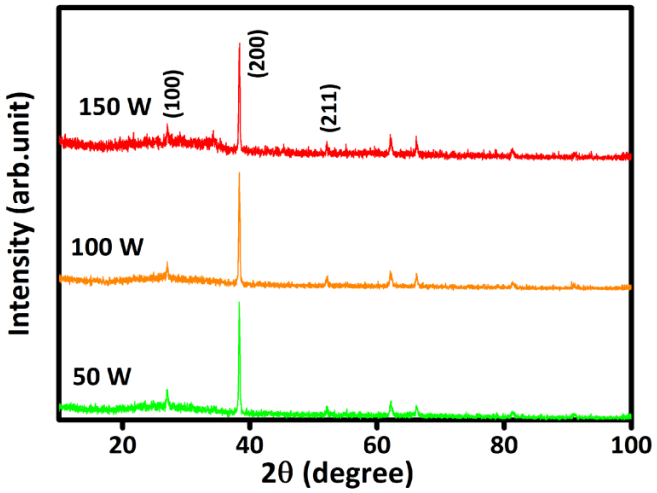

Fig 1: XRD pattern of the films deposited with 50 W, 100 W and 150 W.

The average nano-crystallite size (D) was calculated using the Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the X-ray wavelength, θ is the Bragg diffraction angle, and β is the FWHM of the XRD peak appearing at the diffraction angle θ [11]. The average crystallite size of the films deposited at 50 W, 100 W and 150 W are 56 nm, 64nm and 124 nm respectively.

3.2 Field Emission-Scanning Electron Microscope (FE-SEM)

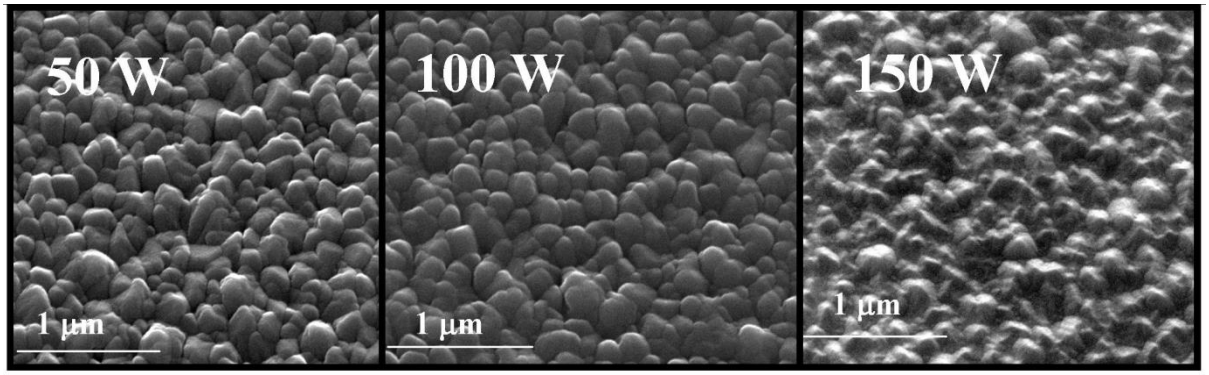

Fig 2: FE-SEM image of the SnO_2 doped films deposited at 50 W, 100 W and 150 W

FE-SEM is an inevitable method to analyze the morphology of the deposited ZnO doped SnO_2 thin films. Figure 2 shows the surface morphology of the films deposited at various sputtering power of 50 W, 100 W and 150 W. A variation in the surface morphology of the film was observed with variation in the RF power. The surface micrographs of films deposited with 50 W and 100 W appeared like closely packed polished angular aggregates. The film deposited at 150 W showed rarely packed polished angular aggregates. This disappearance in angular aggregates may be due to increase in thickness of the film. The films show a uniform deposition with pin hole free surface.

3.3 Energy dispersive X-ray Analysis (EDX)

Figure 3 shows the EDX spectrum of the film deposited at 50 W, 100 W and 150 W. Only Sn, Zn and O elements are observed in the spectrum which confirms the film purity. The atomic percentage of O, Sn and Zn were found to be 77%, 22% and 1% respectively for the films deposited at 50 W and 100 W. The films deposited at 150 W shows atomic percentage of O, Sn and Zn as 78%, 18% and 4% respectively.

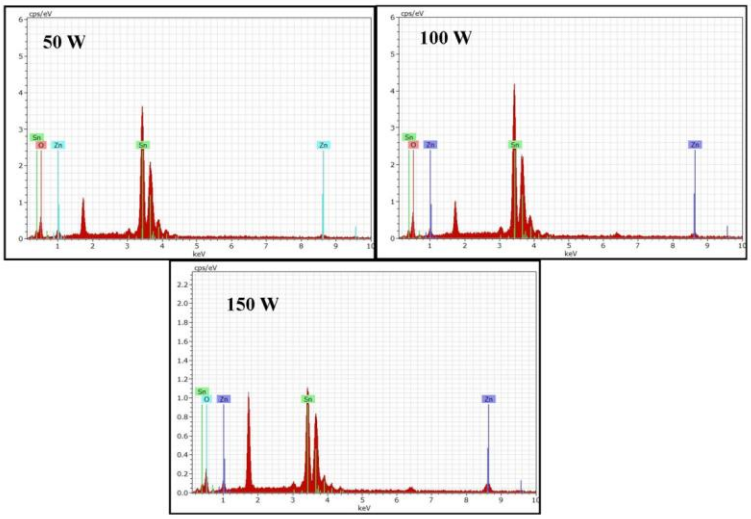

Fig 3: EDX spectrum of the ZnO doped SnO_2 film deposited at 50 W, 100 W and 150 W.

3.4 UV-visible NIR spectrophotometer study

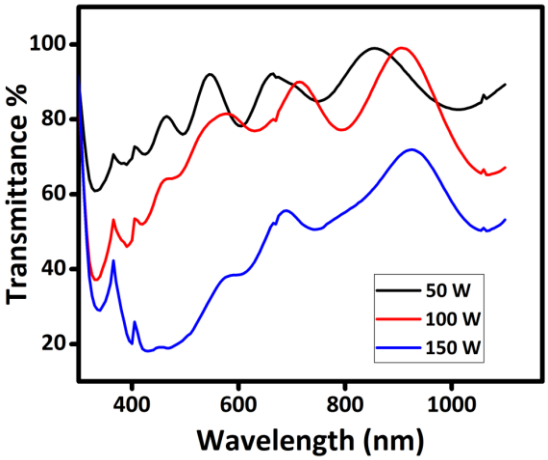

Fig 4: Transmittance of the ZnO doped SnO_2 film deposited at 50 W, 100 W and 150 W.

Figure 4 shows the transmittance spectra of the ZnO doped SnO_2 film deposited at 50 W, 100 W and 150 W. The transmittance of the films decreased with increase in sputtering power. The decrease in transmittance may be due to the increase in thickness of the film with RF sputtering power. The thickness of the films were calculated using the envelope method [12] were obtained as 510 nm, 950 nm and 1400 nm for the films deposited at 50W, 100W and 150 W respectively.

4. Conclusion

In summary thin films of ZnO doped SnO_2 films were deposited successfully by RF sputtering method with various sputtering power of 50 W, 100 W and 150 W. All the films showed tetragonal rutile crystalline structure. The films deposited at 50 W, 100 W and 150 W showed an average crystallite size of 56 nm, 64 nm and 124 nm respectively. The films were deposited uniformly and are pin hole free in nature. EDX spectrum confirmed the film purity. Using envelope method the thickness of the films were calculated as 510 nm, 950 nm and 1400 nm for the films deposited at 50W, 100W and 150 W respectively.

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