Available online at www.sciencedirect.com

Thin Solid Films 515 (2007) 6562 – 6566

www.elsevier.com/locate/tsf

Comparative study of zinc oxide and aluminum doped zinc oxide transparent thin films grown by direct current magnetron sputtering

M. Suchea [a,b,*], S. Christoulakis [a,c], N. Katsarakis [a,d], T. Kitsopoulos [a,b], G. Kiriakidis [a,c]

[a] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, Vasilika Vouton, 711 10 Heraklion, Crete, Greece
[b] University of Crete, Chemistry Department, 711 10 Heraklion, Crete, Greece
[c] University of Crete, Physics Department, 711 10 Heraklion, Crete, Greece
[d] Center of Materials Technology and Laser, Science Department, School of Applied Technology, Technological Educational Institute of Crete,
710 04 Heraklion, Crete, Greece

Abstract

Pure and aluminum (Al) doped zinc oxide (ZnO and ZAO) thin films have been grown using direct current (dc) magnetron sputtering from pure metallic Zn and ceramic ZnO targets, as well as from Al-doped metallic ZnAl2at.% and ceramic ZnAl2at.%O targets at room temperature (RT). The effects of target composition on the film's surface topology, crystallinity, and optical transmission have been investigated for various oxygen partial pressures in the sputtering atmosphere. It has been shown that Al-doped ZnO films sputtered from either metallic or ceramic targets exhibit different surface morphology than the undoped ZnO films, while their preferential crystalline growth orientation revealed by X-ray diffraction remains always the (002). More significantly, Al-doping leads to a larger increase of the optical transmission and energy gap (E_g) of the metallic than of the ceramic target prepared films.

Keywords: Zinc oxide; dc magnetron sputtering; Surface morphology; Sensors

1. Introduction

ZnO thin films are highly attractive in the development of materials area, due to their interesting physical properties as high transparency in the visible and near-ultraviolet (UV–VIS) spectral regions, as well as their wide conductivity range and conductivity changes under photoreduction/oxidation condition. The conductivity and its changes under specific conditions for ZnO thin films depends upon several factors, such as the preparation technique, the in situ preparation parameters, the doping agent, the annealing temperature and atmosphere, and even the measurement conditions [1–4]. When ZnO films are doped with the appropriate metal atoms, such as Al, Sn, Cd, Ga, In, etc., their conductivity can be changed from values as low as 10^{-10} $(\Omega\ \mathrm{cm})^{-1}$ to values as high as 10^4 $(\Omega\ \mathrm{cm})^{-1}$. The wide range of conductivities and conductivity changes upon different environmental conditions make ZnO films suitable materials for oxidant gas sensing layers [5–7]. Dopant presence determines significant changes of film physical properties as crystalline structure (associated to stoichiometry), surface topology (associated to adsorption of species onto surface), optical properties (associated with photoconductivity) which reflect directly on film ability to act as a sensing layer. In the case of ZAO films, previous works have reported that the presence of the dopant determines usually crystallinity alterations [8] or decreases of the transmittance significantly, to values under 70% [9], facts that are highly inconvenient for sensing applications. In this work ZnO and ZAO thin films prepared by dc magnetron sputtering and their structural and optical properties were studied comparatively.

2. Experimental

The deposition of the ZnO and ZAO films was carried out in an Alcatel dc magnetron sputtering system using 99.999% pure

---

* Corresponding author. Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, Vasilika Vouton, 711 10 Heraklion, Crete, Greece. Tel.: +30 2810 391269; fax: +30 2810 391305.
E-mail address: mirasuchea@iesl.forth.gr (M. Suchea).

0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.11.151

Zn, ZnAl2 at% (ZnAl2%) metallic and ZnO, ZnO: 2 at.%Al_2O_3 (ZnAl2%O) ceramic targets all fabricated by Heraeus TMD. The base pressure in the chamber was 5×10^{-7} mbar (5×10^{-5} Pa). Films with thickness about 100 nm were deposited onto Corning 1737F glass and silicon substrates in an oxygen–argon atmosphere (O_2/Ar). The deposition constant parameters were the total pressure (8×10^{-3} mbar), the substrate temperature at 27 °C (RT), and the total gas flow. The depositions were done for plasma current I = 0.44 A. The surface morphology was measured with a Nanoscope III atomic force microscope (AFM) (Digital Co. Instruments, USA) using in Tapping Mode a conventional silicon nitride tip (125 μm) oscillating to its resonant frequency (200–400 kHz). All measurements were made at RT. In the present study the morphology parameters were determined using the Scanning Probe Image Processor (SPIP image processing software for nano- and micro scale microscopy).

X-ray diffraction (XRD) using a Rigaku diffractometer with CuKα X-rays was done in order to determine the crystal structure of the deposited films.

3. Results and discussions

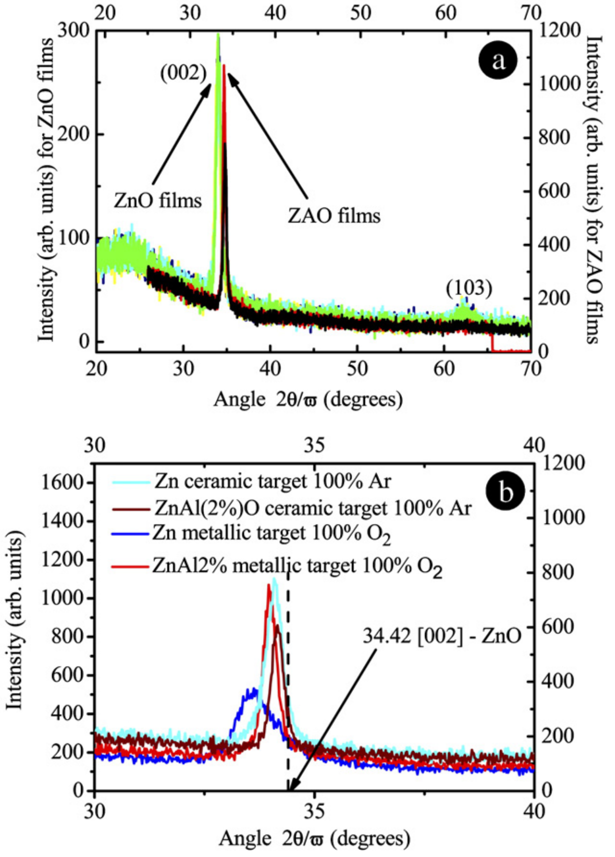

Fig. 1. a) XRD patterns of ZnO and ZAO films deposited on Corning glass; b) zoom on XRD pattern near (002) reflexion plane of ZnO and ZAO films (grown at RT in a 100%O_2 or Ar for ceramic targets).

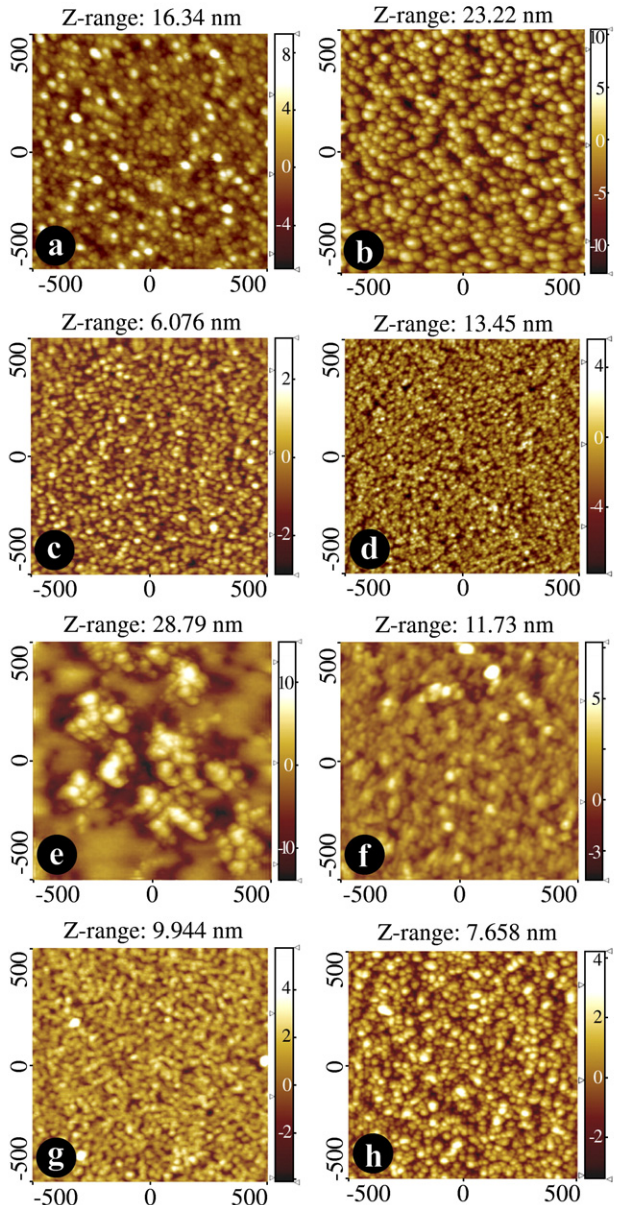

Fig. 2. AFM images of 1 × 1 μm scan size on films grown: a) from Zn metallic target in 80% O_2 concentration in plasma; b) in 100% O_2; c) from ZnAl2% metallic target in 80% O_2 concentration in plasma; d) in 100% O_2; e from ZnO ceramic target in 0% O_2 in plasma; f) in 20% O_2; g) from ZAO ceramic target in 0% O_2 in plasma; h) in 15% O_2.

It is well known that sputtered ZnO films are highly textured with the c axis perpendicular to the substrate surface. The changes in crystal structure for films sputtered from different targets were investigated by X-ray diffraction (XRD). Fig. 1a displays XRD patterns of ZnO and ZAO films deposited on Corning glass. The XRD spectra are dominated by the hexagonal ZnO (002) plane confirming the strong (002) textures. The films exhibit only the (002) peak in the displayed $2\theta/\omega$ region and no metallic Zn or Al characteristic peaks are observed. The characteristic parameters given by XRD from the (002) plane are used to characterize the feature of these ZnO and ZAO films (grown at RT in a 100%O_2 or Ar for ceramic targets), which are shown in Fig. 1b. The diffraction angle of $2\theta/\omega$ ranges from 33.669° for ZnO films grown from Zn metallic target, to 34.16° for ZnO films grown from ceramic target. The