Ceramics International 44 (2018) 16464–16469

Contents lists available at ScienceDirect

Ceramics International

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

Effect of Au ion beam on structural, surface, optical and electrical properties of ZnO thin films prepared by RF sputtering

M. Fiaz Khan[a,d,*], K. Siraj[a], A. Sattar[b,**], S. Majeed[a], H. Faiz[a], M.I. Khan[c], J. Raisanen[d], K. Mizohata[d], M. Kemell[e]

[a] *Laser and Optronics Centre, Department of Physics, University of Engineering and Technology, Lahore, Pakistan*
[b] *Physics Department, COMSATS University Islamabad, Lahore Campus, Lahore, Pakistan*
[c] *Department of Physics, The University of Lahore, 53790, Pakistan*
[d] *Department of Physics, Division of Materials Physics, University of Helsinki, Finland*
[e] *Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, Finland*

ARTICLE INFO

Keywords:
Gold ion irradiation
ZnO thin films
XRD
Nanostructures
Optical band gap energy
Electrical resistivity

ABSTRACT

In the present work, ZnO thin films were irradiated with 700 keV Au^+ ions at different fluence (1×10^{13}, 1×10^{14}, 2×10^{14} and 5×10^{14} ions/cm^2). The structural, morphological, optical and electrical properties of pristine and irradiated ZnO thin films were characterized by X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), scanning electron microscope (SEM), spectroscopy ellipsometry (SE) and four point probe technique respectively. XRD results showed that the crystallite size decreased from pristine value at the fluence 1×10^{13} ions/cm^2, with further increase of ion fluence the crystallite size also increased due to which the crystallinity of thin films improved. SEM micrographs showed acicular structures appeared on the ZnO thin film surface at high fluence of 5×10^{14} ions/cm^2. FTIR showed absorption band splitting due to the growth of ZnO nanostructures. The optical study revealed that the optical band gap of ZnO thin films changed from 3.08 eV (pristine) to 2.94 eV at the high fluence (5×10^{14} ions/cm^2). The electrical resistivity of ZnO thin film decreases with increasing ion fluence. All the results can be attributed to localized heating effect by ions irradiation of thin films and well correlated with each other.

1. Introduction

ZnO thin films have many novel properties and are attracting a lot of attention recently, especially due to wide band gap (3.37 eV) and large exciton binding energy (60 meV). ZnO is a II-VI semiconductor at room temperature. Because of their physical, optical and electrical properties, ZnO thin films have stimulated much interest in application such as light emitting diodes, solarcell, surface acoustic wave devices, opto-electronic devices, transparent conductive electrodes, piezoelectric and chemical sensors [1–11].

ZnO thin films can be deposited using various techniques, such as pulsed laser deposition, chemical vapor deposition, spray pyrolysis, thermal sputtering, molecular beam epitaxy and RF sputtering etc [12–14]. RF sputtering offered some important advantages such as high deposition rate, easy control of composition and uniformity over the substrate [15]. Doping of different kind of anions and cations is the best way to modulate or alter the optical, electrical, morphological and magnetic properties of ZnO [16]. Ions irradiation is a powerful technique for doping ions, such as Fe, Ni [17,18], Ag, Cr etc in the ZnO thin films [19,20]. When a highly energetic charged ion impinges on the ZnO thin films, it loses most of its energy in the process of electron excitation or ionizations. The ion energy delivered to the target generates non-equilibrium phases with nanostructures on the surface of thin films [21–23]. Many research groups have focused their work on ion irradiation induced changes in ZnO thin films. The formation of regular nanostructures 400 nm ZnO thick films with 150 keV argon ion beam irradiation has been observed in the past [24]. The formation of nanostructures due to 120 MeV Au^{9+} ions irradiation on Al_2O_3 thin films and its effect on the optical properties of thin film has also been reported [25]. Effects such as annealing due to 170 keV indium ions implanted on ZnO thin films have been reported [26]. More over irradiation of 60 keV Si and 300 keV Au ions produced defects in ZnO thin films [27]. The irradiation of the ions for implantation purposes is usually accompanied by the defects formation in the thin films. These defects such as interstitials, vacancies and volume defects often lead to considerable structural alterations. The effects of ion implantation

---

[*] Corresponding author at: Laser and Optronics Centre, Department of Physics, University of Engineering and Technology, Lahore, Pakistan.
[**] Corresponding author.
E-mail addresses: fiazkhan.uet@gmail.com (M. Fiaz Khan), asattar@ciitlahore.edu.pk (A. Sattar).

https://doi.org/10.1016/j.ceramint.2018.06.061
Received 27 March 2018; Received in revised form 11 May 2018; Accepted 8 June 2018

warrant comprehensive study of changes in physical and structural properties of thin films that will be proved helpful in understanding ZnO thin film based devices prepared by metal ion irradiation process [28].

In the present work ZnO thin films prepared by RF sputtering have been irradiated by 700 keV Au^+ ions at different fluence. The key feature is the development of nanostructures on the surface of ZnO thin films after irradiation, without any significant change in electrical properties, which remain lying in semiconducting range. If the optical band gap and electrical conductivity of the ions irradiated ZnO thin films are considered, such thin films can be used in the fabrication of optoelectronic devices.

2. Experimental

The experimental part is composed of two steps: first is ZnO thin film deposition and second step is ion irradiation. In the first step five identical ZnO thin films were fabricated on glass substrate (10 mm × 10 mm × 1 mm) by RF Sputtering. A commercially sintered pure ZnO target (99.99%) with diameter 3 in and thickness 3 mm was used for the sputtering process. Before deposition glass substrates were cleaned by mild soap solution then washed thoroughly in de ionized water and later boiling water. Finally, substrates were cleaned by ethanol using ultrasonic bath for 15 min. During the deposition, the pressure was maintained at 3×10^{-3} Torr with 945 V DC biasing and 30 min time. The rate of Argon flow was maintained at 50 sccm. The thickness of all the deposited films was 200 ± 10 nm.

In second step, 700 keV Au^+ ions were implanted in ZnO thin films at four fluences i.e. 1×10^{13}, 1×10^{14}, 2×10^{14} and 5×10^{14} ions/cm^2 and Pelletron tandem accelerator [29] was used for this purpose. The implantation was carried out at room temperature and at high vacuum ~ 10^{-6} Torr. One ZnO thin film was kept pristine to be used as a reference. During the irradiation, the current of ion beam was kept at 20 nA/cm^2. All the samples were tilted through 5° to avoid channeling effect and electrically grounded during irradiation. The projected range of 101 nm and straggling of 29 nm were calculated using SRIM 2010 [30]. The nuclear stopping power is found to be 6.02×10^2 eV/Å while the electronic stopping power is 1.436×10^2 eV/Å. It shows that the energy of incident ions is sufficiently low to be stopped within the thickness of films. Hence the majority of ions were implanted after losing their energy to the ZnO thin films. Pristine and irradiated ZnO thin films were characterized using different techniques. The structural modification was examined by X-ray Diffractometer (PANAlytical X'Pert Powder) using CuK_α (1.5405 Å) radiations in 2Θ range of 20–80°. Surface morphology of pristine and ions irradiated thin films was studied by Scanning Electron Microscope (S4800). Molecular species present in the films were examined using Fourier transform infrared spectroscopy (Thermo-Nicolet 6700P). The optical properties were studied by spectroscopic ellipsometry in transmission mode (JA Woolam Co Ellipsometer-M2000). For electrical properties, four-point probe technique was used.

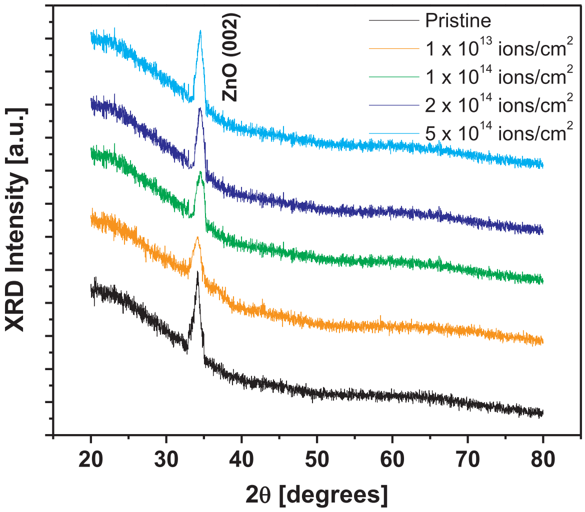

Fig. 1. XRD spectra of pristine, and Au^+ ions irradiated ZnO thin films.

3. Results and discussion

3.1. Structural analysis

The XRD spectra of pristine and Au^+ irradiated ZnO thin films is shown in Fig. 1. The pristine ZnO thin film showed a strong stacking along c-axis with (002) plane at 34.18°. When ZnO thin films were irradiated with 700 keV Au^+ ion with fluence 1×10^{13} ions/cm^2, 1×10^{14} ions/cm^2, 2×10^{14} ions/cm^{2}and 5×10^{14} ions/cm^2, the ZnO remained crystalline in nature after irradiation-No other peaks corresponding to impurity phases were observed after irradiation, which indicates that the grains in ZnO have a strong orientation along c-axis (002) plane [31,32]. The crystallography parameters such as crystallite size and lattice parameter are calculated by using following Eqs. (1) and (2) [33,34];

$$D = \frac{0.9 \quad \lambda}{\beta \cos\Theta} \tag{1}$$

$$C = \frac{\lambda}{\sin\Theta} \tag{2}$$

where λ is the wavelength of X-ray, Θ is the Bragg diffraction angle and β is the observed full width at half maximum (FWHM). The crystallography parameters calculated from XRD spectra are given in Table 1 indicating that the crystallite size of pristine film was 9.63 nm which reduced to 6.97 nm at the fluence of 1×10^{13} ions/cm^2. The decrease in crystallite size at this fluence can be attributed to the generation of defects in ZnO thin films [35]. At high fluence (i.e. 1×10^{14} to 5×10^{14} ions/cm^2) the crystallite size increased from 7.26 nm to 9.01 nm (see Table 1). At high fluence, incident ions transfer enough energy to the lattice due to nuclear energy loss, causing local increase in temperature along the path of ions. This temperature produced localized annealing effect, resulting reduction in compressive stresses among the grains, and agglomeration of the grain occur which increased the crystallinity of the ZnO thin films as explained in Ref. [36]. Thus, main modifications are expected due to nuclear stopping power as compared to electronic stopping power.

3.2. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of glass substrate for reference, pristine and ion irradiated ZnO thin films are shown in Fig. 2. The insets showing the FTIR spectra in the range of 350–600 cm^{-1}. The FTIR spectra of bare glass substrate indicate no vibration peaks of ZnO. Absorption band at 432 cm^{-1} is due to Zn-O stretching vibration and is visible in all samples. It can be seen that a second absorption band at 395 cm^{-1} started appearing in the samples irradiated with different Au^+ ions fluence. The band at 395 cm^{-1} became stronger with the increase in the fluence. The appearance of new absorption band at 395 cm^{-1} is an indication of the formation of ZnO acicular nanostructures in the film as observed in reference [37]. Such acicular structures are clearly visible in the Fig. 3(f). Absorption bands at 2361 cm^{-1} is due to the O=C=O adsorbed from the atmosphere. It can be seen that sample with highest fluence 5×10^{14} ions/cm^2 shows biggest peak at 2361 cm^{-1}, which is clear indication of adsorption of atmospheric CO_2 [39,40]. A broad peak at 2920 cm^{-1} in all the samples is due to presence of hydrocarbons [41]. This feature is also present in the FTIR of the substrate as well and could be a reminiscent of the chemical cleaning process of the substrate.