Journal of Alloys and Compounds 624 (2015) 251–257

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Ti doped ZnO thin film based UV photodetector: Fabrication and characterization

P.S. Shewale [a], N.K. Lee [a], S.H. Lee [a], K.Y. Kang [a], Y.S. Yu [a,b,*]

[a] Convergence of IT Devices Institute, Dong-Eui University, Busan 614-714, South Korea
[b] Department of Radiological Science, Dong-Eui University, Busan 614-714, South Korea

ARTICLE INFO

Article history:
Received 31 July 2014
Received in revised form 1 October 2014
Accepted 13 October 2014
Available online 19 October 2014

Keywords:
ZnO thin film
Spray pyrolysis
XRD
FE-SEM
UV photodetector

ABSTRACT

This paper presents the synthesis of undoped and 2 wt.% titanium (Ti) doped zinc oxide (ZnO) thin films onto glass substrates by chemical spray pyrolysis technique. Both films are deposited at 375 °C substrate temperature. The influence of Ti doping on structural, morphological, optical and UV detection properties of ZnO film was studied. Both films revealed to be of polycrystalline nature with a hexagonal wurtzite structure; and the ZnO film crystallinity improved on Ti doping. Surface morphological observations agreed well with structural results. The Ti incorporation in ZnO thin films were confirmed by an energy dispersive X-ray spectroscopic analysis (EDX). The Ti doping increased the optical transmittance (~96% at 550) and band gap (~3.2927 eV) of ZnO thin film. Further, the metal–semiconductor–metal (MSM) planar ultraviolet photodetectors (UV PDs) were fabricated from deposition of tin (Sn) contacts onto undoped and Ti doped ZnO films using e-beam evaporation technique. To investigate UV photodetection properties, the MSM devices were subjected to current–voltage (*I*–*V*) characteristics measurements of forward and reverse bias in dark and UV light conditions. The photocurrent and responsivity were measured as a function of optical power density and applied voltage, respectively. The reproducibility of the UV detection performance of MSM devices was ensured by constantly switching UV light on and off at regular time intervals. The Ti doped ZnO film based UV PD demonstrates highest responsivity of about 0.051 A/W upon 2 mW/cm^2 illumination at 365 nm peak wavelengths and 5 V applied bias.

1. Introduction

Wide band gap semiconductors such as SnO_2, TiO_2, and ZnO etc. have been paying a great deal of attention due to their potential applications for next-generation electronic and optoelectronic devices [1–3]. Among these materials, thin films of zinc oxide (ZnO), an n-type semiconductor, are most fascinating with their excellent optical and electrical properties, in addition to their high chemical stability [4]. Therefore, ZnO has widespread applications for metal oxide semiconductor (MOS) gas sensors, transparent conducting oxide (TCO) layers, light emitting diodes (LEDs), transparent thin film transistors (TFT's), ultraviolet (UV) lasers and especially the UV detectors [5,6]. In particular, the advantageous features of wide direct band gap ($E_g = 3.37$ eV), high exciton binding energy (60 meV), high radiation hardness, non-toxicity, good sensitivity to UV region and easy as well as inexpensive manufacturing make the ZnO material system an ideal choice for realization of high-performance UV photodetectors (UV PDs) [7–9]. The ZnO based UV PDs are important devices that can be used in various civil and military applications including UV astronomy, environmental monitoring, flame sensing, secure space-to-space communications, and chemical/biological analysis [10]. Therefore, many researchers have been focusing on ZnO as prominent semiconducting metal oxide for possible UV detection. Over the years, different configurations of ZnO based UV PDs had been prepared and characterized by researchers viz. metal–semiconductor–metal (MSM) detector [11–13], Schottky photodiode [14,15], p–n heterojunction photodiode [16,17], etc. Among these, the MSM structured UV PD with two ohmic contacts is typically the simplest to fabricate. Previously, MSM PDs with good responsivity had been demonstrated using undoped ZnO thin films [12,13].

Furthermore, doping is supposed to be a significant and effective way to improve the properties of MSM photodetectors. Accordingly, some researchers have studied the UV photoresponse of ZnO films by doping with transition elements; such as Co, Cu, Ni and Mn [18–20]. Titanium (Ti) is such another transition dopant elements which have an ionic radius (0.068 nm) smaller than that of zinc (Zn) (0.074 nm), and thus Ti^{4+} ions may replace Zn^{2+} ions at substitutional sites [21]. This in turn acts as a donor by providing

---

* Corresponding author at: Department of Radiological Science, Dong-Eui University, Busan 614-714, South Korea. Tel.: +82 51 590 2760, +82 10 3846 9295; fax: +82 51 890 2767.

E-mail address: ysyu@deu.ac.kr (Y.S. Yu).

http://dx.doi.org/10.1016/j.jallcom.2014.10.071
0925-8388/

two free electrons. Therefore Ti doping in ZnO films is expected to modify photoresponse through enhanced electrical properties. Besides, for fabrication of high-performance MSM UV PDs, it is imperative to achieve a large Schottky barrier height at the metal–semiconductor interface that results in a small leakage current and high breakdown voltage; which may possibly increase responsivity and photocurrent to dark current contrast ratio [22]. To realize a large Schottky barrier height on ZnO, researchers have applied high work function metals such as gold (Au), platinum (Pt), and Palladium (Pd) which are considered to be very expensive metals. Tin is an interesting low cost metal that can be used as a stable contact electrode due to its reasonably high work function (4.42 eV). However, to date no one has reported UV photo detection properties of Ti-doped ZnO thin film based MSM PD with Sn contacts. In this paper, we report synthesis of undoped and Ti-doped ZnO thin films by using cost-effective chemical spray pyrolysis technique. The films are characterized as their structural, morphological and optical properties. Finally, we fabricated undoped and Ti doped ZnO photoconductive UV detectors in MSM configurations and their photoconductive UV detection properties have been investigated and discussed.

2. Experimental

2.1. Synthesis of undoped and Ti doped ZnO thin films

The undoped and Ti-doped ZnO thin films were synthesized onto microscopic glass substrates by using chemical spray pyrolysis technique by optimizing its deposition parameters. For undoped ZnO thin film deposition, 0.05 M of zinc acetate was dissolved in methanol and sprayed through a specially designed glass nozzle onto preheated glass substrates. The substrate temperature was kept constant at 648 K. To dope ZnO thin films with 2 wt.% of Ti, the spraying chemical solution was prepared by mixing appropriate volumes of equimolar (0.05 M) solution of high purity zinc acetate [$Zn(CH_3COO)_2{\cdot}2H_2O$] and titanyl acetylacetonate [$TiC_{10}H_{14}O_5$] in methanol. Then, the thin film deposition was carried out by spraying resultant solution onto the preheated glass substrate kept at 648 K temperature. During all the deposition process, the compressed air was used as a carrier gas to control the solution spray rate at ~5 ml/min. The nozzle to substrate distance was 26 cm and the to and fro nozzle oscillation frequency was 28 cycles/min. Throughout the experimentation, the substrate temperature was controlled by using an electronic PID temperature controller. Harmful gases evolved from the thermal decomposition were expelled out.

2.2. Characterization and UV photodetection property measurements

The undoped and Ti-doped ZnO thin films were characterized by means of structural, surface morphological, optical and electrical techniques. The phase and crystalline structure of the thin films were investigated by X-ray diffraction (XRD) using X-ray diffractometer (Rigaku, D/MAX 2100H Model: operating at 40 kV and 30 mA). The Cu Kα (λ = 1.5406 Å) radiation was used. The surface and cross-section micrographs were obtained by Quanta 200 FEG & FEI Company FE-SEM equipment. Cross-sectional FESEM images were used to measure the average film thickness. The chemical composition was determined by an energy dispersive X-ray spectrometer (EDX) attached to FE-SEM. Optical transmittance (at normal incidence) measurements were performed at room temperature using a double-beam UV–Vis–NIR spectrophotometer (Model: Cary-5, Varian, Australia). To fabricate the photoconductive UV detector devices based on metal–semiconductor–metal (MSM) configuration, the ohmic contacts were made by depositing tin metal thin film layers (with ~200 nm thickness) onto the spray deposited undoped ZnO and 2TZO thin films using the e-beam evaporation technique. The forward and reverse current–voltage (*I–V*) characteristics of these MSM devices were measured by applying bias voltage from 0 to 5 V across the junction using Keithley instruments model 2410 Sourcemeter. The MSM devices were kept in the dark for more than 24 h to establish the stable dark current; before measuring the dark *I–V* characteristics in the darkroom. In the UV irradiation experimentation, a mercury arc lamp was used as the UV light source (λ = 365 nm) for illumination of the MSM device. Both the undoped ZnO and 2TZO thin film coated MSM UV photodetectors were studied under UV light exposure at different incident optical powers. Finally, their photocurrent response to UV light was measured by switching the UV light source of 2 mW/cm^2 intensities. All dark and photocurrent measurements were performed at room temperature.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows XRD spectra of undoped and 2 wt.% Ti doped ZnO (2TZO) thin films. Both the samples are preferentially oriented along (002) plane; however weak intensity peaks corresponding to (101) and (103) planes are also observed. Importantly, no additional peaks corresponding to titanium or titanium oxide are observed for 2TZO thin film; although the doping percentage is moderately high. This confirms that titanium substitutes zinc in the hexagonal lattice and/or titanium segregates to the non-crystalline region in grain boundaries. The matching of observed and standard '*d*' values (JCPDS data card No. 36-1451) shows that the samples are polycrystalline with the wurtzite phase ZnO (P63mc) with preferential *c*-axis orientation perpendicular to the substrate surface. The intensity of (002) peak apparently decreased when ZnO is doped with Ti. However the full width half maximum (FWHM, β) of (002) peak that determines the film crystallinity is also decreased from Ti incorporation. For undoped ZnO the β value is 0.00276; that approaches 0.00255 for 2TZO film. This indeed suggests that Ti doping in ZnO films improves its crystallinity. Furthermore, a shift in the (002) diffraction peak to the lower diffraction angle by 0.04° was observed when ZnO film is doped with titanium. Such a shift in diffraction peak position (2θ) can be correlated to the change in crystallographic properties of the doped nanostructures on account of the difference between ionic radii of titanium and zinc. Similar shift in (002) peak position on Ti incorporation in ZnO was observed by Chung et al. [23] and Lin et al. [24]. From the above values of β and 2θ of the (002) peak, the average crystallite size (*D*) was calculated by using the Scherrer's formula [25]. In addition, to get more information on defects in the films the dislocation density (δ) was evaluated by the simple approach from Williamson and Smallman [26]. It is seen that the average crystallite size is increased from ~52.67 to ~56.87 nm and dislocation density is decreased from 3.6047×10^{14} lines/m^2 to 3.0919×10^{14} lines/m^2; when ZnO film is doped with titanium. A large *D* and small δ value obtained for the 2TZO thin film implies its better crystallization. Such thin film having good structural quality is considered as the prerequisite for the fabrication of UV photoconductive devices as it has more photogenerated electrons. Comparable results were reported in the studies carried out by Zhong and Zhang [27].

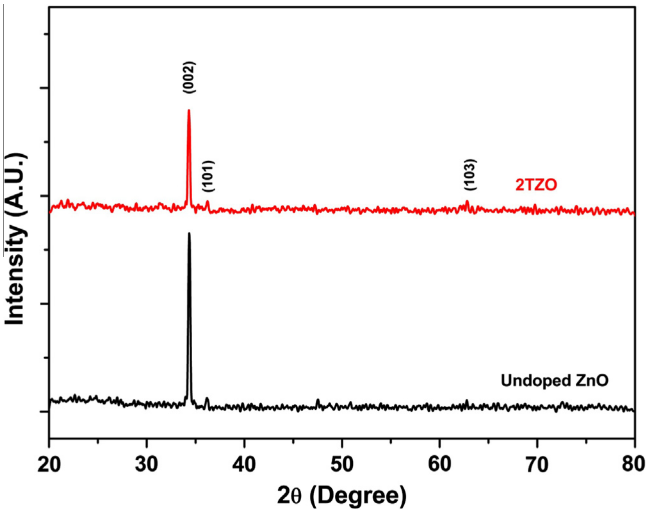

Fig. 1. X-ray diffraction spectra of undoped ZnO and 2TZO thin films.