Applied Surface Science 255 (2009) 4153–4158

Contents lists available at ScienceDirect

Applied Surface Science

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

Structural and optical properties of nano-structured tungsten-doped ZnO thin films grown by pulsed laser deposition

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ARTICLE INFO

Article history:
Received 10 April 2008
Received in revised form 31 October 2008
Accepted 31 October 2008
Available online 14 November 2008

JEL classification:
61.10.–I
68.35.D
85.40.R
74.25.Gz
81.15.Z

Keywords:
Laser ablation
Semiconductor
Thin film
Nano-structures
Optical windows

ABSTRACT

Novel highly c-oriented tungsten-doped zinc oxide (WZO) thin films with 1 wt% were grown by pulsed laser deposition (PLD) technique on corning 1737F glass substrate. The effects of laser energy on the structural, morphological as well as optical transmission properties of the films were studied. The films were highly transparent with average transmittance exceeding 87% in the wavelength region lying between 400 and 2500 nm. X-ray diffraction analysis (XRD) results indicated that the WZO films had *c*-axis preferred orientation with wurtzite structure. Film thickness and the full width at half maximum (FWHM) of the (0 0 2) peaks of the films were found to be dependent on laser fluence. The composition determined through Rutherford backscattering spectroscopy (RBS) appeared to be independent of the laser fluence. By assuming a direct band gap transition, the band gap values of 3.36, 3.34 and 3.31 eV were obtained for corresponding laser fluence of 1, 1.7 and 2.7 J cm^{-2}, respectively. Compared with the reported undoped ZnO band gap value of 3.37 eV, it is conjectured that the observed low band gap values obtained in this study may be attributable to tungsten incorporation in the films as well as the increase in laser fluence. The high transparency makes the films useful as optical windows while the high band gap values support the idea that the films could be good candidates for optoelectronic applications.

1. Introduction

Interest in the research efforts on ZnO film is driven by its various applications in blue and ultraviolet (UV) light emitters regions [1–3], transparent conductors [4–6], solar cell windows [7,8], gas sensors [9], photovoltaic devices [10] and surface acoustic wave devices [11]. Progress made in the area of ZnO-based materials and devices shows that ZnO has a great potential due to its wide and direct band gap of 3.37 eV and a large excitonic binding energy of 60 meV at room temperature [12]. In the past several years, various methods have been employed to prepare ZnO films such as chemical vapor deposition (CVD) [13–15], rf magnetron sputtering [16,17], sol–gel process [18,19], photo-atomic layer deposition [20], spray pyrolysis [21,22], metal oxide chemical vapour deposition (MOCVD) [23], molecular beam epitaxy (MBE) [24,25], filtered cathodic vacuum arc technique (FCVA) [26,27] and pulsed laser deposition (PLD) [28–31].

Pulsed laser deposition has become a widely used deposition technique for thin film growth. PLD presents several advantages with respect to other deposition techniques. In fact, due to the high energetic content of the ejected species, it allows low temperature deposition process. Moreover, its ability to congruently transfer the stoichiometry from the target to the film, allows the growth of complex materials. The technique is based on the vaporisation

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doi:10.1016/j.apsusc.2008.10.122

process induced by focusing a high energy pulsed laser on the surface of the material. When the energy laser density is higher than a threshold value, which depends both on the material and the laser wavelength, a stream of atoms, molecules, and clusters is ejected from the target surface. Such a stream, known as a plume and being also composed of excited neutral and ionized species, emits radiation. Good quality films can be deposited at room temperature due to high kinetic energies (>1 eV) of atoms and ionized species in the laser produced plasma.

The laser energy plays a noticeable role on the growth of ZnO films [32]. At low laser fluence, the growth of ZnO films occurs via a 3D-island mode with a low deposition rate.

These can be related to the low kinetic energy of the species in these experimental growth conditions which decreases their surface mobility and accordingly leads to an island growth mode [33]. On the other hand, too high laser fluency causes a degradation of crystallinity, electrical and optical quality of ZnO films through the bombardment of the growing film by energetic species. So the properties of ZnO are governed by the depositions parameters, dopants [34] and the post-deposition treatments [35]. Therefore, ZnO films have been doped to enhance their properties with elements of Li, Al, Ga, In, Ag, etc.

However, there are scanty reports on the properties of tungsten (W) doped zinc oxide referred to as W-doped ZnO and to the best of our knowledge, this is the first time that the optical properties of W-doped ZnO thin films have been studied.

Tungsten oxide (WO_3) is another material that is widely employed for its electrochromicity [36], as a sensor material for gas sensing [37,38] and in optical data storage and switching [39]. The ionic radius of W^{6+} is 0.062 nm, and Zn^{2+} is 0.074 nm, thus it is theoretically possible for W^{6+} to substitute for Zn^{2+} in ZnO. Moreover, there is a valence difference of 4 between W^{6+} and Zn^{2+}, which is quite attractive because one dopant atom can contribute more electrons. Despite these characteristics, tungsten has not yet been actively employed as a dopant in ZnO, either in bulk or thin film form. Therefore, the aims of the present study are to increase the amount of information already in existence on ZnO by preparing thin films of tungsten-doped ZnO on Corning 1737F glass using pulsed laser ablation and to study their structural and optical properties.

The current contribution reports on the crystallography, surface morphology and optical investigations of tungsten-doped zinc oxide nano-structures grown by PLD technique on corning 1737F glass substrates. The dependence of the structural and optical properties of the grown films on laser fluence was investigated. The structures of the films were studied using X-ray diffraction analysis (XRD) and the morphology using scanning electron microscope (SEM). The thickness and the composition were determined by the use of Rutherford backscattering spectroscopy (RBS). The surface roughness of the films was studied using atomic force microscopy (AFM) and the optical transmittance measurements coupled with the thickness determined from RBS analysis were used to calculate the absorption coefficients and hence the optical band gap of the films.

2. Experimental details

Cylindrical pellets "ø≈15 mm and about 2 mm thick" with a weight composition of 1% of WO_3 and 99% of ZnO were prepared by standard sintering method from pure oxide metal powders "Johnsson Mathey, purity 99.8%" for WO_3 and "Alpha Aesar 99.999% purity" for ZnO. The powders were thoroughly mixed in a mortar and pre-sintered in air at 300 °C for 3 h. The dried mixture was again re-ground and pressed with a load of 20×10^3 kg using a manual hydraulic press to obtain a disc shape of 15 mm diameter.

Sintering was carried out at a maximum temperature of 1200 °C with a dwell time of 2 h, at the end of which the target was allowed to cool down to room temperature before removal. The targets were mounted in the vacuum system with a base pressure of the order of 2.0×10^{-6} mbar, and irradiated with KrF excimer laser (model Lambda Physik LPX-305icc) at 45° incidence having a wavelength λ = 248 nm. By varying the energy output of the laser it was possible to obtain an energy density in the range of 1–2.7 J cm^{-2} on the targets. Prior to the deposition, the substrates were cleaned ultrasonically and then degreased in acetone. The corning 1737F glass substrates used were mounted on a heated stage kept at 350 ± 1 °C during the whole period of ablation. This final heating temperature was measured by a thermocouple located onto the substrates surface. The substrate to target distance was kept at 30 mm and the laser was focused to ablate the centre of the rotating target. These growth conditions were consistent with what had been reported in the literature [40], hence are considered as optimal conditions for the best films. The following three different laser energy densities were used for the film growth at 10 Hz repetition rate: 1, 1.7 and 2.7 J cm^{-2}. The deposition was carried out in an oxygen atmosphere at a pressure of 3×10^{-5} mbar to avoid oxygen deficiency.

The laser ablated nano-structures thickness and composition were determined by Rutherford backscattering spectroscopy. The experimental conditions are as follow: a $4He^{2+}$ ion beam generated from a van de Graaff accelerator was used as the projectile. The scattering angle was 165° and the resolution of the detector was 20 keV. The beam current is in the range 5–20 nA. During the process of acquiring the spectral data, the energy of the ion beam used was 3.05 MeV, and the process was done in an IBM scattering geometry. All the spectra were analysed using the free RBS analysis software RUMP.

The structural properties of the films were investigated using X-ray diffractometer (model Bruker AXS D8 Advance) available at the iThemba LABS in South Africa. The morphology was studied using a Leo-StereoScan 440 scanning electron microscope. Optical properties were measured in the wavelengths region of 200–2500 nm using a CE2000 Series UV–vis–NIR spectrophotometer (from Cecil Instruments) at normal incidence. The atomic force microscopy measurements for surface morphology were carried out using NanoMan V Veeco atomic force microscope while the AFM images were analysed with Nanoscope V700 software. The surface topography mappings were obtained in air subsequent to a special cleaning treatment before scanning. All images were obtained in direct taping mode with standard Si tips of nominal radius 10–20 nm. Topography scanning on the nano-structures' surface was measured over scan range of 4 μm × 4 μm.

3. Results and discussion

In this experiment 1 wt% of WO_3 was used while varying laser fluence to grow different films of the same W concentration. Fig. 1a shows a typical RBS spectrum of tungsten-doped ZnO on Corning 1737F glass substrate sample. For ease of reference, the tungsten-doped ZnO will henceforth be referred to as W-doped ZnO and corning 1737F glass substrate will be referred to simply as glass substrate.

The solid line through winkled data set is the simulation of the spectrum using RUMP and Genplot software. From the simulation of the films grown at different laser fluence, one can determine the thickness and the composition. The thickness of W-doped ZnO layer plotted in Fig. 1b was estimated to be 130, 170 and 220 nm for 1, 1.7 and 2.7 J cm^{-2} leading to growth rate of 4.33, 5.66 and 7.33 nm/min, respectively.

Fig. 1b shows a linear relationship between the film thickness "d" and the laser fluence "f" which can be represented by