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Investigations on opto-electronical properties of DC reactive magnetron sputtered zinc aluminum oxide thin films annealed at different temperatures

B. Rajesh Kumar[a,b,*], T. Subba Rao[b]

[a] Department of Physics, Sri Venkateswara University, Tirupati 517502, A.P., India
[b] Department of Physics, S.K. University, Anantapur 515003, A.P., India

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ABSTRACT

In the present study transparent conducting zinc aluminum oxide (ZAO) thin films were prepared by DC reactive magnetron sputtering technique. The films were deposited on glass substrates at 200 °C and annealed from 200 °C to 500 °C. XRD patterns of ZAO films shows (0 0 2) diffraction peak of hexagonal wurtzite, meaning that the films have *c*-axis orientation perpendicular to the substrate. Crystallite size was calculated from X-ray diffraction (XRD) spectra using the Scherrer formula. The surface morphology of the films was observed by field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). The electrical conductivity increases with increase of annealing temperature. The activation energies of conduction were obtained from an Arrhenius equation. The best characteristics of ZAO films have been obtained for the films annealed at 400 °C with an average transmittance of 88% and a minimum resistivity of $2.2 \times 10^{-4}\ \Omega\,\text{cm}$. The optical band gap, optical constants, and electron concentrations of ZAO films are obtained from UV–vis–IR spectrophotometer data.

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1. Introduction

Transparent conducting oxides (TCOs) have a wide range of applications as transparent electrodes in optoelectronic devices. The development of non- or reduced-indium TCO materials has attracted much attention due to high-cost, scarcity of indium, and toxicity of indium compound powders [1]. Therefore, Al doped zinc oxide thin films have attracted due to good resistivity, high transmittance, non-toxicity, and low cost [2] to replace indium tin oxide (ITO). High optical transparency in the visible region, wide band gap and the high refractive index of 1.8 enables several applications including antireflection coating in solar cells industry [3], heat mirrors and multilayer photo thermal conversion systems [4]. Low resistivity has enabled applications as transparent electrodes for solar cells, liquid crystal displays (LCD) and organic light emitting diodes (LED) [5]. Nowadays, many display and solar cell industries require the large scale production of zinc aluminum oxide (ZAO) films with high deposition rate on glass substrates for its higher productivity and commercial benefits [6]. The magnetron sputtering process has the advantage of facilitating the growth of TCO films due to the high growth rate and large area uniformity [7,8]. ZAO films by sputtering deposition with high mobilities above $40\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ remains a demanding task [9], especially for high-rate sputtering processes.

The aim of the present work is to study the effect of post-annealing temperature treatment on structural, electrical, and optical properties of ZAO films. While in most papers, the film deposition was carried using ceramic oxide targets which is high cost and requires maximum power density. Therefore the deposition rates are limited due to the tolerable thermal load for the targets. In this paper we prepared ZAO films by DC reactive magnetron sputtering technique using two individual high purity metallic targets of Zn and Al. The deposition conditions were optimized for ZAO films to exhibit a good surface roughness for light scattering and low resistivities.

2. Experimental details

ZAO thin films were prepared by DC reactive magnetron sputtering technique. High purity metal targets of Zn (99.999%) and Al (99.99%) with 2 in. diameter and 4 mm thickness are used for deposition on glass substrates. The glass substrates were ultrasonically cleaned in acetone and ethanol, rinsed in an ultrasonic bath in deionized water for 15 min, with subsequent drying in an oven before deposition. The sputter chamber is initially evacuated to a base pressure of 6×10^{-6} Torr and the working pressure was 3 m Torr. Pure argon gas is introduced into the chamber at a flow rate of 25 sccm (standard cubic centimeters per minute)

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[*] Corresponding author at: Department of Physics, Sri Venkateswara University, Tirupati 517502, A.P., India. Tel.: +91 9985672081; fax: +91 8554 255710.
E-mail address: rajphyind@gmail.com (B.R. Kumar).

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through mass flow controller (Model GFC 17, Aalborg, Germany). Pure oxygen is let into the chamber through another mass flow controller with oxygen flow rate of 2 sccm. The distance between the target and substrate is kept at 60 mm and the deposition time is 30 min. Film thickness was measured by Talysurf profilometer. The resulting thicknesses of the films are ∼350 nm. XRD (Philips: PW1830) was used to analyze the crystalline orientation and lattice constant of the ZAO thin films. Surface morphology of the samples has been studied using Hitachi SU6600 Variable Pressure Field Emission Scanning Electron Microscope (FESEM) with Energy Dispersive Spectroscopy (Horiba, EMAX, 137 eV) and AFM (Park XE-100: Atomic Force Microscopy). EDS is carried out for the elemental analysis of prepared thin film samples. The sheet resistance (R_s) of the film was measured with a four-point probe method. The resistivity of the film (ρ) was calculated using the simple relation $\rho = \underline{R}_s d$, where d is the film thickness. The optical transmittance measurements were recorded as a function of wavelength in the range of 300–1200 nm using JASCO Model V-670 UV–vis–NIR spectrophotometer (Tokyo, Japan).

3. Results and discussion

3.1. Structural properties

XRD spectra of ZAO thin films deposited on glass substrates as a function of the annealing temperature is shown in Fig. 1. All the films show the strong peak correspond to their (0 0 2) preferred orientation. The intensity of the main peak corresponding to the (0 0 2) direction increased as the annealing temperature increased. The FWHM values for ZAO films decreased from 0.42° to 0.28° as the annealing temperature increased from 200 °C to 500 °C. The (0 0 2) peak shifts toward the higher angle as the annealing temperature increased. The increase of diffraction corresponds to a reduction in the interplanar spacing (*d*). Since Al^{3+} (0.053 nm) has a smaller ionic radius with respect to Zn^{2+} (0.074 nm), the substitution of Al atoms for Zn atoms at their lattice sites results in the decrease in the lattice constant. The lattice constant of ZAO films decreased with increase of annealing temperature from 200 °C to 500 °C. It was observed that the crystallinity was improved with increasing the annealing temperature, since the (0 0 2) diffraction peak becomes more intense and sharper. This indicates that the crystallite size became larger with increasing annealing temperature.

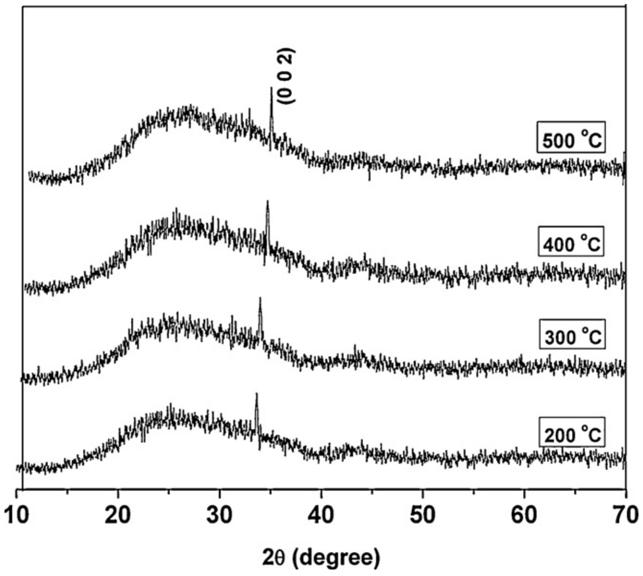

Fig. 1. XRD patterns of ZAO films post-annealed at temperatures of (a) 200 °C, (b) 300 °C, (c) 400 °C and (d) 500 °C.

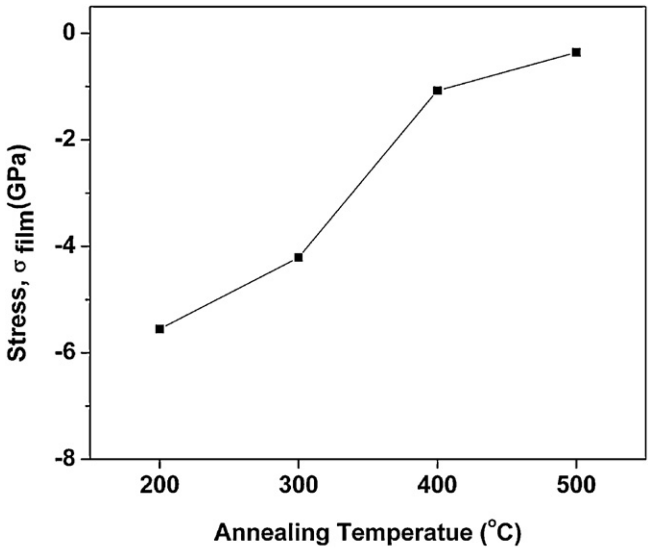

Fig. 2. SEM images of ZAO films annealed at (a) 200 °C, (b) 300 °C, (c) 400 °C and (d) 500 °C.

Crystallite size was estimated by using the Scherrer formula [10]. The crystallite size increased from 19.8 nm to 29.7 nm as the annealing temperature increased from 200 °C to 500 °C. The increase of crystallite size results in decrease of grain boundary, leading to higher conductivity. The higher the *c*-axis preferred orientation the lower the resistivity due to the reduction in the scattering of the carriers at the grain boundaries [11,12]. The residual stress decreased with increase of annealing temperature shown in Fig. 2. According to Chang et al. [13] the residual stress of the film can be reduced by annealing process that resulted in a peak shift of XRD patterns toward high angle, similar results were obtained in this study.

SEM images of ZAO films annealed at different temperatures are shown in Fig. 3. As annealing temperature increases the grain boundary density of a film decrease, subsequently the scattering of carriers at grain boundaries decreased. The possibility of scattering of the grains increases as the annealing temperature increases, which can also be attributed to the increase of grain size and surface density of the films. The high annealing temperature enhances the occupation probability of Al ions on Zn sites, as well as oxygen vacancies and Zn interstitial atoms. In other words, Al atoms can diffuse to the surface, dependent upon the annealing temperature. An increase in crystalline size would be strongly related to a decrease in resistance for free electrons, because of lower grain and grain-boundary scattering. The grain size obtained from SEM image is found to be in the range of 30–42 nm. The relative compositions obtained from EDS for ZAO films annealed from 200 °C to 500 °C are in an atomic ratio of Zn/O/Al are 43.73/52.97/3.30%, 48.86/47.79/3.35%, 54.00/42.60/3.43%, and 56.85/39.36/3.79%. The stoichiometric deviation results the high conductivity of these films. The conduction electrons in these films are supplied from donor sites associated with oxygen vacancies or excess metal ions. The donor sites can be easily created by chemical reduction or intentional doping. It generates a large amount of conduction electrons by the doping effect, and this also creates oxygen vacancies in order to maintain the charge balance.

Fig. 4 shows the AFM images of ZAO films at different annealing temperatures. The surface roughness of ZAO films increased from 1.53 to 2.60 nm as the annealing temperature increased from 200 °C to 500 °C. It is well known that the surface roughness of the ZAO thin

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